of more than two rare earths are to be separated. To achieve this, it may be practical to operate at flow rates much lower than those reported previously.[1,6]

It is difficult to choose optimum conditions when a study of this type is being made. The length of time involved in making a run is so great that it is not practical to study many variables. For this reason, the conditions employed in these runs are not claimed as optimum. To establish such a set of conditions will require a much better knowledge of the equilibrium distribution coefficients of the rare earths between the resin and solution under various conditions and some information concerning the rates at which these reactions approach equilibrium.

Summary

By utilizing a column separations method in which a complexing agent is used to remove the cations from an ion-exchanger and a recently developed exchange resin of high combining capacity, it was possible to get essentially complete separations between several rare earths of the Ce group in a single adsorption–elution cycle. Pr was separated both in trace and bulk amounts from Ce. Ce was separated from La. In one run a mixture of nearly equivalent quantities of Nd, Pr and Ce was separated into its constituent elements. Each of these three rare earths in this run was obtained in a high yield. The impurities were below a detectable level (probably less than 0.1%).

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[CONTRIBUTION FROM THE CLINTON NATIONAL LABORATORY]

The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. IV. The Separation of the Yttrium Group Rare Earths[1]

BY B. H. KETELLE AND G. E. BOYD[2]

Introduction

The current state of development of the quantitative understanding of the physics and chemistry of the rare earth elements has been summarized in an excellent recent monograph by Yost, Russell and Garner.[3] In this work the extraordinary difficulty thus far met with in the separation of the rare earths has been remarked upon. Further, the possible general utility of radio-isotopic tracer techniques was recognized as a means in the overcoming of this classical chemical problem. Since investigation of this unique group of elements evidently has been impeded by the scarcity of pure compounds, it was considered important that any promising method of separation and purification be utilized to its full potentialities. Researches on ion-exchange adsorption techniques during the recent war years[4] had indicated that an efficient method of chromatographic separation was possible, and therefore deserved examination at a later time. In fact, the separation of the following fission product element groups had been achieved[5]: Zr + Cb; La + Ce + Pr + Sr + Ba; and Te + I.

The researches described below had as their objective the production, identification and/or characterization of the radio-isotopes of the yttrium group rare earths. Since separation procedures based on ion-exchange adsorption appeared to offer almost unique possibilities for employment as an analytical tool in this problem, the initial studies were directed toward their development. Prior to the initiation of the present program, a series of empirical studies on the separation and recovery of the uranium fission products had led to the development of a "citrate elution" technique by means of which the possibility of the rapid separation of the alkaline and rare earth ions from each other on a milligram scale was demonstrated.[6] Later this procedure was adapted to the separation of cerium and yttrium,[7] and to the production of gram amounts of pure neodymium from didymium earth mixtures.[8] Shortly thereafter, the method was applied to the separation and chemical identification of two radio-isotopes of element 61 formed by the fission of U-235.[9] Quite recently, decidedly superior fractionations of mixtures of approximately equivalent amounts of Ce, Pr and Nd have been achieved by using the new synthetic organic exchanger, Dowex-50.[10]

In spite of the gratifying success met with by the groups lead by Cohn and Tompkins, and by Spedding, there was good reason, on the basis of

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[1] This work was performed under the auspices of the Manhattan District at Clinton Laboratories, Monsanto Chemical Co., Oak Ridge, Tennessee, during the period May, 1945, to May, 1947.

[2] On leave from the Department of Chemistry, University of Chicago. Present address: Clinton Laboratories, Monsanto Chemical Co., Oak Ridge, Tennessee.

[3] D. M. Yost, H. Russell and C. S. Garner, "The Rare Earth Elements and Their Compounds," John Wiley and Sons, New York, N. Y., 1947.

[4] H. D. Smyth, "Atomic Energy for Military Purposes," Princeton University Press, Princeton, N. J., 1945, p. 137.

[5] J. A. Swartout, E. R. Russell, D. N. Hume and B. H. Ketelle, July, 1944, to be published.

[6] E. R. Tompkins, J. X. Khym and W. E. Cohn, THIS JOURNAL, **69**, 2769 (1947).

[7] F. H. Spedding, A. F. Voigt, E. M. Gladrow and N. R. Sleight, *ibid.*, **69**, 2777 (1947).

[8] F. H. Spedding, A. F. Voigt, E. M. Gladrow, N. R. Sleight, J. E. Powell, J. M. Wright, T. A. Butler and P. Figard, *ibid.*, **69**, 2786 (1947).

[9] J. A. Marinsky, L. E. Glendenin and C. D. Coryell, *ibid.*, **69**, 2781 (1947).

[10] D. H. Harris and E. R. Tompkins, *ibid.*, **69**, 2792 (1947).

the variation of the ionic radius within the lanthanide contraction, to believe that the separation of the yttrium group would, in fact, be considerably more difficult than the separation of the early members of the cerium group. The attainment of optimum conditions for a maximum fractionation seemed to depend upon a balancing and adjusting of several chemical and physical variables. An entirely empirical study of these over a sufficient range for the heavier rare earths would have required a prohibitive effort. Fortunately, in the light of the principles established in earlier researches,[11] the lines along which a rational approach was to be conducted seemed clear. For example, it was possible to assume in the beginning that the mass law would be applicable to the heterogeneous equilibria between the trivalent rare earth ion in solution and in the ion-exchanger. The essential nature of the mechanism governing the adsorption rate was felt to be understood. A satisfactory quantitative theory of rate-dependent adsorption processes as they occur in deep, cylindrical adsorbent beds was at hand. Finally, the classical, or rate-independent, theory of chromatography[12,13,14,15] proved to be of considerable aid in the prediction and interpretation of column separations.

As a result of this study, new information on the radio-isotopes of the heavy rare earths was obtained which will be published elsewhere. This communication will describe the results from the examination of various factors governing adsorption column separations. The unusual power of ion-exchange adsorption column techniques has been demonstrated by the separation of all of the fourteen rare earths. It is possible that the results from this work will lead in diverse ways to an improved understanding of the systematic inorganic chemistry of this most interesting family of elements.

Theoretical Considerations

In order to form a basis for the presentation of the experimental findings in the subsequent sections of this paper, it is desirable to outline the elementary principles governing the separation of cations in deep cylindrical beds of base-exchange substances. First, a consideration of the homogeneous and heterogeneous ionic equilibria existing in the aqueous solution and between this solution and the solid exchanger will make explicit those factors which determine the equilibrium distribution. If the partition coefficient can be made independent of the rare earth concentration, a prediction of the fractionating action of a deep adsorbent bed based on the theory of chromatography becomes possible. However, owing to the finite rate of flow of solution through the bed, the shape of the predicted chromatogram must be regarded as a limiting form, perturbed in actuality by the effect of a finite adsorption velocity. Accordingly, an analysis of the influence of rate-dependent adsorption on the non-steady-state conditions occurring in adsorption columns will be required. The object of these considerations will be to give a qualitative explanation of the observed chromatograms.

The Equilibrium Theory.—Chemical equations for the heterogeneous adsorption reaction may be written as follows, arbitrarily assuming the behavior of a trivalent cerium ion to be typical for any trivalent rare earth

$$Ce^{+++} + 3NH_4R \rightleftarrows CeR + 3NH_4^+ \qquad (1)$$

In addition, the homogeneous equilibrium in the aqueous solution between "free" rare earth ion, and rare earth bound in a complex ion may be written[16]

$$Ce(H_2Cit)_3 \rightleftarrows Ce^{+++} + 3H_2Cit^- \qquad (2)$$

Assuming the mass law may be applied to each of these equilibria,[17] and combining the expressions so obtained, the relation for the equilibrium distribution coefficient, K_d, is[18]

$$K_d = \frac{CeR}{Ce(H_2Cit)_3} = K_{exchange}\,K_{complex}\left(\frac{NH_4R}{NH_4^+}\right)^3 \frac{1}{(H_2Cit^-)^3} \qquad (3a)$$

$$K_d = \frac{n_{CeR}}{Ce(H_2Cit)_3} = K_{exchange}\,K_{complex}\,\frac{n_{NH_4R}}{(NH_4^+)^3}\,\frac{1}{(H_2Cit^-)^3} \qquad (3b)$$

Utilizing the appropriate expression for first dissociation constant of the citric acid, Equation (3) may be written

$$K_d = \frac{K_{exchange}\,K_{complex}}{K_1^3}\left(\frac{NH_4R}{NH_4^+}\right)^3\left(\frac{H^+}{H_3Cit}\right)^3 \qquad (4)$$

Assuming the exchange capacity of the adsorbent remains constant, the dependence of the distribution ratio upon *p*H is revealed by Equation (4). Since the usual procedure for adjusting this variable has been to add ammonia to the citrate

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(11) (a) G. E. Boyd, J. Schubert and A. W. Adamson, THIS JOURNAL, **69**, 2818 (1947); (b) G. E. Boyd, A. W. Adamson and L. S. Myers, *ibid.*, **69**, 2836 (1947); (c) G. E. Boyd, L. S. Myers and A. W. Adamson, *ibid.*, **69**, 2849 (1947).

