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Chemistry
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SEPARATION OF ^{171}Tm FROM IRRADIATED ENRICHED ERBIUM

by

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ABSTRACT

A chromatographic cation exchange process was developed to separate ^{171}Tm from irradiated enriched erbium. 38 mg of pure thulium was separated from a 1-gram sample of irradiated $^{170}Er_2O_3$.

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INTRODUCTION

^{171}Tm may be used as a power source that requires low shielding weight. ^{171}Tm, with a half-life of 1.92 y, decays by beta emission (E_{max} = 0.098 Mev) to stable ^{171}Yb; a 0.067 Mev gamma ray occurs in ∿2% of the transitions. These low energy radiations are easily shielded. Pure ^{171}Tm has a specific power of 0.2 w/g. The oxide, Tm_2O_3 (melting point 2375°C), would probably be a useful fuel form.

Relatively pure ^{171}Tm can be produced only by neutron irradiation of erbium enriched in ^{170}Er, one of six stable erbium isotopes. Irradiation of either natural erbium or natural thulium (^{169}Tm) produces ∿1 Ci of ^{170}Tm per Ci of ^{171}Tm. ^{170}Tm is a high-energy (E_{max} = 0.97 Mev) beta emitter requiring considerable shielding for the bremmstrahlung; potential applications of ^{171}Tm (such as the power source of an artificial heart) require the ^{170}Tm concentration to be no greater than ∿1 ppm.[1]

In previous work,[2] ^{170}Tm and ^{171}Tm were separated from irradiated natural erbium by ion exchange, although separation of thulium from erbium was not complete. Efficient separation is needed if ^{170}Er is to be recycled to a reactor, and to obtain a ^{171}Tm power source of maximum power density.

This report describes an improved ion exchange process developed to separate ^{171}Tm from irradiated enriched Er_2O_3.

SUMMARY

A chromatographic cation exchange process was developed to separate thulium from irradiated erbium oxide. Two sequential cycles were used with ammonium N-hydroxyethylethylene-diamine-triacetate (HEDTA) as the complexing agent. Most of the erbium is removed in a displacement development cycle, with final separation in an elution development cycle. Diffusion kinetics are improved by operation at 85°C.

The process was successfully demonstrated with 630 mg of irradiated Er_2O_3, enriched to 96.07 isotope % ^{170}Er. 38.0 of a total of 40.1 mg of ^{171}Tm (99.61% ^{171}Tm, 0.39% ^{170}Tm) was separated in a fraction that contained <400 ppm of erbium.

DISCUSSION

Target Preparation and Irradiation

1.044 g of Er_2O_3 powder, prepared from erbium that was calutron-enriched to 96.07 isotope % ^{170}Er at Oak Ridge was sealed in a quartz ampoule and placed in an aluminum capsule packed with aluminum powder.

The only chemical impurities found by spectrographic analysis in the Er_2O_3 powder were 100 ppm Yb and <80 ppm Tm. Isotopic composition of the enriched erbium is given in Table I.

TABLE I

Isotopic Composition of Enriched Erbium

Isotope	Atom %
162	<0.05
164	<0.1
166	1.03 ±0.05
167	0.96 ±0.05
168	1.94 ±0.05
170	96.07 ±0.1

The Er_2O_3 powder was irradiated in a thermal flux at a Savannah River reactor to a total exposure of $\sim 2.5 \times 10^{22}$ n/cm^2, yielding ∿65 Ci of ^{171}Tm. Processing was begun two months after discharge from the reactor.

Target Decapsulation and Dissolution

The aluminum capsule and powder were dissolved in hot 2M NaOH - 2M $NaNO_3$. Because the ampoule had been broken prior to dissolution, some of the erbium and thulium oxides entered the alkaline solution. The oxides were filtered from the solution, and were dissolved from the filter with 0.2M HNO_3; 40.1 mg

(44.2 Ci) of ^{171}Tm were separated from this solution by ion exchange as described in a later section. After several weeks, a precipitate formed in the alkaline solution. Filtration gave a filtrate containing 1.9 mg of ^{171}Tm and a precipitate partially soluble in 0.2M HNO_3. The dissolved precipitate contained 19.1 mg of ^{171}Tm contaminated with iron.

