



**CHROMATOGRAPHIC SEPARATION AND CONCENTRATION OF THORIUM  
AND RARE EARTHS FROM URANIUM USING ALUMINA-HYDROFLUORIC  
ACID. PREPARATION OF CARRIER — FREE RADIOTHORIUM AND CON-  
TRIBUTION TO THE FISSION RARE EARTHS**

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ABSTRACT

This paper describes a new procedure for the separation and concentration of thorium and rare earth elements (RE) from uranyl solutions. The method is based upon the sorption of thorium and rare earths when acid solution of uranyl nitrate, chloride, or sulfate, containing 0.3M HF is percolated through a small column of alumina ( $Al_2O_3$ ), the uranyl ion being not sorbed.

This method allows Th and RE present at very low concentration in uranyl solutions to be separated and concentrated on alumina. It is applied to the direct separation and preparation of carrier-free thorium-234 from pure uranyl nitrate, a 2 ml alumina column being sufficient to collect the UX1 from about 2 liters uranyl nitrate of 100 g/l  $U_3O_8$ . For the separation and preparation of carrier free thorium-234 by the method here outlined uranyl nitrate solutions of 50 to 250 g/l  $U_3O_8$  were used.

Also the method is being used for the separation, concentration and determination of thorium-232 and total rare earths in uranium. These elements are eluted together from the alumina with hot 1M HCl or 1M HNO<sub>3</sub>, two or three washings eluted more than 99% of the sorbed elements. Thorium is determined spectrophotometrically by the xylenol orange method at pH 2 and thorium plus rare earths are determined together at pH 6.

Experiments using radioeuropium added to an uranyl nitrate solution demonstrated the availability of this technique to the separation of fission rare earths from irradiated uranium, with the additional advantage of being alumina quite resistant to radiation damage, unlike organic ion exchangers.

The method can be used to separate and collect thorium-230 (ionium) descendant from uranium-238, and thorium-231 and thorium-227, descendants from uranium-235.

INTRODUCTION

The separation of thorium and rare earths elements from uranium is of paramount importance in the nuclear energy technology. The outline of considerable number of schemes for the chemical separation of thorium and lanthanides from uranium has been a remarkable preoccupation in the research and industrial laboratories.

The separation of microquantities of thorium and lanthanides from uranium and its compounds it is a constant challenge to

the analyst. It is considerable the number of papers published searching the best conditions for the above mentioned chemical separation.

The importance of to know the thorium and rare earths elements content in uranium is due to the neutron economy when the uranium is destined to be used as fuel element in the nuclear reactors and due to the reprocessing chemistry for the burned fuel elements. In the first case, mainly the rare earths must be rigorously controlled since, as it is well known, some of them (Sm, Dy, Gd, Eu, Er) have high cross section for thermal neutrons and could interfere seriously in the neutron economy of the reactor. In the second case, the rare earths are present as fission products, and contribute markedly for the increase of radiation level of irradiated uranium.

This paper is a contribution to the thorium and rare earths elements chemistry at extremely low concentration, especially to its separation from uranium.

#### SEPARATION OF THORIUM AND RARE EARTHS FROM URANIUM

The most frequently methods used for the separation of thorium and rare earths from uranium, as for analytical purpose as for preparative techniques as well, are precipitation (coprecipitation), solvent extraction and ion exchange techniques.

Many papers using chromatographic separation of small quantities of thorium from uranium and, in particular, for the isolation of the thorium-234 (UX1) radiotracer have been described using cationic resin, including the excellent papers of Bane<sup>(1)</sup>, Dyrssen<sup>(2)</sup>, Asaro et al<sup>(3)</sup>, and a semi-industrial preparation of thorium-234 published by Eister et al<sup>(4)</sup>. Strelow<sup>(5)</sup> recommended a method which elutes the thorium with oxalic acid, the elution being incomplete, and Hettel<sup>(6)</sup> described the elution of thorium

with 4M  $H_2SO_4$  from the cationic resin after the elution of rare earths and uranium with 4M HCl.

The use of anionic ion exchangers have been suggested taking the advantage of the chemical behavior exhibited by the uranyl ion in the formation of negative charged chloride complexes, while thorium and rare earths remain unaffected as cationic species. Kraus and Moore<sup>(7)</sup> separated uranium-233 and protoactinium from thorium percolating a 8M HCl solution through an anionic resin, uranium and protactinium being fixed on the resin and eluted with 1 to 4M HCl as recommended by Roy and Weiler<sup>(8)</sup>, Kraus and Nelson<sup>(9)</sup>. An excellent method is published by Berman and coworkers<sup>(10)</sup> for the preparation of high activity carrier-free thorium-234 by sorption of the uranyl chloride from 9.6M HCl on an anionic resin.