(12) J. N. Wilson, *ibid.*, **62**, 1583 (1940).

(13) D. DeVault, *ibid.*, **65**, 532 (1943).

(14) J. Weiss, *J. Chem. Soc.*, 297 (1943).

(15) J. E. Walter, *J. Chem. Phys.*, **13**, 229 (1945).

(16) At the present writing the stoichiometric composition of the most important rare earth citrate complex remains indefinite, although it seems probable that an uncharged structure is formed. Preliminary results indicate that either the H_2Cit^- or the $HCit^=$ ions participate, and not the tribasic citrate ion as is the case with the alkaline earth complexes which carry a negative charge (J. Schubert and J. W. Richter, February, 1945, to be published). Preliminary measurements carried out in September, 1945, by B. H. Ketelle and J. W. Richter gave values of 4.3×10^{-8} and 4.5×10^{-9} for the instability constants of the neutral compounds, $La(HCit)_{1.5}$ and $Y(HCit)_{1.5}$, respectively.

(17) An investigation of heterogeneous equilibria of the type indicated by Equation (1) has been carried out by Mr. L. S. Myers, September, 1946, to be published.

(18) In the experimental measurement of the distribution ratio a determination of only the total cation in the solution (*i. e.*, total Ce(III)) is made. The assumption that this is identical with the complex ion concentration may be justified by a simple computation based on approximate values for the complex ion dissociation constants. Concentrations are expressed as thermodynamic activities. Equation (3b) will apply when ideal solid solutions are formed.

buffer,[4] a decrease in hydrogen ion will be accompanied by an increase in NH_4^+ ion concentration so that the magnitude of the distribution coefficient would be expected to decrease sharply with increase in *p*H. The decrease in the concentration of the undissociated citric acid will tend to offset these changes somewhat, of course. It is evident also that the lowering in the magnitude of K_d which will be produced by an increase in the initial citric acid concentration, keeping the *p*H constant, will be caused in part by an increased ammonium ion concentration.

The conditions under which the distribution coefficient changes are of interest, since, if this varies with the concentration in solution much poorer separations are observed. As may be seen from Equation (4), as long as the quantity of rare earth adsorbed is sufficiently small that the activity of the ammonium ion in the exchanger remains constant, the distribution ratio will not vary. A mole fraction of NH_4R constant within experimental error may be realized either with small values of K_d, with low rare earth concentrations, or with a high capacity exchanger.

Although the exact effect of temperature changes upon K_d cannot be predicted, general considerations suggest a direct proportionality will be observed. Thus, the exchange constant will decrease, whereas the complex ion instability constant will increase with the temperature so as to compensate. The variation of K_d, therefore, will be determined largely by the change of the first dissociation constant of citric acid, K_1, with temperature. At room temperatures the third dissociation constant, K_3, for citric acid has been found to decrease with temperature, whereas the first and second constants, L_1 and K_2, increase very slowly.[19] By analogy to the behavior of other organic acids, oxalic acid in particular,[20] at temperatures above 50° both K_1 and K_2 would be expected to decrease; hence, above this latter temperature, K_d should tend to increase.

In as much as the interest in this research was in the separation of the heavy rare earths, a separation factor, α, defined by the ratio of the distribution coefficients for two neighboring rare earths, has been employed. It then follows from Equation (4) that the separability of a pair of rare earths will be independent of the ammonium and citrate ion concentrations in solution, and of the *p*H so long as the composition of the complex ion does not vary. The separation factor would be expected to be virtually unchanged by temperature variations.

By way of illustration, it will be of interest to give a comparison of the partition coefficients for a pair of rare earth ions, say, Ce^{+++} and Y^{+++}. Thus,

$$\alpha = K_d^{Ce}/K_d^{Y} = (K_{exchange}^{Ce}/K_{exchange}^{Y})(K_{complex}^{Ce}/K_{complex}^{Y}) \quad (5)$$

It was predicted[9] and has been shown experimentally[17] that cerium is more strongly adsorbed than yttrium. A value of 1.55 has been observed for the first ratio on the right-hand side of Equation (5). The second ratio is known also, from preliminary measurements,[16] to possess a value of approximately 2.9. The role of the citrate becomes apparent: by its use, the normal difference in adsorbabilities, by means of which a separation of the two ions could be effected, is enhanced by the difference in the homogeneous equilibria in the aqueous phase.

It is desirable to stress a number of additional factors in the adaptation of the foregoing principles to the practical problem of the separation of the rare earths by an adsorption column. If the separation is conducted in such a manner that equilibrium is realized, the behavior of the adsorption column may be interpreted in terms of the theory of chromatography. The prediction made for linear isotherms is that a band with an abrupt leading and trailing edge will be formed. Further, this band will move through the adsorbent bed with a velocity given by $v/(1 + \delta/f)$ where v is the linear flow rate of solution in the bed, δ is the equilibrium distribution coefficient, and f is the fractional bed void space.[21] Correspondingly, that rare earth with the larger δ will move slower and will lag in its relative movement down the adsorption column. Using the example given above, where $K_d^{Ce} > K_d^{Y}$, yttrium would be expected in the effluent from the adsorbent before cerium.

It may be shown that the general expression for the velocity of movement of a band, $v(c)$, depends upon the adsorbate concentration in solution and will be a minimum for the case of linear adsorption. From the dependence of δ on the concentrations in solution, it can be deduced that an increase in *p*H or in citric acid concentration at constant *p*H will increase the migration rate of the band. An increase in temperature would be expected to cause a retardation. Further, the larger the exchange capacity of the adsorbent, the slower the band velocity, all other things being equal. Conversely, the larger the ammonium ion concentration, the greater the band velocity.

A number of additional useful guiding rules are derivable from the elementary theory. Values of δ may be computed from the time, t_x, required for the band to transverse the length of the column, choosing the center or the peak as the point of reference. Thus

$$\delta = (Wt_x/x) - f \quad (6)$$

where W is the volume flow rate (ml./sq. cm./min.) and x is the bed depth. The bed void may

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(19) Bjerrum and Unmack, *Danske Videns Kobenes Selskabs Math. Fys. Med.*, IX, 1 (1929).

(20) H. S. Harned and L. D. Fallon, THIS JOURNAL, 61, 3111 (1939).

(21) The bed distribution coefficient, δ, is related to K_d and to the bed density, ρ, by $\delta = K_d\rho$. If K_d is expressed as (moles/g. oven dry NH_4R)/(moles/cc. solution) then ρ will be given in the units: (g. oven dry NH_4R/cc. bed).

be measured with high reproducibility by determining the time, t_h, for a non-adsorbed (anionic) ion to pass through the bed. Then

$$f = t_h W/x \qquad (7)$$

whereupon

$$\delta = (t_x/t_h - 1)(Wt_h/x) = (W/x)(t_x - t_h) \qquad (8)$$

It is evident, if the correct bed densities are known, that values of K_d may be computed from observations made with adsorption columns. The validity of Equation (8) may then be checked by an independent determination of K_d in an equilibrium experiment.