Cation Exchange Chromatography

The chromatographic separation of thulium from erbium is based on differences in stability of the complexes formed by chelating agents with Er(III) and Tm(III). The metal ions are first sorbed on a column of cation exchange resin, and the column is washed with a dilute solution of the complexing agent. The thulium moves slightly faster down the column than the erbium because thulium forms a stronger complex with the chelating agent.

In general, two types of chromatographic development are possible, displacement and elution. In displacement development (elutriant solution at high pH), the bands are contiguous and move at equal rates. The boundaries between bands are not ideally sharp; a certain degree of overlap occurs. In elution development (elutriant solution at low pH), the bands travel at different rates and thus move apart as they proceed down a column. However, the bands also spread as they move and overlap is sometimes considerable. Displacement development is generally used for separation of multigram quantities of materials; elution development for milligram quantities. In both types, temperatures can be elevated to reduce overlap and to sharpen the bands by improving diffusion kinetics.

For the expected ^{171}Tm-^{170}Er mixture, a two-cycle ion exchange separation process was designed -- most of the erbium was removed in a displacement cycle; final separation of thulium from the remaining erbium was achieved in an elution cycle. HEDTA was selected as the complexing agent because of its large Er-Tm separation factor* and its rapid ion exchange kinetics.[3]

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*Separation factor = the ratio of the stability constants of the complexes, $K_{Tm}/K_{Er} = 10^{15.38}/10^{15.17} = 1.6$.

Cation Exchange Separation of Tm from Er.

Displacement Cycle

The calculational methods of Helfferich[4] and Powell and Spedding[3] and the theoretical plate height data of Sellers and Powell[5] were used to design a displacement development cycle assuming an expected composition of 98.5 mg of ^{171}Tm and 769 mg of ^{170}Er in the irradiated Er_2O_3. (The actual composition of the mixture processed was different from this, as explained in the following paragraphs.) Results of the calculations (shown in the appendix) are summarized in Table II.

TABLE II

Ion Exchange Displacement Cycle Design

Column diameter: 6 mm
Column length: 50.2 cm
Temperature: 85°C
Amount of erbium containing <0.1% thulium to be separated from original Er-Tm mixture: 646 mg
Composition of product (feed to subsequent elution cycle): 123 mg ^{170}Er, 98.5 mg ^{171}Tm

Two ion exchange columns were used in the displacement cycle: the first to remove impurities from the Er-Tm mixture and achieve partial Er-Tm resolution, the second to separate erbium and thulium under the design conditions in Table II. Erbium and thulium were absorbed from the dilute nitric acid solution on "Dowex"* 50W-X8, 100-200 mesh, NH_4^+ form resin in a 1-cm-ID column filled with resin to a height of 27 cm. Elution was begun at 60°C and 0.65 ml/(cm^2)(min) with 0.02M HEDTA at pH 7.9. Impurity bands were eluted rapidly, and the motion of the colorless thulium band was estimated from observation of the pink erbium band following it. After 10 hours of elution, a second column of the same resin (6 mm ID, 45 cm tall) was used to receive the continuing flow of eluate from the first column. When all of the thulium and erbium had been sorbed in the second column, the temperature and flow of the continuing elution through the two columns were increased to 85°C and 1.25 ml/(cm^2)(min). The first column acted as an elutriant degasser for the Er-Tm column. The moving ^{171}Tm band and the eluted ^{171}Tm solution glowed blue-white. The erbium remaining in the second column after the ^{171}Tm elution was eluted rapidly with 0.2M HEDTA at pH 8.2.

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*Trademark of Dow Chemical Co.

