

ION EXCHANGE PROCEDURES

IV. SEPARATION OF ^{234}Th (UX_1) FROM URANYL NITRATE SOLUTIONS*, **

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In studies involving various equilibria and reactions of Th(IV), use of a thorium tracer is sometimes desirable to facilitate analyses. The tracer ^{230}Th (ionium), $T_{1/2} = 8 \cdot 10^4$ years, is often selected for this purpose, but its analysis requires α -counting which is time consuming. A more convenient tracer is ^{234}Th (UX_1), $T_{1/2} = 24.1$ days. Being a γ -emitter, it may readily be determined in liquid samples by scintillation counting. The isotope is also readily available since it arises from decay of uranium (^{238}U).

The procedure described here was developed for routinely separating ^{234}Th from uranium and other activities associated with uranium; it is a modification of the cation exchange method first used by BANE² and DYRSSEN³.

DISCUSSION

The procedure was developed specifically for recovering ^{234}Th from uranyl nitrate hexahydrate, selected because this compound is readily available and very soluble. The procedure was designed for processing *ca.* 400 g of this salt. This contains 63 μC of ^{234}Th at secular equilibrium which is sufficient for a considerable amount of tracer work. If desired, the procedure can readily be adapted to handling substantially larger amounts of uranium.

The method is based on the very high selectivity of cation exchangers of the Dowex 50 type for Th(IV). The salt is dissolved in sufficient 0.1 M HNO_3 to yield a 0.4 M U(VI) solution. This solution is passed into a small bed of cation exchange resin (*ca.* 10 ml bed volume) to concentrate Th on the resin bed. During this step, the bed is converted essentially completely to the UO_2^{2+} form; however, the adsorbed uranium is readily eluted by 6 M HCl while leaving Th(IV) on the resin.

Th(IV) is removed from the resin in a sharp band with 6 M HCl -1 M HF solution, presumably through formation of weakly adsorbed fluoride complexes. Although sulfuric acid or organic complexing agents, *e.g.*, citrates, oxalates, etc., may also be

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used to elute Th(IV) from cation exchangers⁴, use of HCl-HF media is preferred since these acids are readily removed by evaporation in subsequent concentration steps.

The thorium fraction usually still contains small amounts of uranium, Fe(III) and other impurities, such as resin degradation products including traces of sulfate, so that further purification is desirable. Organic matter is destroyed by evaporation to near-dryness with concentrated HClO₄-HNO₃ solution. The residue is dissolved in a small amount of 6 M HCl and added to a second (small) cation exchange column. A fine mesh resin of relatively low cross-linking (4 %) is used in the second purification step to improve rates of elution. This resin should be of "analytical grade". This second column is washed sequentially with 6 M HCl and 4 M HCl to remove U(VI) and Fe(III) impurities; Th(IV) is then eluted with 6 M HCl-1 M HF.

The uranium nitrate solution can be stored; after an appropriate time for growth of the ²³⁴Th daughter, it can be reprocessed.

This method of isolation of UX₁ is relatively slow since about 20 h are required for the concentration step. However, we consider it preferable to a more rapid carrier technique (*e.g.* co-precipitation with LaF₃) since fewer manipulations are required; the column can be operated essentially without attention during the concentration step. A relatively slow flow rate is also recommended for the purification step, since in this way high product purity is assured.

TYPICAL SEPARATION

About 400 g of uranyl nitrate hexahydrate were dissolved in 2 l of 0.1 M HNO₃ and the solution passed into a 1.75 cm² × 5.7 cm (10 ml) column of water-washed Dowex 50-X8 resin (100-200 mesh) in the hydrogen form. Flow rate was adjusted to about 1 cm/min. After the solution had passed through, it was washed with 4 column volumes (c.v.) of 6 M HCl and then with 4 c.v. of 6 M HCl-1 M HF to elute the thorium (UX₁). The eluent containing thorium was collected directly in a Teflon evaporating dish, 1 ml each of concentrated HClO₄ and HNO₃ were added and the solution evaporated to a small volume (0.1 ml). The sample was taken up in 1 ml of 6 M HCl and added to a 0.28 cm² × 3 cm column of Dowex 50-X4 resin (200-400 mesh) which had been pretreated with 6 M HCl. The column was washed with 1 c.v. of 6 M HCl and then with 9 c.v. of 4 M HCl. Fig. 1 gives a plot of counting rate *versus* column volumes of effluent. The elution band which appears with maximum counting rate near 2.5 c.v. was found by decay rate measurements and γ -spectroscopy to consist primarily of 1.18 min ²³⁴Pa (UX₂) and 6.7 h ²³⁴Pa (UZ), arising from decay of ²³⁴Th. Thorium was removed in a sharp band with 6 M HCl-1 M HF solution.

PROCEDURE

(a) Materials and reagents

Resins. Dowex 50W-X8, 100-200 mesh, hydrogen-form cation exchanger. Dowex 50W-X4, 200-400 mesh, "analytical grade" hydrogen-form cation exchanger.

Apparatus. Two sizes of polyethylene tubing, 1.5 cm diameter (area 1.75 cm²) and 0.6 cm diameter (area 0.28 cm²) in 10 cm lengths are used to prepare columns. A one-hole rubber stopper, carrying a small section of plastic tubing containing a porous Teflon plug, is inserted in the larger tube to retain resin. The smaller tube (used for the second column) is softened at one end by heating, pulled to a tip and a

porous Teflon plug is inserted. Additional apparatus includes 2 l glass containers plastic test tubes, Teflon evaporating dishes, plastic transfer pipets, and syringes.