Useful information concerning the minimum bed depth, x_c, or volume of pure solvent,[22] V_c, required to just effect a separation of two substances whose adsorption coefficients are δ_1 and δ_2, where $\delta_2 > \delta_1 > 1$, may be obtained also. If V_0 is taken as the volume from which the initial adsorption onto the top of a bed of cross-section A occurred, then

$$x_c = (V_0/fA)(\delta_1/\delta_2 - \delta_1) = (V_0/fA)(\alpha - 1) \qquad (9)$$

The Influence of Rate Dependent Processes.— Although adsorption bands with sharp front and rear edges are predicted from the rate-independent theory of chromatography for conditions in which the equilibrium adsorption increases linearly with concentration, in actuality such a behavior is virtually never observed. The usual finding is an S-shaped leading and trailing edge in which, generally, a long near-linear middle portion may be found. Frequently these bands are symmetrical in shape, although occasionally asymmetric forms with more abrupt forward than rear edges which resemble those predicted for a nonlinear adsorption isotherm are observed. As was indicated in the preceding paper in this series,[9] for the linear isotherm, the sigmoid character of the adsorption edges may be understood on the basis of a theory of rate-dependent chromatography. In the terms of this theory, the edges of the bands are characterized by a dimensionless parameter, y, related to the rate and equilibrium constant, k and δ; to the bed depth, x; to the linear flow velocity, v; and to the fractional bed void space, f, by the expression

$$y = (k\delta/f)(x/v) \qquad (10)$$

When the value of y becomes infinitely large, bands with abrupt edges are approached, so that under limiting conditions the equilibrium theory and the rate-dependent theory of chromatography become identical. Since relatively small values of y produce broad bands, in general, it is essential to employ conditions leading to as high a value as possible if the separation of several substances by chromatographic techniques is desired.

The factors which determine the rate constant, k, must be examined to predict the variations in y resulting from changes in the variables of the adsorption system. Studies of the mechanism of the rate processes[8] have led to a film diffusion hypothesis by means of which k was shown to depend upon the diffusion coefficient of the ion being adsorbed, D^l, the adsorbent particle radius, r_0, the fluid film thickness, Δr_0, and the equilibrium distribution coefficient, δ, by the equation

$$k = 3D^l/r_0 \Delta r_0 \delta \qquad (11)$$

which, upon substitution into Equation (10), yields

$$y = (3D^l/r_0 \Delta r_0 f)(x/v) \qquad (12)$$

Now, if diffusion through a thin liquid film is rate controlling in adsorption, the same process would be expected to govern the *desorption rate* with an unchanged rate constant. The same y value would describe the forward and rear edges, and therefore the band would possess a symmetrical shape.

Equation (12) reveals that particle size will play an important role; consequently, smaller particles should produce sharper band edges. Furthermore, adsorbent granules of a rather highly uniform size are essential to reduce the classification caused by the back-washing of deep beds. On the other hand, since the film thickness, Δr_0, appears to vary approximately inversely as the linear flow rate, v, the character of the band edge will either be independent of the flow or change quite slowly with it. Deeper adsorbent beds, it is seen, should lead to sharper band edges. The magnitude of the partition coefficient, δ, will be without an effect on the edges of the band, although of course the band width will be determined by this.

From Equation (12) it is seen for maximum values of y that the magnitude of the bed void space, f, should be reduced to a minimum. This factor will be independent of the particle diameter, in the absence of wall effects, although it is determined in part by the particle shape. It is well-known that f will be a minimum for a bed composed of spherical granules of a uniform diameter.

The only temperature dependent quantity in Equation (12) is the diffusion coefficient, D^l, of the exchanging ion. Since this will increase with temperature with an activation energy of 4–5 kcal. mole^{-1}, appreciably higher y values, and hence sharper band edges, will be obtained by conducting the adsorption separations at elevated temperatures. In order to off-set the slowing down in the movement of the band, owing to the increase in δ with temperature, indicated by Equation (4), either the flow rate may be increased, or the magnitude of δ may be lowered by an increase in pH.

An increase in temperature will also bring about several additional advantages. Thus, owing to the reduced fluid viscosity, larger flow rates are

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[22] In the rare earth separations, the "solvent" was the ammonium citrate buffer solution.

possible with the same hydrostatic head. This gain may be utilized by employing finer adsorbent particles thereby additionally sharpening the band edges, or, it may be used to obtain the same degree of separation in a correspondingly shorter time, since the character of the band edge will be nearly independent of flow.

The presence of a rate factor in the adsorption system is seen, therefore, to cause a broadening of the band over that predicted from the classical theory of chromatography. As a result, the separations observed will be less than was anticipated. Although the bands will move with the same velocity as before, the actual value of x_c observed will be greater than indicated by Equation (9). In principle, these observed values may be computed from the rate theory, although the criterion for band separation must be revised.

Experimental Methods and Procedures

The experimental arrangements are illustrated by Fig. 1. In a typical experiment, the ion-exchanger was contained in the Pyrex glass tube, A, 120 cm. long by 6 mm. diameter, which was surrounded by a jacket so that the temperature in the bed could be controlled either by circulation of a liquid from a thermostat, or by the passage of steam through the jacket. The ion-exchanger was retained by a small plug of Pyrex glass wool which rested upon a constriction at the lower end of the column.

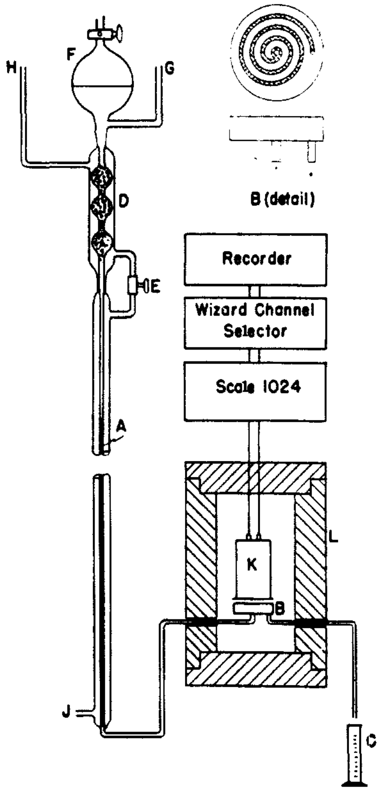

Fig. 1.—Experimental arrangement employed in adsorption column separations: A, adsorbent bed, Amberlite IR-1 or Dowex-50; B, counting cell; C, receiver; D, Allihn condenser; E, throttle valve; F, gas entrainment bulb; G, elutriant inlet; H, thermostat fluid inlet; K, mica end-window Geiger–Müller counting tube; L, two-inch lead radiation shield.

The effluent solution from the column was conducted through a transflex tube of $^1/_{16}''$ inside diameter to the counting cell, B, and finally to the receiver, C, where the various samples were collected. The cell, B, is shown enlarged in the inset diagram of Fig. 1. It consisted of a cylindrical block of Lucite, $1^1/_4''$ in diameter by $^1/_2''$ thick. A spiral groove $^1/_{32}''$ broad and $^3/_{32}''$ deep was cut in one face. This channel was covered by a "window" of 3.2 mg./sq. cm. thick polystyrene which was sealed to the Lucite block with Amphenol cement. Access to each end of the spiral channel was attained through holes and threaded nipples. The volume of liquid held by this cell was 0.6 ml.

In a particular experiment the solution containing the radioactive rare earths was placed on the uppermost portions of the adsorbent bed by means of a small diameter tube inserted into the top end of the column. A separatory funnel containing water was connected by means of an air-filled rubber tube to the top of the column to inject the solution into the exchanger. No water was permitted to flow into the column. The object of this technique was to cause the mixture to be adsorbed as a narrow band with sharp lower edge at the topmost part of the bed. The volume from which adsorption took place was either 1 or else 2 ml. of 1 *M* hydrochloric acid or 5% citrate adjusted to the same *p*H as was employed subsequently to effect a separation. Usually not more than 1 to 3 mg. of rare earth sesquioxide mixture was adsorbed; frequently, only 0.1 mg. quantities were studied.

Following the adsorption step, the air above the resin bed was completely displaced by solution to develop the chromatogram, and an Allihn condenser, D, was attached to the upper end of the column. This condenser was maintained at the same temperature as the column, and thereby served to "pre-heat" the influent elutriant solution. When steam was being passed through the jacket, the temperature of the condenser was controlled by means of the valve, E, in such a manner that the influent solution was caused to boil gently. This was desirable in order that dissolved gas be removed from the solution before it reached the bed. The expelled gas was collected in the bulb, F. Thus, the eluant or wash solution from a constant head tank entered the top of the condenser through inlet, G, under the force of gravity, and then flowed through the packing of glass beads and glass wool, through the exchanger bed, A, through the counting cell, and finally to a receiver. The fluid used to control the temperature entered the condenser jacket at H, passed through valve E before entering the column jacket, and then escaped through outlet J at the lower end of the column.