Separation of thulium from erbium was better than expected, probably because the amounts of erbium and thulium were less than the design quantity. The first cycle elution diagram is shown in Figure 1; product fractions were grouped into four batches as shown in Table III.

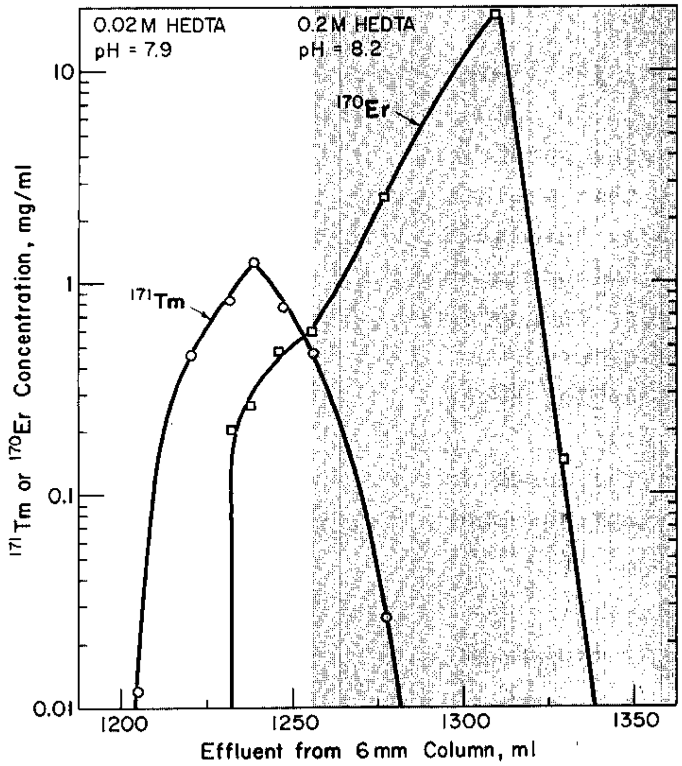

FIG. 1 ^{171}Tm-^{170}Er DISPLACEMENT CYCLE

TABLE III

^{171}Tm-^{170}Er Ion Exchange Product Fractions (Displacement Development)

Product Fraction	^{171}Tm, mg(a)	^{170}Er, mg
1	9.2	<0.01
2	30.3	27.0
3	0.6	92.8
4	<0.05	513
	40.1	632.8

(a) Corrected to the reactor discharge.

Each fraction was processed further by precipitation of erbium and thulium oxalates from 1M oxalic acid followed by calcination to the oxides.[2] Fractions 1, 3, and 4 were stored. Feed solution for the second ion exchange cycle was obtained by dissolving Fraction 2 in 15 ml of hot 0.1M nitric acid.

Elution Cycle

Preparatory tests with nonradioactive erbium and thulium were made in 1-cm-ID columns of "Dowex" 50W-X8, 100-200 mesh resin to determine conditions for the second (elution) ion exchange cycle that would achieve the best separation of the expected mixture. Erbium was determined by atomic absorption spectroscopy; thulium was traced with ^{170}Tm and determined by liquid scintillation counting. In most of these tests, the amount of thulium used was equal to that expected in the product from the first cycle; however, the Er/Tm ratio was somewhat greater. Separations were excellent as summarized in Table IV. Temperature is the most critical variable. The need for degassing the elutriant was shown by the gassing in the column in Run 5.

