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**BASIC PRINCIPLES INVOLVED IN THE MACRO-SEPARATION
OF ADJACENT RARE EARTHS FROM EACH OTHER BY MEANS
OF ION-EXCHANGE**

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Basic Principles Involved in the Macro-Separation of Adjacent
Rare Earths from Each Other by Means of Ion Exchange

by

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Abstract

The separation of rare earth mixtures by ion exchange using ammonium ethylenediaminetetraacetate as an eluting agent and cupric ion as a retaining cation has been discussed in detail. Simple counter-current separation theory has been used to predict the minimum number of displacements of an adsorbed band that are necessary in order to separate the components of a binary mixture. It has been shown how the theory can be applied to even more complex systems and experimental data have been presented for some of the more difficultly separable groups of rare-earth species. Experimental results agree very well with the theoretical predictions.

I. Introduction

In an earlier paper (1) a general theory concerning the use

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- (1) F. H. Spedding and J. E. Powell, J. Am. Chem. Soc., 76, 2545 and 2550 (1954).
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of dilute citrate solution as an eluant for the rare earths was presented in some detail. It is the purpose of this article to extend the original theory to cover the use of ethylenediaminetetraacetate (EDTA) solutions for separating rare earths on cation-exchange columns. Wheelwright, Spedding and Schwarzenbach (2) and

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- (2) E. J. Wheelwright, F. H. Spedding and G. Schwarzenbach, J. Am. Chem. Soc., 75, 4196 (1953).
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Schwarzenbach, Gut and Anderegg (3) have measured the stability

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- (3) G. Schwarzenbach, R. Gut and G. Anderegg, Helv. Chim. Acta, 37, 937 (1954).
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constants of the individual rare-earth-EDTA complexes of the form RY^- in 0.1 M KCl and KNO_3 solutions. The relatively large differences between the stability constants of the adjacent rare-earth-EDTA complexes made this chelating agent attractive as an eluting agent and it was shown, subsequently, by Spedding, Powell and Wheelwright that EDTA solutions could be used to separate adjacent rare earths by the ion-exchange technique, provided a suitable retaining ion was adsorbed on the resin bed ahead of the rare-earth band. In the case of elutions with dilute citrate solutions, H^+ ion was used as the retaining ion, i.e., H^+ ion

adsorbed ahead of the rare-earth band caused the rare earths to redeposit on the resin bed simply by combining with the $\text{Cit}^{\equiv}$ ion to form H_3Cit . Hydrogen ion cannot be used efficiently as the retaining ion when rare earths are being eluted with EDTA, because the free-acid form of EDTA, H_4Y , is insoluble in water and precipitates in the interstices of the hydrogen-form resin bed. In general, any cation which forms a soluble, more stable complex with EDTA than the rare earths do can be used as a retaining ion. Likewise, a cation which forms a soluble complex which is slightly less stable than the rare earth complexes, but which is less tightly held by the resin than the rare earths can also be used as a retaining ion, provided that the combined effects cause the ion to precede the rare earths down the column. Both Fe^{+3} (4) and Cu^{+2} (5)

(4) F. H. Spedding, J. E. Powell and E. J. Wheelwright, J. Am. Chem. Soc., 76, 612 (1954).

(5) F. H. Spedding, J. E. Powell and E. J. Wheelwright, J. Am. Chem. Soc., 76, 2557 (1954).

have been used successfully, but Cu^{+2} was superior to Fe^{+3} . It was found that the pH range was limited when Fe^{+3} was used, since H_4Y tended to form and precipitate when the eluant was too acidic and $\text{Fe}(\text{OH})_3$ when the eluant was too basic. Due to the greater solubility of $\text{Cu}(\text{OH})_2$, Cu^{+2} can be used over a considerably greater pH range than Fe^{+3} . At eluant pH values above 8.0, however, some of the heavier rare earths, such as Lu, Yb, Tm and Er, are not completely retained by a Cu^{+2} bed. This may result in a partial or total loss of these elements unless precautions were taken. High

EDTA concentrations coupled with high pH values cause the formation of a deep-blue insoluble substance, having the empirical composition Cu_2Y , which may clog the column.

In the preliminary experiments with Cu^{+2} as the retaining ion, difficultly separable groups of rare earths were used and the adsorbed bands were eluted for distances just equal to their original lengths. Nevertheless, the separations achieved were considerably better than those obtained by eluting far greater distances with citrate as the eluant. Since the original experiments were performed, further studies have been undertaken and it seems desirable that the results of these investigations be presented.