Using separation in the HCl medium also there are the published papers of Bunney and coworkers<sup>(11)</sup>, Chesne and Regnaut<sup>(12)</sup>, Tommic and coworkers<sup>(13)</sup>, Moore and Nelson<sup>(14)</sup>, Faris and Buchanan<sup>(15)</sup>. Separation from mixtures of HF-HCl acids was made by Kraus and Nelson<sup>(16)</sup>.

Some procedures are published using the property of thorium forming negative complexes with sulfuric and nitric acid, allowing its sorption on anionic resins, as described by Danon<sup>(17)</sup>, Chen<sup>(18)</sup>, Roy Ko and Weiler<sup>(8)</sup>, Buchanan and Faris<sup>(19)</sup>, Carswell<sup>(20)</sup> and Ying-Mao<sup>(21)</sup>.

More recently some papers have been published advising the use of mixture of solvents and anionic ion exchangers for the separation of thorium from uranium, as recommended by Fritz and Pietrzyk<sup>(22)</sup>, Katzin and Gebert<sup>(23)</sup>, Davies and Owen<sup>(24)</sup>, Tuck and Welch<sup>(25)</sup>, Iguchi<sup>(26)</sup>, Burstall and coworkers<sup>(27)</sup>, Berg and Truemper<sup>(28)</sup>, Kojima<sup>(29)</sup>, Yoshimo and Kurimura<sup>(30)</sup>, Korkish<sup>(31)</sup> and Korgaonkar<sup>(32)</sup>.

One of the most spreaded technique for the separation of

thorium and rare earths from uranyl salt solutions is the previous solvent extraction of the uranium, being those elements collected from the raffinate with the use of non-isotopic carriers, as for instance calcium and rare earth fluorides for gathering the thorium, and thorium fluoride or yttrium fluoride for the coprecipitation of radiothorium. It is well known the use of mercuric iodate for the coprecipitation of thorium. Of great use is the coprecipitation of thorium-234 with ferric hydroxide in sodium carbonate medium after the extraction of uranyl nitrate with ether or tributyl phosphate (TBP). A few micrograms of thorium can be coprecipitated by barium or lead sulfate, as described by Sill and Willis<sup>(33)</sup>.

#### CHROMATOGRAPHY ON ALUMINA

Chromatographic procedures using alumina and cellulose as support have been used for the separation of thorium and rare earths (34) and separation of thorium from uranium<sup>(35)</sup>. The behavior of thorium on a cellulose column has been used for the separation of thorium from uranium in a  $\text{HNO}_3$ -ether medium<sup>(35,36,37)</sup>.

Alumina has been applied for the separation and preparation of some carrier-free radioisotopes, as for instance fluorine-18, molybdenum-99, technetium-99m, tellurium-132 and iodine-132. Tucker et al<sup>(38)</sup> published a method for milking iodine-132 from tellurium-132 fixed on an alumina column, and Bressesti and coworkers<sup>(39)</sup> outlined a method for the separation of carrier-free phosphorus-32 using alumina. Alumina has been used for separation of some fission products from irradiated uranium, tellurium-132 and molybdenum-99 being among them<sup>(38)</sup>; also a technetium-99m generator and a method for the separation of fluorine-19 from irradiated lithium is described by Tucker and coworkers<sup>(38)</sup>.

#### DISADVANTAGES AND DIFFICULTIES OF EXISTING METHODS

While in the methods proposed by Dyrssen<sup>(2)</sup> and Chen<sup>(18)</sup>

there is considerable loss of thorium-234 due to the use of relatively concentrated uranyl solutions, and presents some difficulty for the complete elution of radiothorium, the method proposed by Berman<sup>(10)</sup> has the disadvantage of using the sorption of the major component (uranium) on a large column; while the elution of thorium-234 does not present any trouble, the volume of eluent used (HCl) is large. The described methods either involve large volumes of solution or high concentration of the used acid, as for instance in the procedure of Chen<sup>(18)</sup> about 50 grams of uranium in 9.6M HCl are sorbed on a column of 500 ml of resin, the thorium-234 being eluted with 800 ml of 9.6M HCl. The procedure of Berman<sup>(10)</sup> uses a column containing 1800 g of anionic resin for the sorption of 500 ml of a 507 g/l  $U_3O_8$  in 9.6M HCl and requires 800 ml of 9.6M HCl for washing plus 1600 ml of the same acid for elution of 95% of the total UX<sub>1</sub>, this procedure requiring the evaporation of 2400 ml of concentrated hydrochloric acid for the recovery of thorium-234, which finally is coprecipitated by ferric hydroxide.