TABLE IV

Cation Exchange Separation of Thulium from Erbium
(Elution Development)

Column: 0.78 cm^2, "Dowex" 50W-X8, 100-200 mesh
Elutriant: 0.02M HEDTA

Test	1	2	3	4	5
Resin form	NH_4^+	NH_4^+	NH_4^+	H^+	NH_4^+
Column length, cm	12	12	28	29	28
Temperature, °C	22	22	22	22	60
Column load, mg					
Thulium	98.5	98.5	98.5	50.2	98.5
Erbium	167.4	167.4	167.4	73.3	167.4
Elution conditions					
Flow, ml/(cm^2)(min)	0.8	0.5	0.5	0.4	0.4
pH	4.52	4.52	4.30	4.60	4.30
Elutriant to peak, bed volumes					
Thulium peak	22	21	16	40	8.5
Erbium peak	53	46	33	44	-
Tm product fraction					
Tm recovery, % of feed	88	92	94	93	98
Tm purity, wt % Tm	74	78	73	86	97

^{171}Tm and ^{170}Er were absorbed from dilute nitric acid onto "Dowex" 50W-X8, NH$_4^+$ form, 100-200 mesh resin in a column 1 cm ID and 27 cm tall. Elution was begun at 70°C and 0.38 ml/(cm^2)(min) with 0.02M HEDTA at pH 4.3. Progress of the ^{171}Tm band was monitored by observing the fluorescence in a strip of "Cronex"* X-ray screen taped to the column. (Gassing in the column was prevented by first passing elutriant through a similar ion exchange column at 70°C; gassing was severe in this pretreatment column.) Removal of ^{171}Tm began after 20 hours of elution and was complete 8 hours later. Erbium remaining in the column was eluted rapidly with 0.2M HEDTA at pH 8.0.

Separation of thulium from erbium was excellent, as shown in Figure 2. Product fractions were grouped into the three batches listed in Table V.

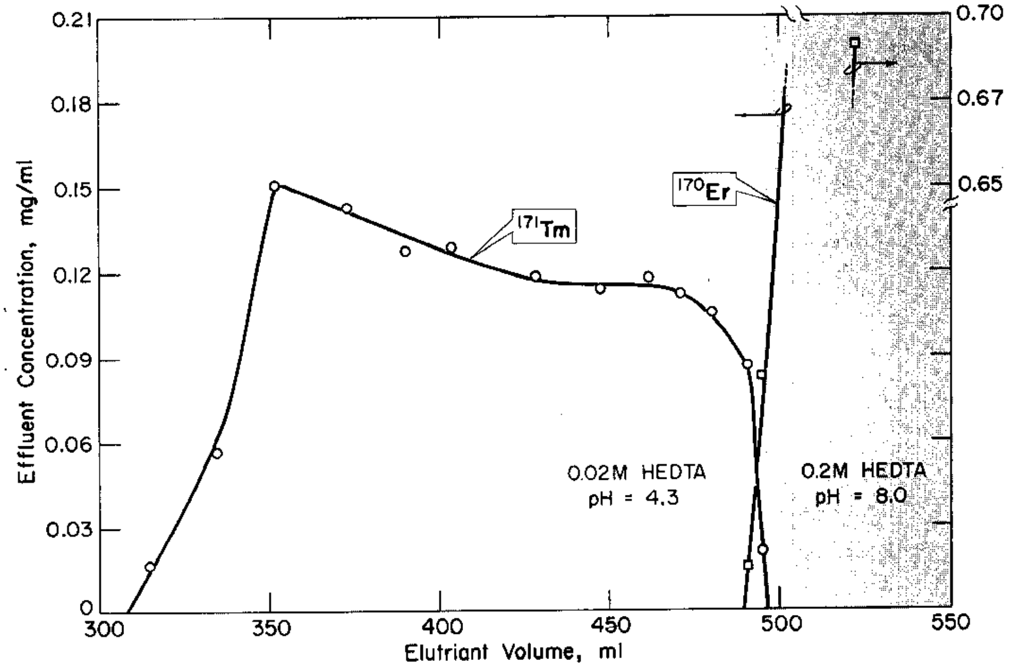

FIG. 2 ^{171}Tm-^{170}Er ELUTION CYCLE

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*Trademark of E. I. du Pont de Nemours & Co.

