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SEPARATION OF CERIUM BY ANION EXCHANGE

AUTHOR

F. P. Roberts

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SEPARATION OF CERIUM BY ANION EXCHANGE*

by

F. P. Roberts

Hanford Laboratories
General Electric Company
Richland, Washington

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INTRODUCTION

The absorption of cerium(IV) on strong base anion exchangers from nitric acid solutions should be very similar to the behavior of thorium. A number of papers have been published[1,2,3] in recent years describing separations of thorium based on absorption on anion exchanges but up to this time no quantitative data on cerium have been reported.

Since there are few metallic nitrate complexes which are strongly absorbed on anion exchangers (notable exceptions are the quadrivalent actinides) [4] separation of cerium from many elements including the trivalent rare earths can be achieved by simply loading the cerium(IV) in nitric acid solution on an anion exchanger and washing the unwanted metals from the resin. However, organic ion exchange resins have reducing properties which make the quantitative absorption of cerium(IV) impossible in the absence of a holding oxidant. We have found that this difficulty can be surmounted by using a column containing a strong base anion exchange resin and a solid oxidant. Lead dioxide was found to be a useful oxidant for this purpose because:

a. It rapidly oxidizes cerium(III) to cerium(IV) in nitric acid and eliminates the need for a pre-oxidation step.

b. It is relatively insoluble in nitric acid and can be mixed with the resin to make an oxidizing anion exchanger.

The behavior of cerium with this oxidizing anion exchanger including batch equilibrium, and column experiments was studied and is discussed in this paper. A method for radiochemical determination of cerium-144 based on this behavior is also presented.

EXPERIMENTAL

Apparatus and Reagents

Dowex 1-X4 resin(100-200 mesh) in the chloride form was converted to the nitrate form by washing repeatedly with 5M nitric acid.

The distribution coefficients as a function of nitric acid concentration were obtained by agitating 5.0 ml of the nitric acid containing Ce-Pr-144 tracer with 0.50 grams of the nitrate form resin (dried in a vacuum at 70C) and 50 mg of lead dioxide for 24 hours. The cerium activity in the aqueous phase was determined by gamma energy analysis. The equilibrium acid concentration was determined by titration with standard sodium hydroxide. The distribution coefficients were calculated from:

$$K_d = \frac{(A-B).(\text{ml of solution})}{B.(\text{grams of resin})}$$

where

A = cerium activity in original solution

B = cerium activity is solution after equilibration with the resin.

The columns were prepared by adding a slurry of the prepared resin to 3 or 4 mm I.D. glass columns to give a settled bed volume of about one ml. Fifty mg of lead dioxide was mixed into the bed by means of a stainless steel wire. The resin was then washed with one ml of 8M nitric acid and was ready for use.

Procedure

Adjust the sample to contain 5-9M nitric acid. Add 1-2 mg cerium carrier and pass through the prepared column. Wash the resin with 10 ml of 8M nitric acid in increments of 2 or 3 ml. Elute the cerium with 6 ml of 0.5 M nitric acid. Allow two hours for Pr-144, the short-lived daughter of Ce-144, to reestablish equilibrium and determine the cerium disintegration rate by gamma energy analysis.

DISCUSSION AND RESULTS

Absorption of Cerium(IV) on Dowex

Distribution coefficients for Ce(IV) on Dowex 1-X4 resin over a wide range of concentrations of nitric acid are shown in Figure 1. The data of Danon[1] for thorium are reproduced here also for comparison. The cerium data show a maximum distribution coefficient at 7M nitric acid and suggest a wide range of conditions for quantitative cerium absorption. Favorable conditions for elution are indicated by the small values below 2M nitric acid.