II. Theoretical Considerations

A. Exchange Constants for the System

When a rare earth is eluted down a cupric-state resin bed with an ammonium salt of EDTA the following equilibria take place in the column.

The barred symbols refer to the resin phase and the unbarred symbols to the aqueous phase. The over-all reaction can be written as follows:

The equilibrium constant for this reaction is given by equation (4).

$$K_R = \frac{a^3(\overline{\text{NH}}_4^+) \cdot a(\text{RY}^-)}{a^3(\text{NH}_4^+) \cdot a(\overline{\text{R}}^{+3}) \cdot a(\text{Y}^-)} \quad (4)$$

When two rare earths, designated by the symbols R_1 and R_2 , are present as a mixture in a column the following equilibrium occurs.

$$K_{\frac{R_1}{R_2}} = \frac{K_{R_1}}{K_{R_2}} = \frac{a(\overline{R}_2^{+3}) \cdot a(R_1 Y^-)}{a(\overline{R}_1^{+3}) \cdot a(R_2 Y^-)} \quad (6)$$

As long as conditions are such that $R_1 Y^-$ and $R_2 Y^-$ are the only rare-earth-containing ions which are present in any appreciable amount in the aqueous phase, $K_{\frac{R_1}{R_2}}$ represents the separation factor which is defined as the ratio of R_1 to R_2 in solution divided by the ratio of R_1 to R_2 in the resin phase.

Since the resin itself is not highly selective as far as two adjacent rare earths are concerned, then

$$\frac{a(\overline{R}_1^{+3}) \cdot a(R_2^{+3})}{a(\overline{R}_2^{+3}) \cdot a(R_1^{+3})} = K_a \approx 1. \quad (7)*$$

* Actually the value of K_a for $\text{Nd} = R_1$ and $\text{Y} = R_2$ has been measured and found to be 1.8. These elements are six elements apart in the actual elution order observed with citrate and EDTA. Although K_a is near enough to unity that it can be ignored in the case of adjacent elements in the rare earth series, it should be taken into consideration for elements which are far apart. The values of $K_{\frac{R_1}{R_2}}$ are so large for elements which are far apart, however, that an additional factor of 2 or 3 would make little difference in the calculations which follow. See equations (16) and (18) in which ϵ is equal to the separation factor minus one.

Multiplying equation 6 by equation 7 gives

$$K_{R_2}^{R_1} \approx \frac{a_{(R_2^{+3})} \cdot a_{(R_1 Y^-)}}{a_{(R_1^{+3})} \cdot a_{(R_2 Y^-)}} \quad (8)$$

This means that one should be able to use data obtained from aqueous solutions alone to predict the behavior of two rare earths when they are eluted down an ion-exchange bed with EDTA.

For the rare earths, the activity coefficients are so nearly identical that they cancel out in the expanded form of equation (8) to give

$$K_{R_2}^{R_1} \approx \frac{m_{(R_2^{+3})} \cdot m_{(R_1 Y^-)}}{m_{(R_1^{+3})} \cdot m_{(R_2 Y^-)}}, \quad (9)$$

where m refers to the molal concentration rather than the activity. The stability constants of Wheelwright, Spedding and Schwarzenbach (2) for the EDTA complexes of the rare earths were defined as follows:

$$K_{R_1 Y}^{\prime} = \frac{m_{(R_1 Y^-)}}{m_{(R_1^{+3})} \cdot m_{(Y^{\equiv})}} \quad (10)$$

and

$$K_{R_2 Y}^{\prime} = \frac{m_{(R_2 Y^-)}}{m_{(R_2^{+3})} \cdot m_{(Y^{\equiv})}} \quad (11)$$

Consequently,

$$\frac{K_{R_1 Y}'}{K_{R_2 Y}'} = \frac{m(R_2^{+3}) \cdot m(R_1 Y^-)}{m(R_1^{+3}) \cdot m(R_2 Y^-)} \approx K_{R_2}^{R_1} \quad (12)$$

It is possible, therefore, to use the stability constants of the EDTA-rare-earth complexes in aqueous solutions to predict the behavior of rare earths when they are eluted down ion-exchange columns with EDTA. It is unfortunate that 0.1 m solutions, for which the apparent stability constants have been measured, are too concentrated to be used conveniently for eluting rare earths, but these data can still be used as a guide in predicting what will occur. $K_{R_2}^{R_1}$ would be expected to be virtually independent of ionic strength, since nothing but rare earth species are involved. Changes in activity coefficients would be mutually compensatory in this case.