A NEW TECHNIQUE FOR THE SEPARATION OF THORIUM AND RARE EARTHS FROM URANIUM: CHROMATOGRAPHY ON ALUMINA-HYDROFLUORIC ACID.

This paper describes a new, simple, rapid and efficient procedure for the preparation of carrier-free thorium-234 for use as tracer, the method serving for the separation and determination of microquantities of thorium and rare earths elements from uranyl solution as well.

The method is based upon the sorption of thorium and rare earths elements on an alumina column from uranyl nitrate having 0.3M HF.

It was verified by the author that it is easily feasible to retain the thorium contained in the uranyl chloride, sulfate or nitrate solutions when to these solutions a small



quantity of hydrofluoric acid is added and the solution is percolated through a small column of alumina. In this condition thorium (thorium-234 and thorium-232) is total and firmly fixed, while uranyl ion is not. An extension of this work led to conclude that equally the rare earths elements are efficiently retained on the alumina as well.

This method is applied to the separation and concentration of extremely low thorium and rare earths content in uranyl salts, allowing for instance the determination of the mentioned elements in concentration as low as one part per million in uranium and its compounds. In the author's laboratory radiothorium was easily separated and identified by gamma-ray spectrometry of thorium-234 contained in one gram of uranium, which means a separation of approximately  $0.8 \times 10^{-5}$  micrograms of thorium-234.

#### SEPARATION OF THORIUM-234 FROM URANYL SOLUTION

The separation of thorium-234 (UX1, 24.1 days) from uranyl solutions is of great importance in radiochemistry, this radiothorium being a valuable tracer for many chemical separations involving thorium.

The new method here outlined consists in the chromatographic separation of thorium on a small alumina column, the thorium being separated from nitrate, chloride or uranyl sulfate solutions previously ascertained to be 0.3M HF. Depending upon the desired activity it is possible to percolate on a 6 mm internal diameter column containing 2 ml of alumina, solutions of uranyl nitrate (nitrate solutions are preferred) of concentration in the 50 to 250 g/l  $U_3O_8$  range, the solutions being 0.3M HF and pH 0.2 to 2.5, volumes from 100 to 1000 ml could be passed through.

The uranyl nitrate is percolated at room temperature at a flow rate of 1 to 5 ml/min. In such conditions the sorption of

thorium-234 is between 95 and 98%, a 100% sorption being possible if larger column is used.

In this work were used uranyl nitrate solutions prepared by dissolution of nuclear grade  $U_3O_8$  (less than 1 ppm of Th) with nitric acid.

As can be seen from Table I the retention of thorium-234 is a relatively fast process, the fixation of radiothorium being reasonably good for flow rates of 0.5 to 5.0 ml/min. for an alumina column with two milliliters of  $Al_2O_3$  (chromatographic neutral active alumina, E.Merck Ag. Darmstadt).

TABLE I: Retainment of thorium-234 as function of flow rate

Column: 6 mm i.d., with 2 ml. of  $Al_2O_3$ . Each experiment used 100 ml of uranyl nitrate 0.3M in HF.

$U_3O_8 = 100 \text{ g/l, pH 1.30}$			$U_3O_8 = 200 \text{ g/l, pH 1.50}$		
Exp. nr.	Flow rate ml/min.	Th-234 retained (%)	Exp. nr.	Flow rate ml/min.	Th-234 retained (%)
1	5.0*	95.5	1	4.0*	97.5
2	4.0*	98.5	2	2.0	96.5
3	2.0	94.2	3	1.5	91.6
4	1.7	99.0	4	1.4	93.6
5	1.7	96.0	5	1.4	94.5
6	1.4	97.3	6	1.2	95.6
7	1.4	97.2	7	1.0	96.2
8	1.1	98.5	8	0.8	95.2
9	0.8	97.0	9	0.7	96.0
10	0.6	96.0	10	0.5	96.0
11	0.5	95.0	11	0.4	93.5

\* vacuum; others experiments by gravity

The concentration of hydrofluoric acid added to the uranyl solution must be controlled. Table II contains the results of retention of thorium-234 when the HF molarity in the uranyl nitrate solutions was varied. As demonstrated the retention of thorium by alumina is low at 0.02M HF, increasing to a maximum from 0.2M to 0.6M HF.

TABLE II Retention of thorium as function of HF molarity

Column: 6 mm i.d., with 2 ml of  $Al_2O_3$ . Each experiment used 100 ml uranyl nitrate. Flow rate: two ml/min.