The radioactivity in the effluent solutions was detected by a thin mica window bell-type G.-M. counter tube, K, which was surrounded by a two inch thick lead shield, L. The tube was connected to a scale of 1024 which in turn transmitted impulses to a Wizard recorder. The latter, through electrical contacts and relays, could be adjusted to close any of four channels on a Simplex time stamper. These channels corresponded to the digits, tens, hundreds, and thousands wheels of the Wizard recorder. By means of a selector switch, it was possible to record the time at which any channel carried a pulse, or, to record only every tenth or one-hundredth scaler when the level of radioactivity was sufficiently high that such a record sufficed. In this way, a continuous record of the radioactivities emerging from the adsorbent bed was made possible. The time between pulses was proportional to the reciprocal of the activity in the solution contained in the counting cell. It was possible, therefore, either to plot the concentration history of the effluent solution in terms of the reciprocal activity, expressed in terms of minutes per 640 counts, or else to convert the data to counts per minute and to plot this as a function of the time from the beginning of the elution. With the former type of plot inverse peaks are obtained when the activity of the emergent solution passes through a maximum.

A peak in the effluent activity was recorded for each rare earth element if a separation had been effected, and if a suitable radio-isotope indicator were present. The magnitude of the activity level reached in these peaks depended upon (a) the concentration of rare earth in solution; (b) the neutron capture cross-section and isotopic abundance of the stable isotope from which the tracer radio-isotope was formed; (c) the neutron flux during the bombardment; (d) the duration of bombardment; (e) the ability of the radiation to penetrate water, polystyrene and mica and, finally, (f) the half-life of the active isotope formed. No attempt has been made to obtain a record of beta activities having maximum energies less than 0.4 Mev. It was felt, however, that under proper conditions somewhat softer radiation might be detected.

A summary of the half-lives and energies of the rare earth isotopes which were measured in the foregoing experimental arrangement is given in Table I. Several of these activities, it will be noted, are new.

TABLE I

DECAY PERIODS AND BETA-RAY ENERGIES FOR RARE EARTH ISOTOPES

Isotope	Half-life[a]	Maximum energy, Mev.
Lu^{177}	3.4 h[b]	1.2
Yb^{177}	2.6 h[b]	1.3
Tm^{170}	125 d	1.1
Er^{171}	7.5 h[b]	1.6
Ho^{166}	27 h	1.9
Y^{90}	65 h	2.2
Dy^{165}	2.5 h	1.2
Tb^{160}	72 d	0.7
$Gd^{159,161}$	8.0 d[b]	0.7
Eu^{152}	9.2 h[b]	1.9
Sm^{153}	47 h	0.8
61^{149}	47 h[b]	1.1
Nd^{147}	11 d	0.9
Pr^{142}	19.3 h	2.1
Ce^{141}	28 d	0.6
La^{140}	40 h	2.1

[a] h = hours; d = days. [b] Longer periods present in addition.

Experimental Results

The continuous beta ray recording equipment described above was employed to determine the optimum conditions for separation, and subsequently to demonstrate a variety of rare earth fractionations. The effects on adsorption column performance of pH, citrate and ammonium ion concentration had been studied previously[6,7,8] and are in accord with the deductions presented in an earlier section. Preliminary investigations of the influence of eluant flow rate on the separation of the rare earths at room temperatures served to confirm the earlier prediction based on Equation (12) of the relative unimportance of this variable at rates below 2 ml./sq. cm./min. The limitation imposed by the mass of the adsorbed ions on the separations was found to be in agreement with earlier findings of Khym and Tompkins[23] and of the Ames group.[7]

Effect of Adsorbent Particle Size on Band Width.—The importance of the mesh size of the exchanger in determining the character of the desorption band had been demonstrated in several early studies.[24] Also, adsorbent particle size had been shown to determine the velocity of exchange regardless of whether diffusion in and through the solid, or through a film surrounding the particle, controls.[10] In either case, the rate increased as the particles became smaller. In terms of column separations, if the speed of exchange is increased, a more rapid flow may be employed, or, two elements can be separated to the same extent in less time. Irrespective of the flow rate, a smaller granule should give an improved separation. Several experiments were conducted to ascertain the influence of particle size in rare earth separations by ion-exchange columns.

A quantity of the synthetic organic ion-exchanger, Amberlite IR-1, was placed in a Pyrex tube and was converted to the hydrogen form (HR) by washing with ten bed volumes of 3 M hydrochloric acid. After rinsing with distilled water, the exchanger was air-dried and screened to give samples of known ranges of mesh size.

Two-tenths gram of adsorbent of a pre-determined particle size was shaken for ten minutes with 5 ml. of hydrochloric acid solution of pH 1.0 which contained 0.025 ml. of carrier-free Y^{91} stock solution after which the suspension was slurried into a glass column to form a shallow bed approximately 4 mm. long by 1 sq. cm. cross-section. The yttrium was displaced by washing with a buffer solution prepared by dissolving 50 g. of citric acid monohydrate in 1000 g. of water and adjusting the pH to 2.64 by the addition of concentrated ammonium hydroxide solution. The flow rate was 0.35 ml./sq. cm./min. The effluent solution was passed through a counting cell to measure its activity continuously. The plots of the desorbed activity as a function of time for each of four particle size ranges are shown in Fig. 2.

The "tailing-out" of the desorption band produced by the large particles would cause unnecessary overlapping of the successive bands and poor resolution of the earths. Consequently, a better separation would be expected with small particles of exchanger if hydrostatic pressure sufficient to maintain satisfactory flow rates were available. Although 270/325 mesh adsorbent was clearly superior, the labor involved in preparing sufficient quantities for deep beds forced a compromise on the use of 170/200 mesh size particles in the subsequent work with Amberlite IR-1.

Heavy Rare Earth Separations with Amberlite IR-1 at Room Temperatures.—The initial degree of success met with in the separation of the yttrium group rare earths may be illustrated by the results from a series of experiments whose primary objective was the isolation and characterization of the radioisotopes of erbium. Samples of Hilger's spectrographically pure erbium oxide (Lab. No. 10,374) were activated

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(23) J. X. Khym and E. R. Tompkins, July, 1945, to be published.

(24) E. R. Russell, private communication, April, 1944.

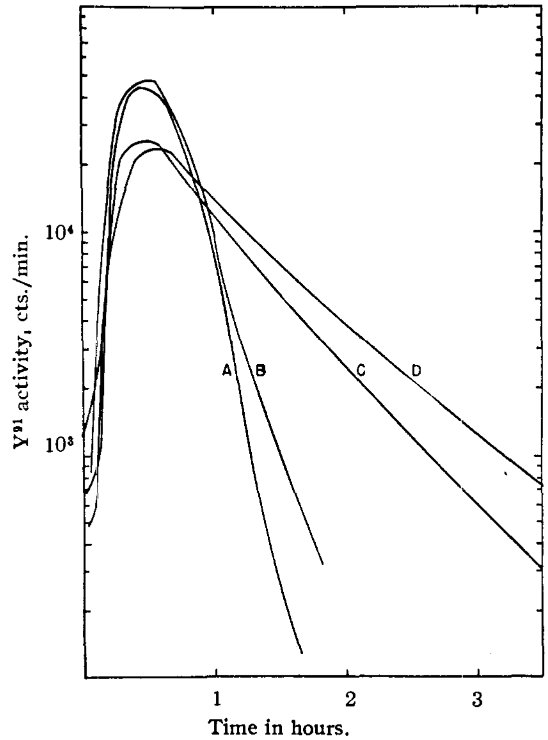

Fig. 2.—Effect of mesh size of Amberlite IR-1 on desorption band width: A, 270/325 mesh; B, 170/200 mesh; C, 50/60 mesh; D, 30/40 mesh.