In Table I the data of Wheelwright, Spedding and Schwarzenbach (2) have been used to calculate values of K_Y^R . R refers to a particular rare-earth species and Y stands for yttrium in this notation.

From the values of K_Y^R it is apparent that all the rare earths, with the exception of Dy and Tb, will separate from Y very readily* when eluted with EDTA down a cation-exchange column. Values of $K_{R'}^R$, for adjacent elements, where R refers to one rare earth and R' to the next less tightly complexed member of the

* A value of K_Y^R or $K_{R'}^R$, equal to unity signifies no tendency to separate. Values very much greater than unity or very much smaller than unity indicate that the elements R and Y or R and R' separate readily.

Table I

Values of K_Y^R and $K_{R'}^R$, Calculated from EDTA Stability Constants
(from data of Wheelwright, Spedding and Schwartzbach (2))

Rare Earth (R)	$\log K_Y^R$	K_Y^R	$K_{R'}^R$
Lu	2.09	123	1.8
Yb	1.83	68	2.1
Tm	1.51	32	3.3
Er	0.99	9.8	1.8
Ho	0.75	5.6	3.6
Dy	0.19	1.5	1.5
Y	0.00	1.00	1.5
Tb	-0.18	0.66	4.8
Gd	-0.86	0.138	1.02
Eu	-0.87	0.135	1.4
Sm	-1.01	0.098	3.1
Nd	-1.50	0.032	2.0
Pr	-1.81	0.016	2.3
Ce	-2.17	0.0068	4.7
La	-2.84	0.0014	

series, are also given in Table I. From these values it is apparent that all adjacent pairs of rare earths, except Gd and Eu, can be separated fairly easily from each other. Four pairs of rare earths, which separated poorly with citrate as the eluant, namely Lu and Yb, Dy and Y, Y and Tb, and Gd and Sm, should separate fairly readily using EDTA, since the values of $K_{R_1}^R$ for these groups are 1.8, 1.5, 1.5 and 1.4, respectively. With $K_{R_1}^R$ values of this magnitude, almost complete separation is accomplished by eluting a distance equal to 2 or 3 times the length of the adsorbed band as will be shown in the next section.

B. Distance Required to Separate a Pair of Rare Earths

The minimum distance of elution, required to attain virtually complete separation of a pair of rare earths under idealized conditions, can be calculated from the exchange constant $K_{R_1}^{R_2}$ (K_Y^R and $K_{R_1}^R$ of Table I are special cases of this more general constant). Spedding and Powell have shown previously how the equilibrium constant can be used to calculate the number of displacements required to separate the isotopes of nitrogen by an ion-exchange method (6).

(6) F. H. Spedding and J. E. Powell, submitted for publication June 23 (1955).

The conditions required in the development which follows are: (1) that the height equivalent to a theoretical plate (HETP) of the ion-exchange bed used must be sufficiently small, and (2) that the value of $\epsilon = K_{R_1}^{R_2} - 1$ must be sufficiently large that the region of overlap between adjacent rare earths in the fully developed band is small compared to the length of the individual adsorbed bands. By adjusting the diameter of the column used to

the amount of rare earths to be separated, it is possible to apply this treatment with some accuracy even though the HETP is fairly large or the value of ϵ is fairly small.

Consider an adsorbed band containing a mole of mixed rare earths in which the mole fractions, N_0 and $(1-N_0)$, of the rare earths, R_1 and R_2 , respectively, are initially constant throughout as in Figure 1.*

When a complexing eluant such as EDTA is passed downward through the column, the band is progressively displaced down the resin bed. In this model, using units of distance occupied by a mole of adsorbed rare earth, the initial spread out, which may be considerable in citrate elutions but which is quite small in elutions with EDTA, can be ignored. As the band is displaced, the mixture desorbed at the rear edge of the band must pass through a region of the adsorbed band where the mole ratio of R_1 to R_2 in the resin phase is equal to $\frac{N_0}{1-N_0}$. As long as any of this region of normal abundance remains in the adsorbed band, the eluate passing through the region will be forced to approach an equilibrium in which the mole ratio of R_1 to R_2 in the eluate will be

$$\frac{N}{1-N} = K \frac{R_1}{R_2} \frac{N_0}{1-N_0} = (1 + \epsilon) \frac{N_0}{1-N_0} \quad (13)$$

*This condition is obtained when a pair of rare earths is adsorbed on the resin from a solution containing no complexing agent which would cause a partial separation during the adsorption step-- provided, of course, that the resin itself exhibits no appreciable selectivity for one rare-earth ion over the other.