$U_3O_8 = 100$ g/l			$U_3O_8 = 200$ g/l			$U_3O_8 = 250$ g/l			$U_3O_8 = 500$ g/l		
Exp.	HF(M)	Th-234 fixed (%)	Exp.	HF(M)	Th-234 fixed (%)	Exp.	HF(M)	Th-234 fixed (%)	Exp.	HF(M)	Th-234 fixed (%)
1	0.02	15.0	1	0.20	96.0	1	0.20	92.5	1	0.20	65.0*
2	0.04	30.0	2	0.20	93.0	2	0.30	95.0	2	0.30	70.0
3	0.05	73.0	3	0.30	96.0	3	0.40	95.8			
4	0.10	48.5	4	0.30	96.5	4	0.60	96.0			
5	0.10	56.0	5	0.40	97.0						
6	0.20	96.0	6	0.60	97.5						
7	0.20	97.0									
8	0.20	98.5									
9	0.30	98.7									
10	0.40	97.5									
11	0.40	98.1									
12	0.60	98.6									

\* at 500 g/l  $U_3O_8$  the percolation is difficult and needs vacuum

Table III has the results of retention of thorium when the concentration of uranium is varied, concluding that the highest uranium concentration recommended is 250 g/l  $U_3O_8$ . For solutions of higher concentration than 250 g/l  $U_3O_8$  the retention is markedly lowered. Solutions as high as 400 or 500 g/l  $U_3O_8$  presented difficulty to be percolated through the column.

TABLE III Retention of thorium as function of uranium concentration

Column: 6 mm i.d., with two ml alumina. Flow rate: 2 ml/min. Each experiment used 100 ml uranyl nitrate 0.3M HF and pH = 1.30

Exp. nr.	$U_3O_8$ g/l	Thorium-234 retained (%)
1	100	97.2
2	100	98.5
3	100	94.7
4	100	96.5
5	100	99.0
6	200	96.0
7	200	94.7
8	200	96.2
9	200	97.5
10	250	94.0
11	250	93.2
12	500	74.3
13	500	65.0

The alumina capacity for fixation of thorium-234 is quite high, as can be seen by data in Table IV. For the conditions se-

lected it is possible to percolate volumes greater than one liter of uranyl nitrate of 200 g/l  $U_3O_8$ , the retention of UX1 remaining high.

TABLE IV Alumina capacity for retention of thorium-234

Successive percolations of uranyl nitrate through the same 2 ml  $Al_2O_3$  column. Each run used 100 ml uranyl nitrate at pH 1.30 and flow-rate = 2 ml/min.

$U_3O_8 = 100$ g/l			$U_3O_8 = 200$ g/l		
alumina column nr.	1	2	3	4	5
HF(M).	0.2	0.3	0.2	0.2	0.3
run. nr.	thorium-234 retained by the column (%)				
1	99.0	98.5	96.0	93.6	95.2
2	98.5	94.2	96.0	94.6	95.1
3	97.0	93.8	92.6	93.6	96.2
4	94.0	93.3	91.4	91.6	96.5
5	80.7	94.5	82.7	84.9	93.1
6	62.0	91.5	75.0	59.5	95.7
7	60.0	93.1	66.1	62.0	97.1
8		91.8			96.5
9		85.3			96.4
10		81.0			94.9
11		68.4			97.5
12					96.0

Table V presents the data concerned with the re-use of a same uranyl nitrate solution from which the thorium-234 has been removed before by the process here described. This solution was kept into a polyethylene bottle during 50 days and the thorium-234 that has grown in was again recovered by percolating the same solution through a new alumina column, without extra addition of hydrofluoric acid.

TABLE V Re-use of uranyl nitrate for the preparation of carrier-free Thorium-234

Uranyl nitrate from which Th-234 was removed before, originally 0.3M in HF. Stored during 50 days for the ingrowth of UX1. Vol. = 2 liters.  $U_3O_8 = 100$  g/l, pH = 1.30. Re-used without extra HF addition. Column: 6 mm i.d., 2 ml  $Al_2O_3$ . Each successive run used 100 ml uranyl nitrate solution at a flow rate of 2 ml/min.

Successive runs through the same column			
run nr.	Th-234 retained (%)	run nr.	Th-234 retained (%)
1	95.5	11	96.7
2	97.0	12	94.3
3	94.0	13	94.3
4	94.0	14	94.8
5	96.5	15	94.3
6	97.2	16	96.8
7	97.2	17	94.6
8	97.1	18	89.0
9	97.6	19	67.0
10	94.0	20	56.0

REMOVAL OF THORIUM FROM ALUMINA

Thorium-234 retained on alumina can be removed by treatment with hot 1 HCl or 1M  $HNO_3$ . Preferably the alumina is transferred to a beaker and covered with enough acid, warmed during 5 minutes and filtered. With a second acid treatment the removal of thorium is about 95% and a third acid treatment the removal of thorium is practically complete.