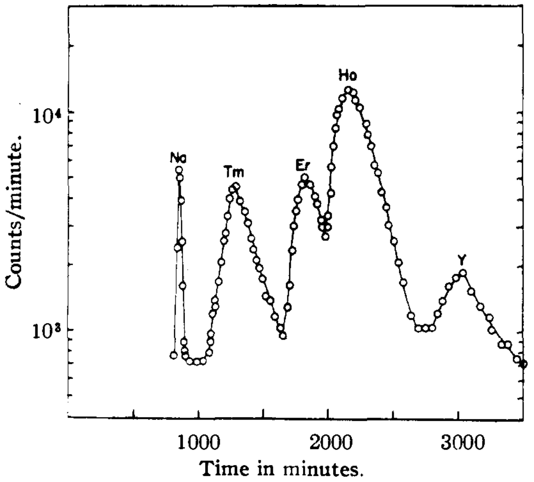

Fig. 3.—Yttrium group separation with a 170/200 mesh Amberlite IR-1 column at room temperature: bed dimensions, 125 cm. × 0.79 sq. cm.; flow rate, 1.2 ml./sq. cm./min.; 5% citrate buffer at *p*H 2.64.

with slow neutrons and the decay of the activity was measured. The slope of the decay curves changed more or less continuously, although the data could be represented by assuming several activities with different half-lives to be present. This behavior might be expected since there are four possible radio-isotopes of erbium which could have resulted from slow neutron bombardment. Since the relative isotopic abundance of stable Er^{162} is but 0.1%, it would probably be difficult to detect Er^{163} activity. There was some reason to believe that active isotopes other than those of erbium were produced, for it was impossible to obtain the same decay periods from bombardments of varying duration. Since three (at the most, four) activities with quite different half-lives would be expected, it should be possible to determine these from the decay curves observed following differing periods of irradiation. Since such an analysis proved impossible, it was suspected that the erbium oxide contained appreciable quantities of impurities. Therefore, a column purification was undertaken.

About 0.1 mg. of neutron activated Er_2O_3 was adsorbed on a 125 cm. by 0.79 sq. cm. bed of 170/200 mesh Amberlite IR-1, and a separation was obtained at room temperature in 3300 minutes by elution with 5% citrate buffer of *p*H 2.64 at 1.2 ml./sq. cm./min. As may be seen in Fig. 3, five partially overlapping activity peaks were obtained. In spite of the mediocre separation, it was possible by means of the radiation characteristics of samples of the eluate to establish the presence of thulium, holmium and yttrium impurities. The lower *p*H of 2.64 used in this fractionation of the yttrium group is to be compared with the higher values of 2.74 to 2.95 employed to separate the cerium group.[7] The almost symmetrical shape of the activity peaks in Fig. 3 is to be noted. This behavior is to be expected if a linear isotherm is obeyed. Clearly, it would be impossible to utilize the Hilger Er_2O_3 oxide preparation without further purification or separation of the activities produced in it.

The Effect of Temperature on the Separation of Thulium and Ytterbium with Dowex-50.—Further study of the separation exhibited in Fig. 3 showed that a better fractionation could be effected if the leading and trailing edges of the activity peaks could be made more abrupt. The slope of these edges, as was pointed out in the section on Theoretical Considerations, is determined by the dimensionless parameter *y*, which, by Equation (10), is dependent upon the rate constant, *k*. The rate of exchange, as shown earlier in both shallow and deep bed studies was known to increase with temperature and with decreasing particle size. These earlier investigations also disclosed, however, that work with the Amberlite IR-1 exchanger must be limited to temperatures less than 60° owing to an increasingly objectionable decomposition of this material at higher values. Fortunately, during the course of these considerations, Dr. L. A. Matheson of the Dow Chemical Company informed us of the demonstrated stability of a new ion-exchanger,[25] Dowex-50, at temperatures as high as 100°. Accordingly, we were encouraged to take up the use of this syn

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(25) See W. C. Bauman, THIS JOURNAL, 69, 2830 (1947).

thetic exchanger for studies at elevated temperatures even though preliminary rate measurements by L. S. Myers had indicated an exchange velocity at 25° of only one-third of that for Amberlite IR-1.

A comparative study of the degree of separation effected at 25° and 100° was conducted using the heavy rare earths, Yb and Tm, which had been tagged by neutron irradiation of 0.1 mg. of each element. The same 91 cm. by 0.26 sq. cm., 270/325 mesh Dowex-50 column and a flow rate of approximately 0.5 ml./min. was used at both temperatures. Since the exchange capacity of the Dowex-50 is roughly twice that of Amberlite IR-1, it was necessary to increase the *p*H of the 5% citrate eluant so as to decrease the value of the distribution ratio, δ, in order to effect the differential desorption in approximately the same time as demonstrated in Fig. 3. An initial *p*H value of 3.12 caused the appearance of Yb activity in the column effluent in only 280 minutes, and therefore was considered undesirably high. The degree of separation achieved at 25° with a *p*H of 2.98 is shown in Fig. 4 together with the fractionation observed at 100°. The predicted increase in δ with temperature was confirmed apparently by the finding that a higher *p*H (3.20) was required at 100° to accomplish the separation in the same time, although the reliability of the *p*H measurement (glass electrode) at 100° was not established.

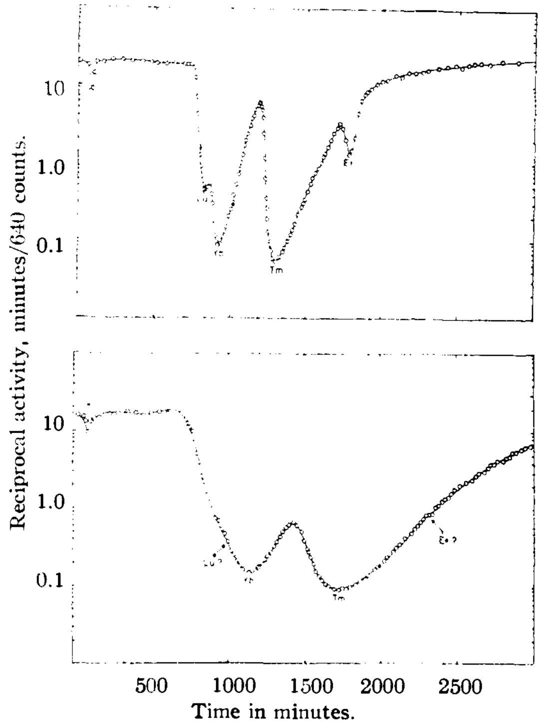

Fig. 4.—Effect of temperature on the separation of the yttrium group earths with a 270/325 mesh Dowex-50 column: bed dimensions, 91 cm. × 0.26 sq. cm.; upper curve for 100°, flow rate 0.35–0.45 ml./sq. cm./min., and 5% citrate buffer at *p*H 3.2; lower curve for 20°, flow rate 0.55 ml./sq. cm./min. and *p*H 2.98.

An examination of Fig. 4 will reveal the superiority of the rare earth fractionation at the higher temperature. Not only are the peak edges sharper at 100° than at 25°, but the presence of unsuspected Lu and Er impurities was also clearly indicated in the higher temperature experiment. Only an inconclusive suggestion of the occurrence of these elements may be determined from a careful examination of the 25° curve. Subsequent to these studies, many additional separations have been carried out at 100°. Thus far, there has been no indication of the decomposition of the Dowex-50 exchanger even after several months of operation of the same bed.

The Effect of Particle Size in the Separation of the Heavy Rare Earths at 100° with Dowex-50.—The initial shipments of Dowex-50 exchanger contained sizeable quantities of 120/140 and 270/325 mesh granules so that it was possible to determine the role of particle size in the yttrium group separations by preparing beds of the same depth from these two fractions. Separations of an identical rare earth mixture at 100° were then conducted. The fractionation obtained with the 120/140 mesh size range contained in a 98 cm. by 0.75 sq. cm. bed when a flow rate of 2.2 ml./sq. cm./min. was used is shown in Fig. 5. The eluant was a 4.75% citrate solution adjusted to a *p*H of 3.2. The mixture studied was the same Hilger Er_2O_3 used in the separation illustrated by Fig. 3. A quantitative intercomparison of the data in these two figures is not possible owing to the differing temperatures, bed dimensions and particle diameters. Qualitatively, however, it may be seen that a vastly improved separation is demonstrated in Fig. 5.