Fig. 1 - Model of a mole of binary rare-earth mixture adsorbed on an ion-change bed.

As long as any appreciable amount of the normal region remains in the band, the net number of moles of R_1 transported from the rear of the band to the front of the band, through this normal region, per mole of rare earth mixture displaced by the eluant is

$$\Delta n = N - N_0. \quad (14)$$

Substituting the value of N , obtained by solving equation (13), into equation (14).

$$\Delta n = \frac{N_0(1 + \epsilon)}{1 + \epsilon N_0} - N_0 = \frac{\epsilon N_0(1 - N_0)}{1 + \epsilon N_0}. \quad (15)$$

Referring to Figure 2, it can be seen that the number of moles of R_1 which must be transported to obtain complete separation of the species R_1 and R_2 is $N_0(1 - N_0)$.

Consequently, the minimum number of band displacements required to effect separation of the bulk of the mixture into pure components, leaving only a relatively small region of mixed rare earths, under these idealized conditions is

$$V = \frac{N_0(1 - N_0)}{\Delta n} = \frac{1 + \epsilon N_0}{\epsilon} \quad (16)$$

When ϵ is very small compared to one, the number of displacements required is

$$V = 1/\epsilon \quad ; \quad \epsilon \ll 1. \quad (17)$$

For large values of ϵN_0 , the number of displacements required is

$$V = N_0; \quad \epsilon N_0 \gg 1. \quad (18)$$

Fig. 2 - Model showing the net number of moles of rare earth that must be transported from the front to the rear of the band and vice versa to completely separate the constituents in a mole of the original mixture.

III. Experimental

In order to test the theory just presented, a number of experiments were performed using a crude concentrate from gadolinite ore and certain selected groups of adjacent rare earths.

A. Rapid Concentration of the Heavy Rare Earth and Light Rare Earth Groups from Gadolinite Ore Concentrate

It is not as simple to predict the behavior of a complicated mixture of rare earths as it is to calculate the behavior of a simple binary mixture. In general, however, it is safe to assume, that the distance of elution required to separate the constituents of a simple binary mixture of adjacent rare earths, such as 80% Y and 20% Dy, would be more than sufficient to separate the main constituent from a more complicated mixture, such as 80% Y and 20% total of Dy, Ho, Er, Tm, Yb and Lu. For computing $\underline{V}$ one would use the mole fraction 0.2, in this case, because the elements Ho, Er, Tm, Yb and Lu separate from yttrium even more readily than does Dy. A rough analysis of a previous batch of gadolinite ore concentrate was presented in an earlier paper (7). Assuming

(7) F. H. Spedding and J. E. Powell, Chemical Engineering Symposium Series, 50, No. 14, 7 (1954).

that the present source has the same composition as this earlier lot of ore, one can calculate the approximate number of band displacements required to free the bulk of the yttrium from each of the other components, i.e., to concentrate this other constituent either at the front or at the rear of the adsorbed band. The

values of $\underline{V}$ have been calculated and are given in Table II.

Fifteen kilograms of crude R_2O_3 concentrate, dissolved in 30 liters of 15N HCl and 100 gallons of water were adsorbed on the first seven of a series of 20-30 mesh, ammonium-form, Nalcite HCR resin beds, each 48-52 inches long. The last of the 100 gallons of solution was flushed on through the beds with distilled water and, when the first trace of rare earth appeared in the effluent solution from the 7th column, column number 8 was connected into the series. Column 8 was originally in the cupric state and only about 5 inches of the cupric bed was converted to the rare-earth cycle during the loading step. The entire rare-earth band was 362 inches long at this time. The adsorbed band was then eluted down the series of beds with 0.0153 M EDTA at a pH of 8 and a flow rate of 800 ml per min.