This solutions of thorium-234 contains a few milligrams of aluminum. If necessary, the UX1 can be coprecipitated with 1-5 mg of Fe-III by precipitation with 1M NaOH. The ferric hydroxide is dissolved with concentrated HCl, the resultant solution percolated through a small anionic resin (2-5 ml of resin, chloride form) previously washed with 7-9M HCl. After loaded, the resin is washed with 7-9M HCl, the Fe-III being fixed by the resin and thorium passed through in the effluent. Alternatively, the carrier-free thorium-234 can be prepared by dissolution of the ferric hydroxide with 2-3M HCl and this solutions extracted with 5% tri-n-octylamine diluted with metil-isobutyl-cetone or xylene, the Fe-III being completely extrated by the solvent and the thorium-234 being in the raffinate.

The thorium-234 radioisotope separated from uranium by the method here described is radioactively pure, others radioisotopes genetically related to the natural uranium family were not found by gamma-ray spectrometry.

#### RE-USE OF URANYL NITRATE

The uranyl nitrate effluent from the alumina column can be stored into plastic bottles for posterior use. After observing sufficient time for thorium-234 has grown in, the effluent can be percolated again for the removal of UX1. This recovery of radiothorium can be done repeatedly many times. Table V shows the results of re-use of the uranyl nitrate solution kept during 50 days for the ingrowth of UX1. Of course, after several percolations of the same solution, the HF content should be restored, since the  $Al_2O_3$  retain some F'-ion.

#### IONIUM AND OTHERS RADIOTHORIUM

This method allows, for the case of enough old uranyl solutions, the separation of thorium-230 (ionium,  $8.0 \times 10^4$  years), an uranium-238 descendant. Ionium presents interest as an alpha emissor source. The method can also be used to separate an collect thorium-231 and thorium-227, both descendants from uranium-235.

#### DETERMINATION OF THORIUM AND RARE EARTHS IN URANIUM

The procedure described above is applicable to extremely low thorium and rare earths elements concentration in uranyl salts, allowing for instance the determination of those elements in concentration lower than one part per million. The lanthanides are collected along with thorium when the uranyl nitrate-0.3M HF solution is passed through the alumina.

Experiments were performed for the separation of thorium and lanthanides from uranyl nitrate of 50-250 g/l  $U_3O_8$  and adjusted to be 0.3M in HF and pH 0.5 to 2.5. The retention of thorium and rare earths is higher than 98%. In these experiments thorium was followed by UX1 tracer and the lanthanides by Europium-152-154 tracer.

After the percolation of the uranyl solution through a 3-5 ml  $Al_2O_3$  column, a washing step with 1% HF solution is followed for the complete elimination of uranium. For the determination of thorium and rare earths the alumina is transferred to a beaker and treated with hot 1M HCl or 1M  $HNO_3$ . This treatment is repeated twice, being the fixed elements eluted completely. The determination is followed by coprecipitation of thorium and lanthanides with 1-5 mg of Fe-III precipitated with hot  $NH_4OH$ , the hydroxides are dissolved with nitric acid and again precipitated with hot NaOH. The hydroxides are dissolved with HCl and the resultant solution is ascertained to be 1-2M in HCl, and then extracted twice with equal volume of 5% tri-n-octylamine in methyl-isobutyl-cetone, the Fe-III being completely extracted; thorium plus rare earths are determined in the raffinate.

The determination of thorium and rare earths can be done in the aqueous phase by the procedure of Mukherji<sup>(40)</sup>, using xylenol orange at controlled pH. Thorium is determined at pH 2 and measured spectrophotometrically at 525 mu. Thorium plus rare earths are determined at pH 6, the rare earth content being calculated by difference.

The precipitation with  $NH_4OH$  and then with NaOH, followed by extraction with tri-n-octylamine was made for the elimination of traces of calcium, aluminum and iron, that give colored complexes with xylenol orange and interfered with the determination of thorium and lanthanides.

## FISSION RARE EARTHS CHEMISTRY

The procedure here described contribute also to the chemistry of the fission rare earths elements. With the HF-Al<sub>2</sub>O<sub>3</sub> method the fission rare earths can be easely removed from the uranyl nitrate solution, with the purpose of recovery of these important fission radioisotopes or facing the problem of wasce disposal. In this particular alumina is a very resistant material to stand the radiation damage, unlike organic ion exchangers. Some methods described for the dissolution of fuel elements use HF to facilitate the chemical dissolution for the reprocessing.

## SORPTION MECHANISM FOR THORIUM AND LANTHANIDES ON ALUMINA-HF

A search of literature on chromatography with alumina reveals that the mechanism of sorption of cations on alumina is not well established. Only a few papers describing the sorption of cations are published, the great majority of the papers are concerning to the fixation of anions. Either for anions or for cations, the general tendency is to point out the sorption from acid medium as a consequence of an ion exchange mechanism.