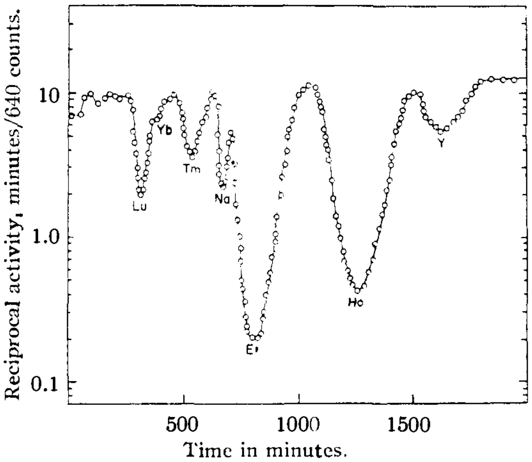

Fig. 5.—Effect of adsorbent particle size on the separation of the yttrium group rare earths with Dowex-50 columns at 100°; bed dimensions, 98 cm. × 0.75 sq. cm.; flow rate, 2.2 ml./sq. cm./min.; 5% citrate buffer at *p*H 3.2; adsorbent particle size, 120/140 mesh; compare with curve for 270/325 mesh exchanger shown in Fig. 6a.

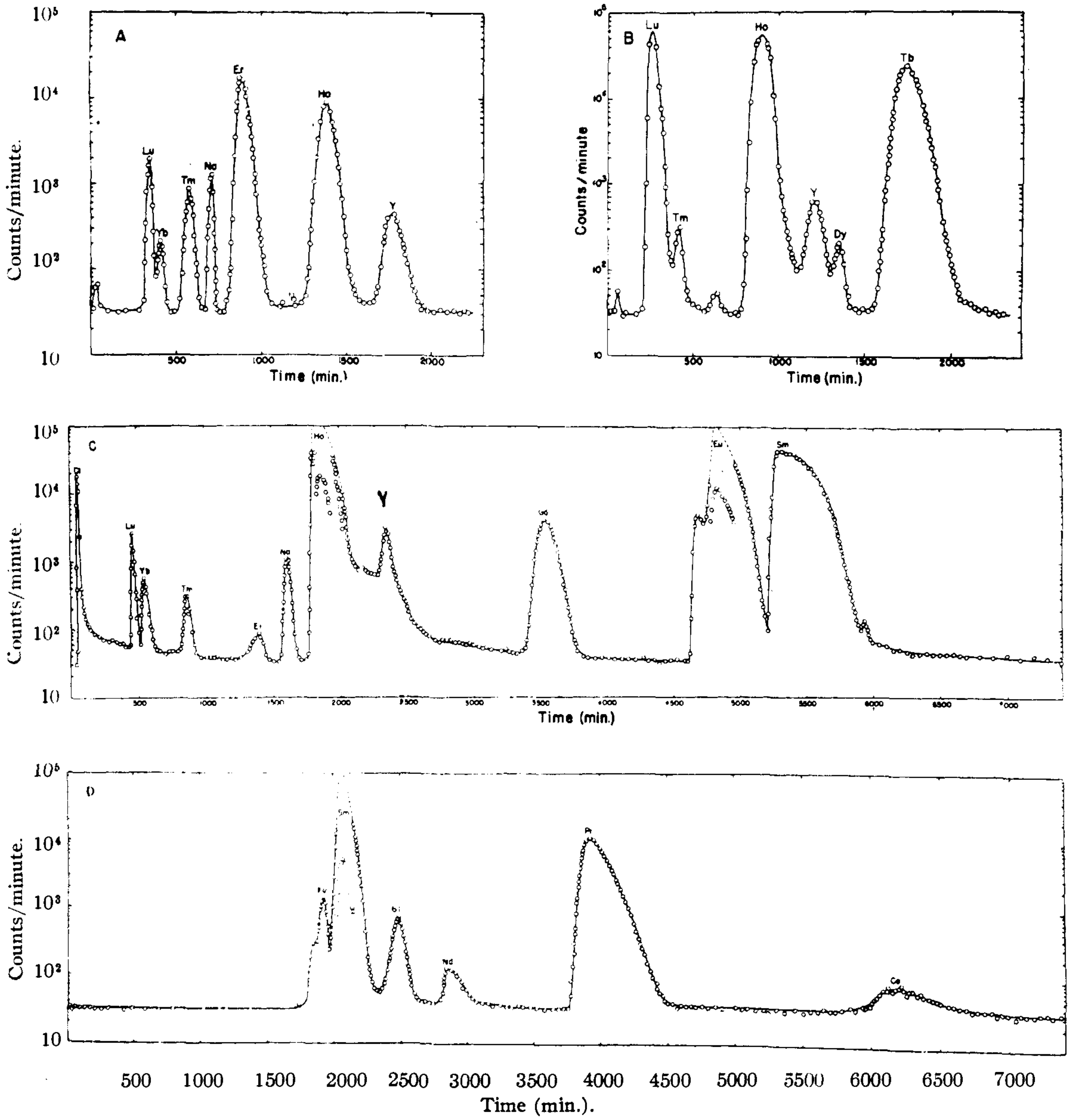

Fig. 6.—Demonstrations of rare earth separations effected with a 270/325 mesh Dowex-50 column at 100°: bed dimensions, 97 cm. by 0.26 sq. cm.; flow rate, 1.0 ml./sq. cm./min. except in *a* where 2.0 ml./sq. cm./min. was used: (a) fractionation of activities produced by neutron irradiation, 0.8 mg. spectrographic grade Er_2O_3 (Hilger) (*p*H 3.20); (b) fractionation of heavy rare earth mixture consisting of 0.1 mg. each of Lu_2O_3, Yb_2O_3, Ho_2O_3 and Tb_2O_3 [Tm, (Er), Y and Dy present as impurities] (*p*H 3.20); (c) fractionation of intermediate rare earth mixture consisting of 0.1 mg. Ho_2O_3 and 1.0 mg. each of Dy_2O_3, Gd_2O_3, Eu_2O_3 and Sm_2O_3 (Cl, Lu, Yb, Tm, Er and Na present as impurities, *p*H 3.25 for 4550 minutes, then *p*H 3.33); (d) fractionation of light rare earth mixture consisting of 0.1 mg. each of Sm_2O_3 and Nd_2O_3 plus 0.01 mg. each of Pr_2O_3, Ce_2O_3 and La_2O_3 (Eu present as impurity, 61 produced by 1.7 h Nd^{149} → 47 h 61^{149}. *p*H 3.33 for 1610 minutes, then *p*H 3.40).

The degree of separation achieved with the bed of 270/325 mesh Dowex-50 particles may be seen in Fig. 6a. Here, except for the particle size and the bed cross section which was 0.26 sq. cm., the conditions were the same as those for the fractionation exhibited in Fig. 5. As in the previous experiments, samples of the eluate were taken and the activity was reclaimed on a small column. The identification of the activity peaks was made by a characterization of the decay periods and energies of these samples.

A comparison of Figs. 5 and 6a serves to establish the improved separation made with 270/325 mesh adsorbent. Whereas about the same time was required for a peak due to a particular element to appear in the effluent, these peaks possessed less abrupt edges with the 120/140 mesh bed and hence were broader. Also, the activity between the peaks was never less than *twice* the instrument background. Furthermore, with the larger particles, the resolution of the Lu and Yb peaks (Fig. 5) was very much less than was found with the 270/325 mesh preparation. The relatively high flow rate of 2 ml./sq. cm./min. used in both of these experiments is to be noted. In fact, because of the decrease in viscosity of the buffer solution as the temperature increased, it was possible to operate the column at flow rates well in excess of this value using a hydrostatic head of only twelve feet.

A comparison of Figs. 3 and 6a shows that in the latter the separation of the Lu, Yb, Tm, Er, Ho and Y activities was accomplished in about two-thirds the time required for the fractionation made at 25° with 170/200 mesh Amberlite IR-1. The activity peaks were well separated in the 100°, 270/325 mesh Dowex-50 experiment, for it may be seen that the activity decreased to background between the bands.

The position of the peak of sodium activity observed in Figs. 3, 6a, and 6c was of interest. It is apparent that the rare earths were desorbed in the order of increasing crystal radius. However, not only is the ionic charge of sodium less than those of the trivalent rare earths, but its ionic radius is smaller even than that of lutecium (r_{Na^+} = 0.98 Å.; $r_{Lu^{+++}}$ = 0.99 Å.). In most base-exchange reactions univalent ions are much less tightly bound and therefore more easily desorbed than are more highly charged ions. The position of sodium among the rare earths in these experiments is to be explained on the basis that the value of δ for the former comes in the same range as those for the rare earths. Alternatively, the movement of sodium through the bed was slow because of the low cation content of the buffer, ($c_{NH_4^+}$ = 0.2 M at pH = 3.2), whereas the movement of the rare earths was increased relative to sodium because they formed complex ions with the anions of the citrate buffer.