Separation of Cerium from Trivalent Rare Earths

Figure 2 shows elution behavior of promethium-147 and cerium-144 from columns containing 1 ml of the Dowex 1-X4 resin and 50 mg of lead dioxide. The promethium elution was very sharp with 8M nitric acid. Ten ml removed greater than 99.9% of the promethium with no detectable loss of cerium. The elution of cerium with 0.5M nitric acid was also very sharp, although a slight tailing effect was observed. Six ml of 0.5M nitric acid removed 99.3% of the cerium. Elution of cerium with hydrochloric acid was similar to nitric acid. Hydrochloric acid, however, does dissolve the lead dioxide.

Effect of Lead Dioxide Concentration on Cerium Recovery and Decontamination

The effect of the amount of lead dioxide on cerium recovery and separation from some fission products was measured. Columns containing varying amounts of lead dioxide and one ml of the Dowex 1 resin were used to separate samples of mixed fission products. The results shown in Table I indicate that 50 mg lead dioxide per ml of resin is adequate for quantitative cerium absorption. The major fission products remaining are Zr-Nb-95 and Ru-106.

TABLE I

Effect of Lead Dioxide Content on Cerium Recovery and Decontamination from Fission Products

PbO_2 mg/ml resin	Amount of Fission Product in Cerium Fraction %					
	Ce-144	Sr-90	Ru-106	Cs-137	Zr-Nb-95	Pm-147
5	16.2	< 0.1	< 1	< 0.1	< 1	< 0.1
10	96.6	< 0.1	< 1	< 0.1	2.0	< 0.1
50	100.00	< 0.1	2.2	< 0.1	1.58	< 0.1
100	99.6	< 0.1	1.2	< 0.1	3.8	< 0.1
200	98.7	< 0.1	1.4	< 0.1	7.4	< 0.1

Determination of Cerium-144 in Strontium-90

The technique suggested above has been applied to the determination of trace amounts of cerium activity in the strontium-90 product recovered at Hanford. Direct determination of cerium-144 by gamma energy analysis is not feasible in this material because the bremsstrahlung from the decay of Sr-Y-90 masks the major photo-peak of cerium-144 and a separation from both strontium and yttrium is required.

Typical recoveries obtained with this method based on synthetic samples are shown in Table II. The general procedure is applicable to samples containing larger amounts of Sr-90 if greater sensitivity is required.

TABLE II

DETERMINATION OF CERIUM-144 IN SYNTHETIC STRONTIUM-90 SAMPLES

No.	D/M Sr-90	D/M Ce-144 added	D/M Ce-144 Found	% Recovered
1	$3x10^6$	36200	35900	99
2	$3x10^6$	18100	18500	102
3	$3x10^6$	3620	3490	96
4	$3x10^6$	1810	2050	113
5	$3x10^7$	3620	3750	103

SUMMARY

It was found that cerium(IV) nitrate complexes exhibit very similar anion exchange behavior as thorium. Cerium can be quantitatively absorbed on columns of strong base anion exchange resin containing 50-200 mg lead dioxide per ml of resin. The columns can be washed extensively with nitric acid without loss of cerium. The cerium can be eluted from the columns with dilute nitric acid or hydrochloric acid quantitatively. The technique described provides a rapid method for radiochemical determination of cerium and can be used as a means of preparing pure carrier free cerium tracer. The technique may also find application in determination of non-radioactive cerium.

REFERENCES

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3. Korkisch, J. and F. Tera, Anal. Chem. 33, 1264 (1961).