Ours experiments for fixation of thorium and lanthanides on alumina using acid solutions of these elements through an alumina column demonstrated that the retention of thorium and rare earths is negligible for nitrate, chloride and uranyl sulfate, from 25 to 250 g/l U<sub>3</sub>O<sub>8</sub>. When to these solutions HF was added, the retention for thorium and rare earths was increased from 0.01M HF and reached a maximum from 0.2M to 0.6M HF, at 0.2M HF being practically quantitative. The concentration of hydrofluoric acid here mentioned is nominal, that is, it does not mean "free" HF, since it is well known that the UO<sub>2</sub><sup>++</sup> ion form relatively strong complexes with F<sup>-</sup> ion. In the experiments here discussed the HF added was not sufficient to



complex the total uranium present. On the other hand it is well established that thorium does not form anionic complexes with  $\text{NO}_3^-$  ion at concentration below 4M  $\text{HNO}_3$ , so the possibility of fixation of thorium as an anionic species with  $\text{NO}_3^-$  ion is excluded for the uranyl nitrate solutions at pH 0.5 to 2.5 as were used.

There are no anionic thorium and rare earth fluorides described in the literature, while for  $\text{Al}^{3+}$  and  $\text{UO}_2^{++}$  anionic complexes do exist.

Also, for very low concentration of thorium and rare earths in uranyl solution the possibility of precipitation of  $\text{ThF}_4$  and  $(\text{RE})\text{F}_3$  is excluded, even though the HF added is not sufficient for the precipitation. There is no precipitation of  $\text{ThF}_4$  when the molar ratio of fluoride ion is below two, due the formation of cationic soluble complexes of  $\text{ThF}^{3+}$ ,  $\text{ThF}_2^{2+}$ , and  $\text{ThF}_3^+$  type (41). It is well known that the  $\text{UO}_2^{++}$  ion has a solubilization effect upon the rare earth fluorides and thorium fluoride, as mentioned by Short and Dutton (42). In the precipitation of a few micrograms of thorium and rare earths, the presence of 10 or 20 grams of uranoium has a solubilization effect which does not permit the recovery of these small amount of thorium and rare earths that could be quantitatively recovered from the aqueous solution in the absence of uranium.

Some experiments were run to determine the capacity of  $\text{Al}_2\text{O}_3$  in the retention of  $\text{F}^-$  ion. Using an excess of 0.3M HF through an alumina column the fixed  $\text{F}^-$  was determined to be about 0.55 g of HF per ml of  $\text{Al}_2\text{O}_3$ .

So, it seems reasonably to us that a mechanism of ion exchange could be ascribed as the responsible for the fixation of thorium and rare earths, the ion exchange being accomplished by the  $\text{AlF}_4^-$  ( $\text{pK} = 17.75$ ),  $\text{AlF}_5^{--}$  ( $\text{pK} = 19.37$ ) and  $\text{AlF}_6^{---}$  ( $\text{pK} = 19.84$ ), anionic species formed by the percolation of HF acid through alumina, when the uranyl nitrate solution adjusted to 0.3M HF are used, and the  $\text{Th}^{4+}$ ,  $\text{ThF}_3^+$ ,  $\text{ThF}_2^{++}$  and  $\text{ThF}^{3+}$  cationic species. The same mechanism

could be admitted for the fixation of lanthanides, as for instance with the  $GdF^{2+}$  ( $pK = 3.46$ ) and  $LaF^{2+}$  ( $pK = 2.77$ ) species.

#### LIMITATION OF THE $Al_2O_3$ - HF METHOD

The method above discussed is limited by the concentration of thorium and rare earths solutions since the presence of HF starts the precipitation of their fluorides. The author's experiments led to the conclusion that when the thorium or rare earths are above 20 ppm in the uranyl nitrate solutions of 100-200 g/l  $U_3O_8$  the corresponding fluorides begin to precipitate after 20 - 30 minutes the addition of HF acid. But even at these conditions the thorium or rare earths fluorides precipitation is not complete. If the fluorides are filtered or centrifuged off, the remainder soluble thorium or lanthanides can be recovered in the filtrate or supernate by percolation through the alumina column as yet described.

#### CONCLUSION

From the foregoing discussion of alumina-HF method for sorption of thorium or rare earth from uranyl nitrate solutions, it follows that:

1) chromatography of dilute HF solutions- $Al_2O_3$  allows a fast, simple and highly efficient separation for thorium-234 (UX1), thorium-230 (ionium), thorium-227 and thorium-231, these radioisotopes being easily separated from uranyl solutions. Equally the technique permit the separation of micro-quantities of lanthanides and its concentration from uranyl salts, followed by their determination, as for instance by the xylenol orange spectrophotometric method. As an example a 100 g/l  $U_3O_8$  uranyl nitrate solution containing 10 ppm of thorium was percolated through an alumina column, the thorium removed as described

and precipitated with oxalic acid, a total of 4mg of thorium being recovered, so giving the possibility of a macrotest for thorium an rare earths.