TABLE V

^{171}Tm-^{170}Er Ion Exchange Product Fractions (Elution Development)

Product Fraction	^{171}Tm, mg	^{170}Er, mg
1	28.8	<0.007
2	1.5	0.8
3	<0.02	26.2

^{170}Er was precipitated as the oxalate from Fraction 3 and calcined to $^{170}Er_2O_3$. The oxalates could not be precipitated from Fractions 1 and 2, probably because a strong complexing agent had been formed by radiolytic degradation of HEDTA during two months storage following the elution cycle. The ^{171}Tm could be absorbed onto cation exchange resin indicating that the complexing agent had a charge $\geqslant -2$. The ^{171}Tm was successfully precipitated as the fluoride.

Overall Product Composition

Product composition through both cycles of ion exchange is summarized in Table VI.

TABLE VI

^{171}Tm-^{170}Er Ion Exchange

Product Fraction	^{171}Tm, mg	^{170}Er, mg
1 (Fraction 1, Table III & Fraction 1, Table V)	38.0	<0.017
2 (Fraction 3, Table III & Fraction 2, Table V)	2.1	93.6
3 (Fraction 4, Table III & Fraction 3, Table V)	<0.07	539

^{171}Tm was determined by isotope-dilution mass spectrometry and liquid scintillation counting and ^{170}Er by isotope dilution. The sensitivity of the isotope dilution method fixes the ^{170}Er concentration in Fraction 1 at <450 ppm and the ^{171}Tm concentration in Fraction 3 at <130 ppm.

The isotope dilution method was used to determine the erbium and thulium isotopic compositions after irradiation. The results are shown in Table VII.

TABLE VII

Isotopic Compositions of Erbium and Thulium at Reactor Discharge

Thulium		Erbium	
Isotope	Atom %	Isotope	Atom %
170	0.39	162	<0.002
171	99.61	164	0.024
		166	0.800
		167	0.020
		168	3.55
		170	95.60
		171	None

Although the thulium is isotopically quite pure by ordinary standards, the ^{170}Tm content is ~10^3 greater than desired for ^{171}Tm power sources for medical uses.[1] Erbium enriched to >99.99% ^{170}Er would probably be required for production of ^{171}Tm with sufficiently low ^{170}Tm content.

RECOMMENDATIONS

As a result of this work, the following recommendations can be made for more efficient production and ion exchange separation of ^{171}Tm.

(1) ^{170}Er must be highly enriched (>99.99%) to produce ^{171}Tm of the isotopic quality required for medical applications.

(2) In a large-scale production operation, one cycle of displacement cation exchange separation (with a small recycle fraction) with HEDTA would probably be sufficient to yield ^{171}Tm of the required purity.*

(3) Thulium must be precipitated as the oxalate immediately after elution to avoid formation of strongly complexing HEDTA radiolysis products which inhibit formation of the oxalate.

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*In any future tests or in large-scale application, the newly developed technique of using fine particle resin in pressurized columns would be used. Similar chromatographic separations of lanthanides have been performed in this laboratory at flows up to 16 ml/(cm^2)(min), 13 times faster than the flow used in this work.[6,7]

APPENDIX

CALCULATION OF CONDITIONS FOR DISPLACEMENT DEVELOPMENT CYCLE

Basis: Separation of 769 mg ^{170}Er and 98.5 mg ^{171}Tm

Elutriant: 0.02M HEDTA

Resin: "Dowex" 50W-X*, 100-200 mesh

Er and Tm Band Lengths[4]

$$Z_i = \frac{M_i \quad Q_i}{q(X + \beta C)}$$

Z_i = band length of species i, cm

M_i = valence of species i = 3 for Tm and Er

Q_i = amount of i (Q_{Tm} = 0.576 mmoles, Q_{Er} = 4.52 mmoles)