Table II shows that under ideal conditions all the Lu, Yb and Tm and most of the Er in the mixture would have concentrated near the front of the band by the time the band front reached the bottom of the 8th column, having been driven 47 inches or about an eighth of a band length by the eluant. Therefore, the first foot of the adsorbed band was allowed to pass off the 8th column onto a 4-inch diameter bed of 100-200 mesh Dowex 50-X12 in the cupric state, whereupon it formed a band 27 inches long. This band was rapidly eluted off the short column in order to ascertain how much separation had been accomplished by eluting one-eighth of a band length.

The eluate was collected in a series of 12-gallon carboys and the rare-earth content was recovered as the oxalate, ignited to the oxide and analyzed for the individual components

Table II

The Minimum Distance of Elution Required to Separate the Major Constituent Yttrium from Other Rare Earths Present in Gadolinite Ore Concentrate

Component	Actual N_o	N_o Used	<u>ϵ</u>	<u>v</u>
Lu	0.003	0.003	122	0.011
Yb	0.027	0.030	67	0.05
Tm	0.003	0.033	31	0.06
Er	0.027	0.060	8.8	0.18
Ho	0.008	0.068	4.6	0.28
Dy	0.044	0.112	0.5	2.11
Tb	0.003	0.840*	0.5	2.84
Gd	0.038	0.840	6.2	1.00
Eu	0.000	0.840	6.4	1.00
Sm	0.038	0.840	9.2	0.95
Nd	0.041	0.840	31	0.87
Pr	0.016	0.840	64	0.86
Ce	0.016	0.840	147	0.85
La	0.008	0.840	690	0.84
Y	0.728			

*From this point on the assumption is made that the problem is equivalent to separating a mixture of 0.84 mole per cent Y and 0.16 mole per cent Tb, Gd, Eu, Sm, Nd, Pr, Ce or La.

spectrophotometrically. The results are given in Table III.

Table III
Breakdown of Fractions Collected from the First Diversion
Column

Fraction	Wt. R_2O_3 (grams)	% Lu_2O_3 (and ThO_2) (by difference)	% Yb_2O_3	% Tm_2O_3	% Er_2O_3	% Ho_2O_3	% Dy_2O_3
1	84.0	21	79	tr.	--	--	--
2	120.4	16.4	83	0.4	--	--	--
3	116.2	16.5	82	1.5	tr.	--	--
4	116.2	8.6	80	10	1.4	--	--
5	119.6	tr.	53	21	20	tr.	--
6	113.2	--	26	12	61	0.4	--
7	108.8	--	tr.	5	94	1	--
8	92.1	--	--	tr.	85	15	tr.
9	0.8	--	--	--	67	13	20
Total (1-9)	871.3	7.7	51.4	6.5	31.6	1.72	0.02

As predicted, virtually all of the Lu, Yb and Tm, as well as a major portion of the Er, appeared in this material. Some Ho and Dy are also present, but the theoretical predictions are well substantiated by these results. One would not expect a clear separation of Er, Ho and Dy at this point.

Column 8 was then disconnected from the diversion bed and coupled to columns 9 and 10 of the 6-inch series, which were also in the cupric state, and elution was continued at 800 ml per min. Another foot of the adsorbed band was diverted onto an auxiliary

resin bed when the band reached the bottom of column 10 and was handled in exactly the same manner as described above. The data are given in Table IV.

Table IV

Breakdown of Fractions Collected from the Second Diversion Column

Fraction	Wt. R_2O_3 (grams)	%Yb ₂ O ₃ (by difference)	%Tm ₂ O ₃	%Er ₂ O ₃	%Ho ₂ O ₃	%Dy ₂ O ₃	%Y ₂ O ₃
1	29.0	21	14	65	--	--	--
2	121.3	8	2	90	tr.	--	--
3	117.7	tr.	1	82	17	tr.	--
4	107.1	--	tr.	14	80	4	--
5	109.1	--	--	0.6	57	42	tr.
6	80.7	--	--	tr.	0.6	90	9
7	71.0	--	--	--	tr.	65	35
8	63.8	--	--	--	--	16	84
9	4.1	--	--	--	--	6	94
Total (1-9)	704.8	2.2	1.1	34.1	24.0	25.5	12.7

From Table II it was predicted that the diverted material would contain the remainder of the Er, the Ho, part of the Dy and perhaps a little yttrium. Actually, this second batch of diverted material contained some Yb and Tm in addition to the elements predicted, but the general agreement with theory is considered good.