2) The technique allows the separation and recovery of fission rare earths, its use in the reprocessing chemistry could be thought. In this particular alumina has the requirements of high rate of percolation and it is well resistant to radiation damage.

3) The technique allows the study of solubility of thorium and RE fluorides, traces of these elements that were not precipitated or complexed by  $F^-$ -ion could be retained on alumina.

4) Finally it allows a spectrographic determination of thorium and rare earths, the matrix of  $Al_2O_3$  containing these elements could be excited at the electrodes and the spectra examined. Investigation in this area was initiated at the Instituto de Energia Atômica Spectrographic Laboratory.

#### RESUMO

Este trabalho descreve um novo procedimento para a separação e concentração de tório e elementos das terras raras (RE) em soluções de U-VI. O método é baseado na sorção de tório e terras raras quando soluções ácidas de nitrato, cloreto ou sulfato de urânio contendo  $HF$   $0,3M$  são percoladas numa coluna de alumina ( $Al_2O_3$ ), o íon urânio não sendo retido.

O método permite que tório e terras raras presentes em concentrações muito baixas nas soluções de U-VI sejam separados e concentrados na alumina. É aplicado à separação direta e preparação de tório-234 livre de carregador a partir de soluções de nitrato de urânio, uma coluna de 2 ml de alumina sendo suficiente para coletar o  $UX_1$  de aproximadamente dois litros de nitrato de urânio de 100 g/l em  $U_3O_8$ . Para a separação de tório-234 livre de carregador pelo método aqui descrito são usadas soluções de 50 a 250 g/l em  $U_3O_8$ .

O método também tem sido usado para a separação, concentração e determinação de tório-232 e terras raras totais em urânio. Estes elementos são eluídos juntamente da alumina com  $HCl$   $1M$  ou  $HNO_3$   $1M$  quente, duas a três lavagens eluem mais que 99% dos elementos fixados. Tório é determinado espectrofotometricamente por alaranjado de xilenol a pH 2 e tório mais terras são determinados juntos a pH 6.

Experiências usando radioeúrópio adicionado à solução de nitrato de urânio demonstraram a viabilidade desta técnica à separação de terras raras de fissão a partir de urânio irradiado, com a vantagem adicional de ser a alumina muito resistente aos efeitos de radiação, ao contrário dos trocadores iônicos orgânicos.

O método pode ser usado para separar e coletar tório-230 (iônio), descendente do urânio-238, tório-231 e tório-227, descendentes do urânio-235.

RÉSUMÉ

L'auteur décrit un nouveau procédé pour séparer et concentrer le thorium et les éléments des terres rares dans les solutions d'uranium VI.

Le thorium et les terres rares sont fixés sur une colonne d'alumina par passage de solutions acides de nitrate, chlorure et sulfate d'uranyle contenant HF 0,3M. L'ion uranyle n'est pas fixé dans ces conditions.

Il est possible, par ce technique, de séparer et concentrer sur la colonne, le thorium et le terres rares même s'ils sont présents en très basse concentration.

La méthode est appliquée pour la séparation directe et préparation du thorium-234 sans entraîneur, à partir de solution de nitrate d'uranyle, étant suffisante une colonne de 2 cm<sup>3</sup> d'alumina pour fixer l'UX<sub>1</sub> de deux litres d'une solution de nitrate d'uranyle:100 g/l en U<sub>3</sub>O<sub>8</sub>. On utilise solutions de 50 à 250 g/l en U<sub>3</sub>O<sub>8</sub>.

La méthode est aussi utilisée pour la séparation, la concentration et la détermination du thorium-232 et de terres rares dans l'uranium. Ces éléments sont élués ensemble avec HCl 1M ou HNO<sub>3</sub> 1M à chaud de telle façon que deux ou trois lavages suffisent pour séparer 99% des éléments fixés.

Le thorium est déterminé par spectrophotométrie à l'aide de l'orangé de xylénol à pH 2, et le Thorium avec les terres rares à pH 6.

Des expériences faites avec la radioeuropium ajouté à la solution de nitrate d'uranyle ont montré que la méthode est valable pour séparer les terres rares de fission à partir de l'uranium irradié. L'alumina est plus résistante aux effets de radiation que les .... échangeurs organiques d'ions. On peut également séparer le thorium-230, descendant de l'uranium-235, le thorium 231 et le thorium-22 descendants de l'uranium-235.