q = column cross-sectional area = $\frac{\pi}{4}$ d^2 = 0.786 cm^2

X = resin capacity = 1.9 meq/ml

β = fractional bed void space = 0.31

C = concentration of elutriant = 0.06 meq/ml

d = column diameter, cm

$$Z_{Tm} = \frac{(3)\ (0.576)}{0.786\ d^2\ [1.9 + (0.31)(0.06)]} = \frac{1.14}{d^2}$$

$$Z_{Er} = \frac{(3)\ (4.52)}{0.786\ d^2\ [1.9 + (0.31)(0.06)]} = \frac{9.00}{d^2}$$

$$Z_{Tm} + Z_{Er} = 10.14/d^2$$

Distance Required for Steady-State Resolution[4]

$$Z_{sep} \cong Z_{B+C} \frac{M_C Q_C + \alpha_B^C M_B Q_B}{(M_B Q_B + M_C Q_C)(\alpha_B^C - 1)}$$

where

Z_{sep} = distance a band must travel to attain steady-state resolution of its two components, cm

Z_{B+C} = length of band being displaced, cm

For B = Tm and C = Er, $\alpha_B^C = 1.6$, $M_BQ_B = 1.73$ meq, and $M_CQ_C =$ 13.56 meq

Therefore,

$$Z_{sep} = 10.14/d^2 \; \frac{13.56 + (1.6)(1.73)}{(1.73 + 13.56)(1.6-1)} \cong 18.1/d^2 \text{ cm}$$

Length of Overlap Region[3]

$$L = \frac{6h}{\log \alpha_B^C}$$

L = length of overlap region between 99.9% C and 99.9% B, cm

h = theoretical plate height, cm. At 85°C and HEDTA flow of 1.25 ml/(cm²)(min), h ≅ 0.25 cm for Er-Tm separation.[5]

Therefore,

$$L \simeq \frac{(6)(0.25)}{0.204} = 7.4 \text{ cm}$$

Selection of Experimental Conditions

Band lengths and separation distances can now be calculated as a function of column diameter. Results are tabulated below.

Band Lengths and Separation Distances
(Displacement Development)

d, cm	Z_{Er}, cm	Z_{Tm}, cm	Z_{sep}, cm
2	2.2	0.3	4.5
1	9.0	1.1	18.1
0.8	14.2	1.8	28.2
0.6	25.0	3.2	50.2
0.5	36.0	4.6	72.3
0.4	56.2	7.1	113
0.3	100	12.7	201

A 0.6-cm-ID column was chosen to give the best separation compatible with ease of column fabrication and space in the containment facility.

Expected ^{171}Tm-^{170}Er Separation and Composition of Product (Elution Cycle Feed)

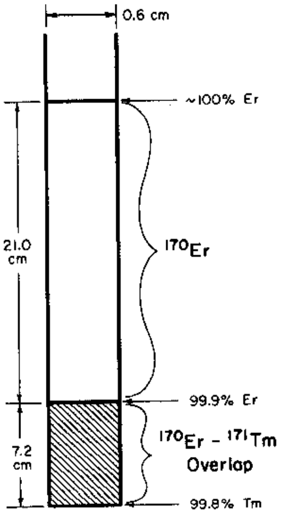
The following figure shows the Er-Tm distribution in a 0.6-cm-ID ion exchange column just as the first metal ions are eluted from the column. This distribution is based on an overlap distance of 7.4 cm and the distances for a 0.6-cm column given in the table. Assume that all ^{170}Er above the overlap region will be separated. Material in the overlap region will compose the feed for the ion exchange elution cycle.

$$\% \text{ of } {}^{170}\text{Er separated} = \left(\frac{21.0 \text{ cm}}{25.0 \text{ cm}}\right) 100 = 84.0\%$$

16.0% of original ^{170}Er in elution cycle feed

$(0.16)(769) = 123$ mg ^{170}Er

Assuming negligible ^{171}Tm losses, elution cycle feed will contain 98.5 mg of ^{171}Tm



^{171}Tm - ^{170}Er DISPLACEMENT CYCLE

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