Columns. The columns used are given in Table I.

Solutions. 6 M HCl; 4 M HCl; 6 M HCl-1 M HF; conc. HClO₄; conc. HNO₃.

TABLE I

	Column 1 Concentration step	Column 2 Purification step
Resin	Dowex 50	Dowex 50
Cross-linking	X8	X4
Form	H ⁺	H ⁺
Mesh size	100-200	200-400
Column length (cm)	5.7	3
Flow rate (cm/min)	1	0.4
Temp. (°C)	25	25
Load solution	0.4 M UO ₂ (NO ₃) ₂ -0.1 M HNO ₃	6 M HCl
Load solution volume	2 l	1 ml
Wash solution and volume (column volumes, c.v.)	6 M HCl (6 c.v.)	(1) 6 M HCl (1 c.v.) (2) 4 M HCl (9 c.v.)
Eluent for UX ₁ fraction and volume (c.v.)	6 M HCl-1 M HF (6 c.v.)	6 M HCl-1 M HF (6 c.v.)

(b) Feed preparations

400 g of uranyl nitrate hexahydrate are dissolved in 2 l of water containing 14 ml of concentrated HNO₃. Final composition is about 0.1 M HNO₃-0.4 M UO₂(NO₃)₂.

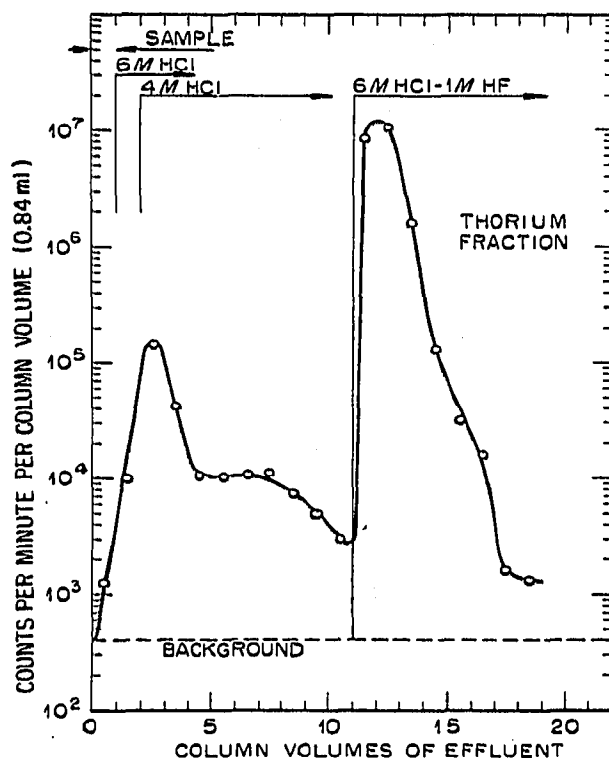


Fig. 1. Counting rate of effluent fractions in purification of Th(IV) by cation exchange (Dowex 50-X4, 200-400 mesh, 3 cm × 0.28 cm² column, 25°).

(c) *Column operations and effluent treatment*

1. *Concentration of ^{234}Th .* Resin as a slurry in water is added to the larger column to form a bed about 6 cm in length. Uranyl nitrate solution is introduced through tubing connected to the top of the resin column by a one-hole rubber stopper. The reservoir of feed solution is placed at a sufficient height (about 20 in.) above the resin bed to produce the desired flow rate. About 20 h are required for the concentration step.

After the feed has passed through the resin bed, the bed is washed with 4 c.v. of 6 M HCl to elute excess U(VI); Th(IV) is eluted with 4 c.v. of 6 M HCl-1 M HF.

2. *Purification of ^{234}Th .* The HCl-HF effluent is collected in a Teflon dish; 1 ml each of concentrated HClO_4 and concentrated HNO_3 are added and the solution is evaporated to a small drop of about 0.1 ml. This is taken up in 1 ml of warm 6 M HCl to yield a Th(IV) concentrate of about 1 c.v. for the next operation.

Dowex 50W-X4 "analytical grade" resin as a slurry in water is added to the smaller plastic column until a bed about 3 cm in length is formed. The column is pretreated with 6 M HCl and the ^{234}Th concentrate is added. The column is operated at a flow rate of 0.4 cm/min. When the sample has passed into the resin bed, 1 c.v. of 6 M HCl is added as rinse. This is followed by 9 c.v. of 4 M HCl. The Th (IV) is eluted into a Teflon dish with 5 ml (6 c.v.) of 6 M HCl-1 M HF. This effluent may be reduced in volume, and the HF driven off by fuming with concentrated HNO_3 or HClO_4 . About 2 h are required for the final purification step.

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SUMMARY

A cation exchange procedure is described for recovering microcurie amounts of carrier-free UX_1 (^{234}Th) from uranyl nitrate solution. Two ion exchange columns are employed, one for initial concentration and the other for final purification.

REFERENCES

- ¹ F. NELSON, D. C. MICHELSON AND J. H. HOLLOWAY, *J. Chromatog.*, 14 (1964) 258.
- ² R. W. BANE, *Rept. CC-3336*, Nov. 23 (1945).
- ³ D. DYRSSEN, *Svensk Kem. Tidskr.*, 62 (1950) 153.
- ⁴ E. K. HYDE, *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva, 1955* (United Nations, 1956), Vol. VII, p. 281.