BIBLIOGRAPHY

- (1) R.W.Bane, U.S. Atomic Energy Comm. CC-3336, Nov. 1945
- (2) D.Dyrssen, Svensk Kem. Tidkr, 62, 153 (1950)
- (3) F. Asaro, F.S. Stephens, I. Pelman, Phys. Rev. 92, 1495 (1953)
- (4) W.K.Eister, G.P.Monet and F.L.Steshly - Report Mon. N-139, Aug. 1946
- (5) F.W.Strelow, Anal. Chem. 31, 1201 (1959)
- (6) H.J.Hettel, The quantitative separation of small amount of rare earths from thorium, uranium and zirconium by ion exchange. M.S. thesis, Iowa State University, Ames, Iowa, 1956
- (7) K.A.Kraus and G.E.Moore, J. Am. Chem. Soc. 72, 4293 (1950)
- (8) Roy Ko and M.R.Weiler, Anal. Chem. 34, 85 (1962)

- (9) K.A.Kraus and F.Nelson, Inter. Nat. Conf. Geneva 1955, 7, 113-131
- (10) S.S.Berman, L.E. Mckinney, M.E.Bednas. Talanta 4, 153 (1960)
- (11) L.R.Bunney and N.E. Ballon, J.Pascal, Anal. Chem. 31, 324 (1959)
- (12) A.Chesney and P.Reynaut, Intern. Nat. Conf. Geneva 1955, 9, 667
- (13) E.Tommic, I.Ladenbauer and M.Pollak, Z. Anal. Chem. 161, 28 (1958)
- (14) A.Kraus, F.Nelson and G.E.Moore, J. Am. Chem. Soc. 78 , 2692 (1956)
- (15) J.P.Faris and R.F. Buchanan, Anal. Chem. 30, 1909 (1958)
- (16) K.A.Kraus and F.Nelson, Inter. Nat. Conf. Geneva 1955, 7, 113
- (17) J.Danon, J. Am. Chem. Soc. 78, 5983 (1956)
- (18) Y.Chen, J.Chinese Chem. Soc., Ser II, 4, 47 (1957)
- (19) R.F.Buchanan and J.P.Faris, RICC/173, USA 1960
- (20) D.J.Carswell, J.Inorg. Nucl. Chem. 3, 384 (1957)
- (21) Ying Mao Chen, Chem. Abstr. 49, 156199 (1955)
- (22) J.S.Fritz and D.J. Pietrzyk, Talanta 8, 143 (1961)
- (23) L.I.Katzin and E.Gebert, J. Am. Chem. Soc. 75, 801 (1953)
- (24) C.W.Davies and B.D.R. Owen, J. Chem. Soc. 1676-1681 (1956)
- (25) D.G.Tuck and G.A.Welch, J. Inorg. Nucl. Chem., 9, 302 (1959)
- (26) A.Iguchi, Bull. Chem. Soc. Japan, 31, 600 (1958)
- (27) F.H.Burstall, P.S.Forrest, N.F.Kember and R.A.Wells, Ind. Eng. Chem., 45, 1648 (1953)

- (28) E.W.Berg and J.T.Truemper, Anal. Chem. 30, 1827 (1958)
- (29) M.O.Kojima, Japan Analyst 6, 369 (1957)
- (30) Y.Yoshimo and Y.Kurimura, Bull. Chem. Soc. Japan, 30 ,  
563 (1957)
- (31) J.Korkisch, USAEC - Rept. TID-13676
- (32) Vasant Kargaonkar, CEA-R-3222, Out. 1967
- (33) Claude W.Sill and Conrad P.Willis, Anal. Chem., 36, 622  
(1964) and Report USAEC-IDO 12034, Dec. 1963
- (34) W.Ryan and A.F.Williams, Analyst 77, 293 (1952)
- (35) A.F.Williams, Analyst 77, 297 (1952)
- (36) F.H.Burstall and R.A.Wells, Analyst 76, 396 (1951)
- (37) D.A.Everest and J.V.Martin, Analyst 82, 807 (1957)
- (38) Walter D.Tucker, M.W.Greene, A.J.Weiss, Alex Murrenhoff,  
BNL-3746, Brookhaven National Laboratory, Upton, Long  
Island, New York
- (39) Marcello Breseti, Renato Lanz and Anna Maria Del Turco,  
Annali Di Chimica, 51, 352 (1961)
- (40) Anil K. Mukherji, Microchemical Journal 11, 243-254  
(1966)
- (41) H.W.Dodgen, Report DYO-5223 (1957) and J. Am. Chem. Soc.  
71, 2600 (1949)
- (42) H.G.Short and W.L.Dutton, Report BR-142 (1942)