In order to confirm the assignment of the sodium and yttrium peaks in Fig. 6a, about a milligram each of sodium, holmium and yttrium were irradiated, adsorbed, and separated at 100° under the same conditions and on the same 270/325 mesh column as was used for the erbium study. The relative positions of the activities were the same as in the experiment in which these activities were found in Hilger erbium, thus verifying the assignments made in that case.

Separation of both the Yttrium and Cerium Group Rare Earths at 100° with Dowex-50.—The same 97 cm. 270/325 mesh Dowex-50 column employed to separate the heavy rare earth impurities in the Hilger erbium oxide was used next in three consecutive experiments in which the rare earths from lutecium through lanthanum were separated. In each of these, the column was operated at 100°, and at flow rate of 1 ml./sq. cm./min.

In the first experiment 0.1 mg. each of the neutron irradiated oxides of lutecium, ytterbium, holmium and terbium were adsorbed. The elutriant solution had a pH of 3.2. The activity history of the column is plotted in Fig. 6b. The lutecium and ytterbium bands were not completely resolved, probably because the elutriant pH was somewhat higher than the optimum of 3.1. The elements thulium, erbium, yttrium and dysprosium were present as impurities in the lutecium and holmium.

The second experiment consisted of the bombardment and separation of 0.1 mg. of holmium oxide and 1.0 mg. each of the oxides of dysprosium, gadolinium, europium and samarium. The results are presented in Fig. 6c.

The desorbing buffer used during the first 4550 minutes had a pH of 3.25, and thereafter another buffer with a pH of 3.33 was used. Before the change of buffers a portable Eck and Krebs G.-M. counter tube was used to scan the column. There were two well separated activity maxima. It is believed that the upper band of activity, the last peak to be eluted, (*i. e.*, Sm) was moved appreciably closer to the lower band (*i. e.*, Eu) by the advancing boundary between the two solutions. This resulted in the europium and samarium peaks being less well separated than would ordinarily have been the case, and also in the anomalous double peak in the former.

During the early part of this separation the minima between peaks was much above the instrument background of 32 counts per minute. It is believed that the high level of these minima was due to the radiation coming from the unshielded column and not to activity in the effluent solution. Although the counter was protected by a two-inch thick lead shield, the γ radiation of the 2.5 h dysprosium and the 9.2 h europium could penetrate this easily. In fact, the level of radiation from the column was quite high until sufficient time had lapsed for these activities to decay.

With several elements the activity in the eluate increased to such a high level that it exceeded the maximum the counting equipment could accept. Therefore, aluminum absorbers were placed between the counting cell and the counter tube while the peak activity of holmium and europium passed through the counting cell. In this way it was demonstrated that the peaks, which would have been too high to measure without absorbers, were not multiple peaks due to poorly separated adjacent earths.

In the third experiment 0.1 mg. each of samarium and neodymium oxides and 0.01 mg. each of praseodymium, cerium and lanthanum were bombarded and separated. The elutriant solution had a pH of 3.33 for the first 1610 minutes, and a value of 3.4 thereafter. The results are plotted in Fig. 6d.

In this experiment again it was necessary to increase the *p*H of the elutriant to increase the rate of movement of the bands. This compressed the first three peaks which came from the column so that they appeared to have been less well separated than would have been the case had the same buffer solution been used throughout the entire experiment. The relative smallness of the neodymium activity peak was caused partially by its weak beta radiations and likewise partially by its long half-life. Actually, as much Nd as Sm was present. The clearly defined position of element 61 between Nd and Sm (see Fig. 6d) is of interest. This finding is in agreement with earlier observations,[9] and in fact serves to establish the place of this radio-isotope in the rare earth adsorption sequence beyond a reasonable doubt.

At the time the cerium had been displaced completely from the column, another peak could be detected well up in the column; this presumably was the lanthanum band.

A higher *p*H value was required to differentially desorb the cerium earths (*ca.* 3.4) compared with that for the yttrium group (*ca.* 3.2) at 100° also. A similar difference was found with the room temperature separations wherein Amberlite IR-1 was employed, and is to be interpreted as a consequence of the greater stability of the citrate complex ions of the heavy rare earths.

The Application of Ion-exchange Separations Techniques to Rare Earth Analysis.—The above described study of the impurities in Hilger erbium oxide constituted a qualitative analysis for the most difficultly recognizable impurities, namely, the other rare earths. One experiment has been made which might be classed as semiquantitative analysis. The material used was erbium which had been purified to a high degree on an ion-exchange column.[26] Spectrographers skilled in rare earth analyses had failed to detect the spectral lines of any other rare earth except erbium in this sample. A 5-mg. aliquot was bombarded in the pile before processing it on the 97 cm. Dowex-50 column. An extremely good separation was obtained of traces of lutecium, ytterbium, thulium, and sodium from the erbium (see Fig. 7). No rare earths lighter than erbium were detected although the column was operated for a sufficiently long time that holmium and yttrium, if present, should have been desorbed.

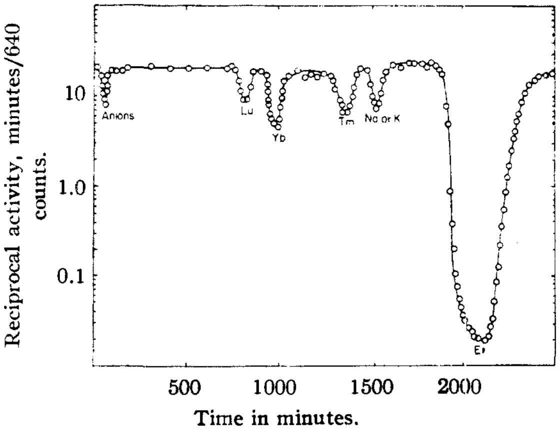

Fig. 7.—Neutron activation analysis of spectrographically pure erbium oxide: bed dimensions, 97 cm. × 0.26 sq. cm.; flow rate, 0.5 ml./sq. cm./min.; 5% citrate buffer at *p*H 3.2; temperature, 100°; 5.0 mg. of Er_2O_3 irradiated in Clinton neutron chain reactor and then fractionated by Dowex-50 ion exchange column.

The entire sample of eluant which contained the thulium was processed on a small column to reclaim the activity. This activity was assayed on apparatus at known counting geometry so that the number of disintegrations, and, therefore, the total number of atoms of Tm^{170}, could be computed from the known half-life. The activation cross-section of Tm^{169} is about 10^{-22} sq. cm. per atom. From the neutron flux of the pile, the cross-section, the duration of the bombardment, and the number of Tm^{170} atoms produced, it was possible to compute the number of Tm^{169} atoms present as impurity in the original erbium. Since the mass of erbium which was irradiated was known, it was possible to express the thulium impurity in per cent. of the total. This erbium contained not more than 0.001% (*i. e.*, 10 p.p.m.) thulium.

A considerably smaller amount of Tm impurity could have been detected if longer bombardments were made to activate the thulium more nearly to saturation.

Discussion

Taken all together, the data of Fig. 6 reveal that the sequence of relative adsorbability among the rare earths was as follows: La > Ce > Pr > Nd > 61 > Sm > Eu > Gd > Tb > Dy > Y > Ho > Er > Tm > Yb > Lu. This progression is in the same order as that of the crystal ionic radii.[27] The variation of the basicity predicted by von Hevesy[28] from theoretical considerations is likewise the same. In these terms, then, adsorbability follows basicity in the sense that strong bases will replace weaker bases from the adsorbent.

The relative position of yttrium, which fell between dysprosium and holmium, was in excellent agreement with the predictions based on the ionic radius. Owing to the very close similarity of Y with these two elements, the triad: Dy, Y,

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(26) The authors wish to thank Mr. Darwin Harris for this material. Efforts to produce purified heavy rare earths on a gram scale were initiated in December, 1946, by D. H. Harris and E. R. Tompkins. By June, 1947, 10 milligram quantities of pure Lu, Tm and 100 mg. amounts of spectrographic grade Yb and Er had been separated from crude yttrium salts by successive chemical and exchange column refining procedures. This work will be published soon; private communication, E. R. Tompkins, May 28, 1947.