Column 10 was attached next to column 11 of the 6-inch series and elution was continued at 800 ml per min., as before. When the

band front reached the bottom of column 15, the elements Gd through La should have been concentrated at the rear of the band according to Table II. As a matter of fact, the Nd band appeared to be fairly well formed and was passing between columns 8 and 9 at this point. Consequently, the band was divided between columns 9 and 10 to give one band six columns long (294 inches), consisting primarily of adsorbed Y with traces of Dy and Tb and a second band somewhat more than a column long (more than 52 inches) containing the light rare earths, La through Gd, and perhaps some Tb and Y.

It will be noted that the entire adsorbed band, counting the two feet diverted previously, was slightly longer than the original 362 inches at this point. In coming to equilibrium with the EDTA eluant, an adsorbed band expands by 5-10% of its original length.

B. Resolution of the Dysprosium, Yttrium and Terbium Group

As the yttrium-rich portion of the adsorbed band started down the 16th column, samples of the solution in contact with the band were withdrawn at the bottoms of columns 9 through 15. As the band moved on down column 16, additional samples were withdrawn from time to time. In this manner, it was possible to obtain a complete profile of the adsorbed yttrium band within a 24 hour period. Six days later, after the yttrium had progressed down six additional columns or one more band length, another profile was taken in the same manner. The data are plotted in Figure 3.

Due to the coarse particle size of the resin and the rapid rate of elution used, the HETP was fairly large in this experiment.

Fig. 3 - Profiles of the separation obtained as elution progresses. Conditions in this experiment were far from ideal, due to the coarseness of the resin and the fast flow rate used.

It can be seen that the plateau of the Dy curve was disappearing rapidly at the time the first profile was taken. The Tb plateau, however, was still fairly pronounced. By the time the second profile was taken both plateaus had been pretty nearly consumed. A final profile was taken as the band front moved down the 30th column and is compared to the earlier profiles in Figure 3. As might be expected, the separation of Dy and Y did not improve significantly with continued elution at this flow rate, but the Y-Tb separation increased somewhat.

It is apparent that, after eluting the band just slightly more than twice its length, a steady state condition was approached as far as the dysprosium-yttrium separation was concerned. If one desires to achieve a more complete resolution of the dysprosium-yttrium-terbium mixture, it is necessary to use conditions which produce more favorable values of the HETP, and hence a narrower region of overlap at the steady state. Since it is necessary from theory to elute nearly three band lengths in order to resolve the yttrium and terbium in the mixture, the following method of operation appears to be in order. After eluting about two band lengths over coarse resin at a rapid flow rate in order to accomplish the bulk of the transport, as rapidly as possible, the flow rate and the size of the resin particles over which the band must travel should be reduced to improve the HETP. This is done to steepen the gradients in the overlap regions so that a larger fraction of the total rare earths on the column can be removed at the desired purity.

To test the above procedure 15 kilograms of a mixture containing 0.1% Ho_2O_3 , 6.0% Dy_2O_3 , 85.5% Y_2O_3 , 1.6% Tb_4O_7 and 6.8% Gd_2O_3 was adsorbed on the first 7 1/2 units of a series of 6-inch diameter, 20-30 mesh beds of Nalcite HCR each 48-52 inches long, in the manner described above. This adsorbed band was eluted down 18 1/2 additional resin beds of the same kind with 0.0153 M EDTA at a pH of 8 and a flow rate of 800 ml per min. Then the band was eluted through 4 beds of 100-200 mesh Dowex 50-X12 resin at a flow which gradually decreased as the finer resin beds were added, until it was reduced to 100 ml per min. with all four beds in the series. When the front of the band neared the bottom of the last bed of fine resin, the eluant was changed to 0.0307 M EDTA at a pH of 8.5. This was done to reduce the time required for collection of the separated rare earth fractions and was permissible since there was no longer any copper ahead of the rare earths to form Cu_2Y in the resin bed. In Figure 4 the percentages of Dy and Tb in the collected fractions are plotted versus the amount of rare earth recovered. The HETP was about 1/2 inch under these conditions--about 1/10 the HETP observed with the conditions used previously.* About 90.5% of the available Y_2O_3 was recovered greater than 99.9% pure in this experiment. A good deal of this material actually had a purity greater than 99.99%. The Dy, Tb and Gd were concentrated very nicely at the

*In the system under consideration, the rate of exchange of one rare earth for another in the EDTA complex is slow and for a given flow rate is the dominant factor which controls the HETP. Therefore, as a very rough approximation, decreasing the flow rate decreases the HETP proportionately.