4. Ryan, J.L., E.J. Wheelwright, Ind. Eng. Chem., 51 60 (1959).

EQUILIBRIUM DISTRIBUTION COEFFICIENTS ON DOWEX 1

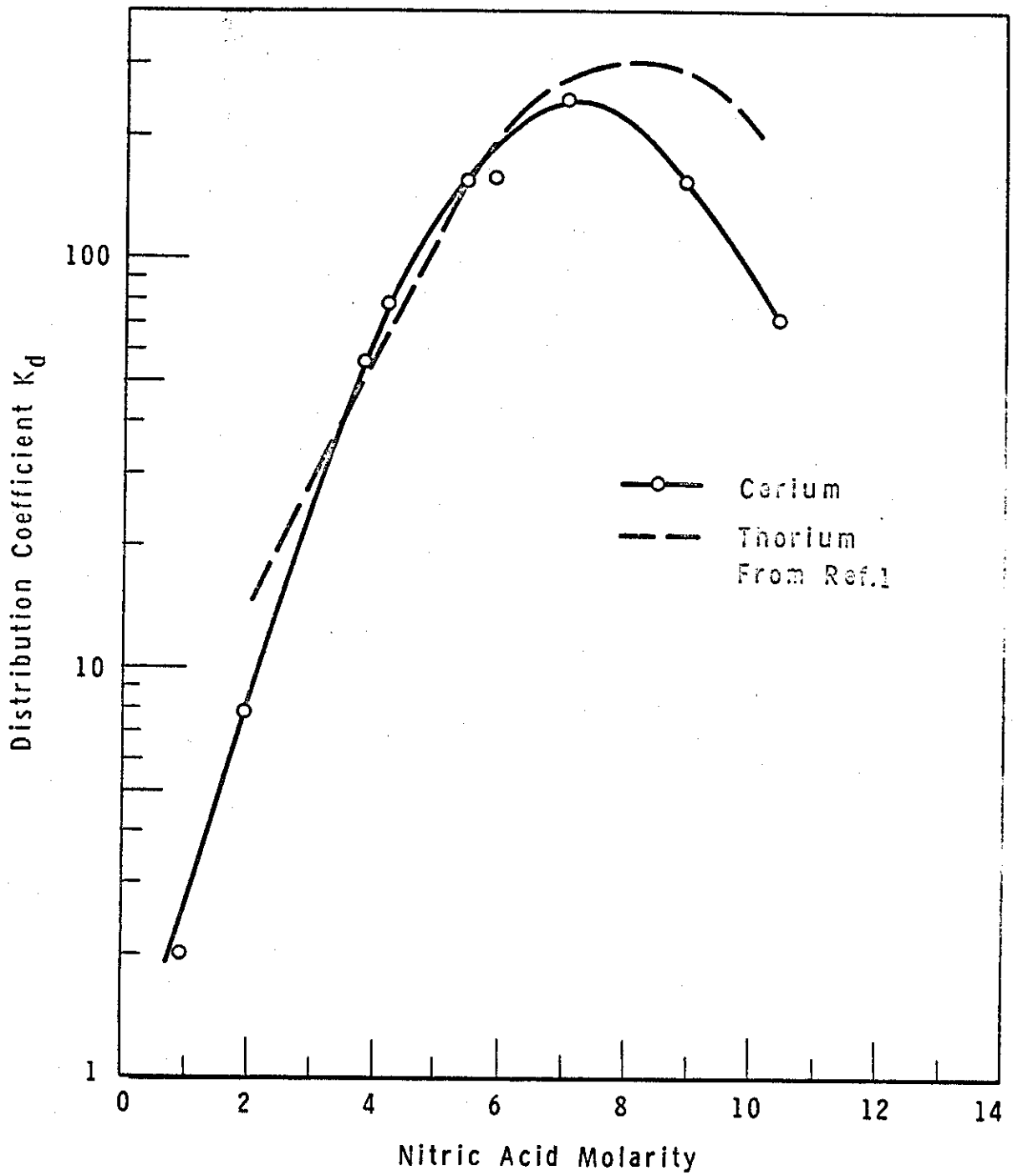

FIGURE 1

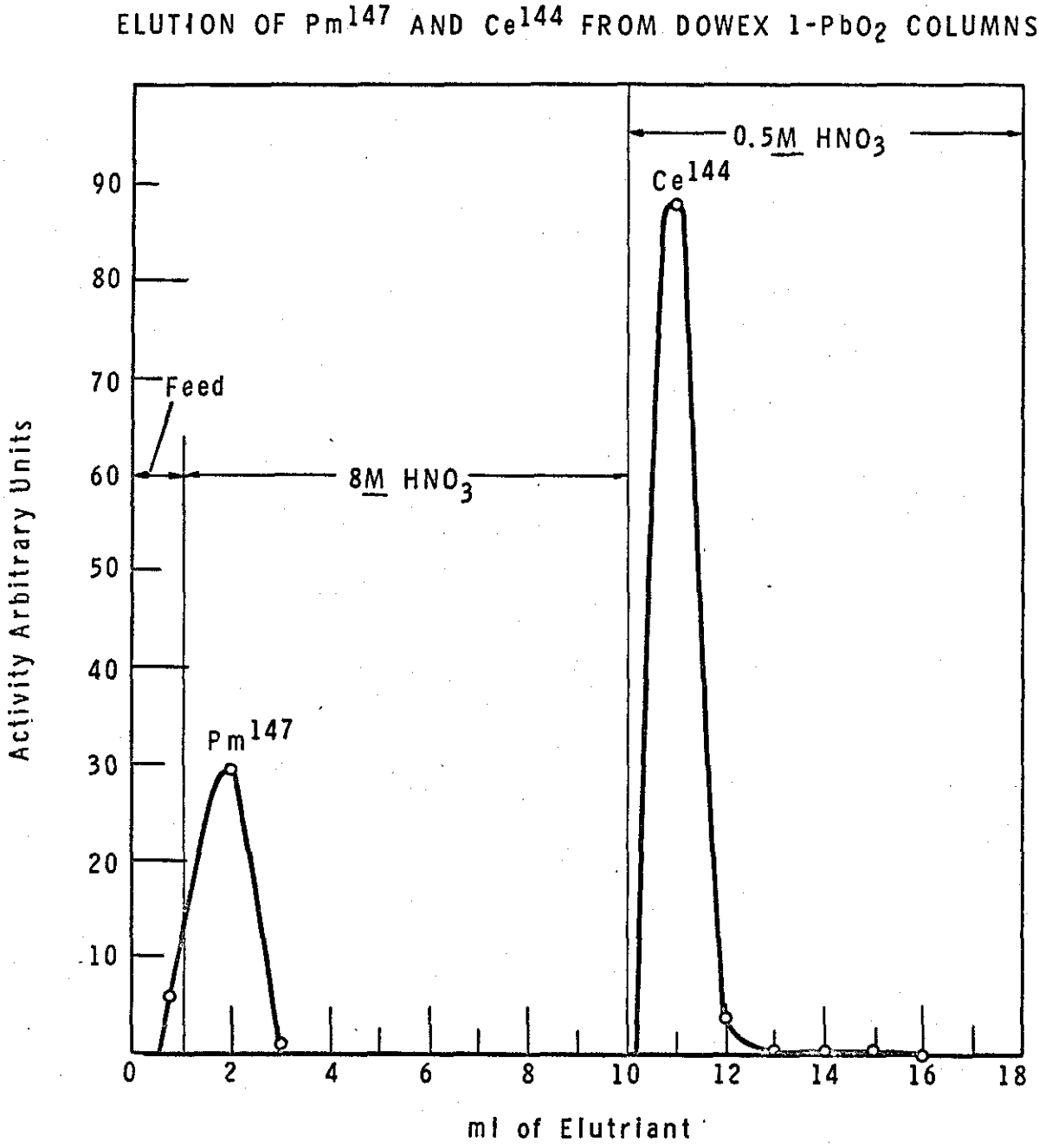
ELUTION OF Pm^{147} AND Ce^{144} FROM DOWEX 1-PbO_2 COLUMNS
0.5M HNO_3
Ce^{144}
Feed
8M HNO_3
Pm^{147}
Activity Arbitrary Units
90
80
70
60
50
40
30
20
10
0
2
4
6
8
10
12
14
16
18
ml of Elutriant

FIGURE 2