Fig. 4 - Elution curve obtained by eluting a mixture of Dy, Y, Tb and Gd with EDTA, under more nearly optimum conditions.

front and rear ends of the band. It is, therefore, advantageous when a high yield of high purity material is desired to operate under conditions which give a small HETP. In practice, however, it would be expedient to balance the increase in time required by the slower flow rate against the purity of product which was actually required in order to arrive at an economically optimum set of conditions.

It is also possible to increase the percentage yield of highly purified product even at fast flow rates by using a total band length which is long compared to the steady-state overlap region between adjacent elements. Overlap regions 8-10 feet long, such as are obtained with 20-30 mesh resin at 800 ml per min., would probably be permissible with yttrium bands 100 or more feet long, but with a band only 25 feet long--eluted under these conditions--most of the yttrium lies in regions of overlap, i.e., the regions containing greater than 0.1% Dy or Tb.

C. Recovery of Pure Dysprosium

A number of enriched dysprosium fractions such as those obtained from the previous experiment were combined to give a sample of R_2O_3 weighing 11,090 grams. This material was dissolved in hydrochloric acid and adsorbed on a series of 30-40 mesh Nalcite HCR beds, 6 inches in diameter and 48-52 inches long, as described previously. The adsorbed band was about 4 1/2 columns long and was eluted with 0.0153 M EDTA at a pH of 8 down 13 1/2 additional, cupric state, 30-40 mesh, resin beds at 800 ml per min. and 2, 100-200 mesh, cupric-state, Dowex 50-X12 beds at a flow rate of 200 ml per minute. When the rare-earth band neared

the bottom of the last column the eluant was changed to 0.0307 M EDTA at a pH of 8.5 and the flow rate was reduced to 100 ml per min. The data are plotted in Figure 5. About 89% of the available Dy_2O_3 and about 87% of the Y_2O_3 were recovered greater than 99.9% pure.

D. Recovery of Pure Terbium

A number of enriched terbium samples like those obtained in experiment B were combined to give a sample weighing 3,100 grams. This material was loaded on a series of 30-40 mesh Nalcite HCR resin beds, 4 inches in diameter and 48 inches long. The mixture was eluted a distance three times the length of the original band down 30-40 mesh, cupric-state resin with 0.0153 M EDTA at a pH of 8 and a flow rate of 300 ml per min. The band was finally eluted down a bed of cupric-state, 100-200 mesh Dowex 50-X12 at a flow rate of 100 ml per minute and collected in 5-gal. carboys. The rare earths were recovered and analyzed. The results are given in Figure 6. About 72% of the Y_2O_3 and 84% of the available Tb_4O_7 were obtained greater than 99.9% pure. Some pure Gd_2O_3 was also obtained, but the separation of the Gd and Eu was not very clean-cut, due to the unfavorable value of $K_{\text{Eu}}^{\text{Gd}}$.

IV. Comments

When a flow rate of 100-200 ml per minute is used toward the end of an elution with 0.0153 molar EDTA at a pH of 8.0, a precipitated zone of H_4Y forms at and moves along with the rear edge of the rare-earth band. Because this causes channeling and

Fig. 5 - Elution of a mixture of Er, Ho, Dy and Y with EDTA.

Fig. 6 - Elution of a mixture of Dy, Y, Tb, Gd and Eu with EDTA.

blockage of the bed, it has been found expedient to raise the pH of the eluant to 8.5 as soon as the heavy rare earths, which tend to leak through the cupric-state resin bed with eluant pH's above 8.0, have been diverted from the main stream. Mixtures which do not contain the elements Ho through Lu may be eluted from the start with pH 8.5 eluant.

The light rare earths, La through Tb, which were diverted from the main yttrium band, as described in Section III-A, were eluted off and recovered. Since eight elements were present in this mixture, and no single species was present in a particularly high concentration, the individual bands were all less than 18 inches long. Consequently, the yields of pure Gd, Sm, Nd, etc. were not impressive. If it is desired to obtain these elements in high purity, it would be necessary to increase the lengths of the adsorbed bands, either by eluting through columns of smaller diameter, or by accumulating mixtures of this sort on a bank of storage columns until enough of each rare earth was present to give adsorbed bands of the required length. In our pilot plant the latter method is being used with the heavy rare earths, Dy through Lu, as well as with the light rare earths, La through Tb.