(27) V. M. Goldschmidt, T. Barth and G. Lunde, *Skrifter Norske Videnskaps Akad. Oslo*, 1 Math. Nat. Kl. no. 7 (1925).

(28) G. von Hevesy, "Die selten Erden vom Standpunkte des Atombaues," Julius Springer, Berlin, 1927, pp. 16–21.

Ho, in fact, constitutes what may be taken as the most difficultly separable of all of the rare earths. Although the similarities were not so great, the adsorbabilities in two other positions within the rare earths were found to be comparable, namely, the triads: Tm, Yb and Lu; and, Sm, Eu and Gd. It was of interest to find that the most recent and exact X-ray diffraction measurements on the rare earth sesquioxides[29] have indicated a dependence of the lattice spacing in these compounds on the number of electrons in the 4f shell of the atom. As may be seen from Fig. 8 where the relative radii ($r_{La^{+++}} = 1.000$) are plotted, the rare earths are conveniently divided into two groups. The first of these, which corresponds to the filling in of the first seven 4f electrons, begins with cerium and ends with gadolinium. Likewise, the relative adsorbability decreases steadily as the atomic number increases so that the maximum similarity between pairs is reached with Eu and Gd, in excellent conformity with the known parallelism between ionic radii and adsorbability. The second subgroup, which begins with terbium and ends with lutecium, corresponds to the filling in of the second seven 4f electrons, and a maximum similarity in both the relative radii and adsorbability is found with Yb and Lu. However, the differences from member to member in the second sub-group are smaller than those between corresponding members of the first. Consequently, taken as a whole, cerium and praseodymium are the easiest of the rare earths to separate from one another, and ytterbium and lutecium are the most difficult, excepting for the separation of the quasi rare earth yttrium from dysprosium. The separability of Eu and Gd corresponds roughly to that of Er and Tm in difficulty.

Quantitative comparisons of the relative adsorbability within the yttrium group earths were made possible by utilizing the data from a much larger number of chromatograms than those shown in Figure 6, together with Equation (8) above. The ratios of the distribution coefficients of neighboring members of the sequence, presented in Table II, clearly bears out the foregoing statements. The average deviation found for these ratios from experiment to experiment, in spite of differing conditions of flow rate, *p*H and temperature, is seen to have been less than 2%, emphasizing the highly reproducible character of adsorption column performance, as well as confirming some of the predictions made in an earlier section. Although the absolute values for the distribution coefficients derived from column data have been computed, they will not be reported until a comparison with values of K_d determined by simple equilibrium measurements becomes possible.

TABLE II

RELATIVE RARE EARTH ADSORBABILITIES

Element	$\delta_{n+1}:\delta_n$
Lu	
	1.21 ± 0.01
Yb	
	1.44 ± .02
Tm	
	1.55 ± .02
Er	
	1.57 ± .02
Ho	
	1.30 ± .02
Y	
	1.20
Dy	

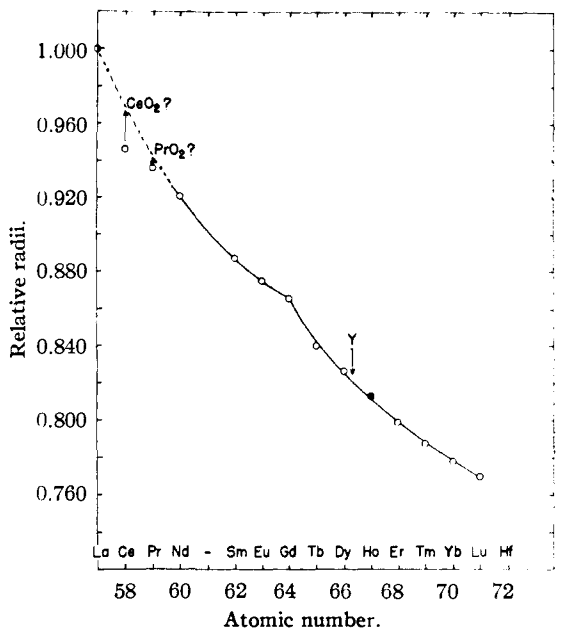

Fig. 8.—Relative (cubic) radii of trivalent rare earth ions: $R_{La^{+++}}$1.291 Å. for cubic sesquioxide; O, H. Bommer, *Z. anorg. allgem. Chem.*, **241**, 273 (1939); ●, V. M. Goldschmidt, *Ber.*, **60**, 1263 (1927); these data were computed by Dr. M. Bredig.

Acknowledgments.—The authors wish especially to thank Dr. W. C. Bauman of the Dow Chemical Company for his invaluable assistance in supplying the needs of our research with special laboratory scale preparations of spherical Dowex-50. The help given by Dr. L. A. Matheson in this and in other ways is gratefully acknowledged. The initial stages of this work were facilitated by the receipt of small quantities of spectrographically analyzed lutecium, thulium holmium and terbium sesquioxides through the generosity of Dr. C. J. Rodden of the National Bureau of Standards. Thanks are also due to Dr. E. M. Gladrow of Iowa State College for his donation of gram quantities of neodymium oxide which had been purified by him to a high degree using ion-exchange column techniques.

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[29] Bommer, *Z. anorg. allgem. Chem.*, **241**, 273 (1939). We wish to thank Dr. Max Bredig for his helpful discussion of this point.

Summary

1. A demonstration of the separation of all the rare earths by chromatographic techniques based on the use of synthetic organic ion-exchange adsorbents was made. With a 97 cm. by 0.26 sq. cm. bed of 270/325 mesh Dowex-50 adsorbent maintained at 100°, the optimum *p*H of the 4.75% citric acid eluant was 3.2 for the separation of the yttrium earths and 3.4 for the cerium earths.

2. The employment of a temperature of 100° permitted the use of elutriant flow rates of as high as 2 ml./sq. cm./min., thereby greatly reducing the time required for a separation. In a typical experiment, milligram quantities of lutecium, ytterbium, thulium, erbium, holmium, and yttrium were separated in thirty hours.

3. The fractionation of the heavy rare earths could be made sufficiently complete that the method was established as a promising procedure for the quantitative analysis of rare earths for cationic impurities. A previously exhaustively purified sample of erbium oxide, in which all other rare earths were reported as absent by spectrographic analysis, was shown to contain 10 p.p.m. of Tm by irradiation of the Er_2O_3 with neutrons and subsequent chromatographic separation.

4. The adsorbability of yttrium was shown to lie intermediate between holmium and dysprosium in quantitative agreement with the expectations based on considerations of the ionic radii. As a result, the separation of these elements was even more difficult to accomplish than the separation of the heavier rare earths.

5. The adsorbability of ytterbium and lutecium were shown to be more nearly the same than any other pair of rare earths in conformity with the trend in ionic radii. Predictions based upon crystal radii suggested that samarium, europium and gadolinium would be the most difficult of the cerium earths to fractionate.

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[CONTRIBUTION NO. 20 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Separation of Rare Earths by Ion Exchange.[1] III. Pilot Plant Scale Separations

BY F. H. SPEDDING, E. I. FULMER, T. A. BUTLER, E. M. GLADROW, M. GOBUSH, P. E. PORTER, J. E. POWELL AND J. M. WRIGHT

Introduction

The previous papers[2,3] of this series dealt with the development of procedures for separating macro-amounts of the rare earths by adsorption on Amberlite IR-1 and subsequent elution with 5% citric acid–ammonium citrate[4] solutions at regulated *p*H. The use of this concentration of citrate proved costly in large scale operations. Therefore, experiments were undertaken to find the minimum concentration of the citrate consistent with efficient separations using Amberlite IR-100. Data also are presented on the development of the working conditions for pilot plant separation of the rare earths. For convenience of discussion, the data will be presented under the two headings: I. The Light Rare Earths (Cerium group), and II. The Heavy Rare Earths (Yttrium group.)

The separation of the rare earths was stepped up to pilot plant scale using the general procedures established for the smaller scale operations.[2,3] There was urgent need not only to furnish pure rare earths to other members of the Manhattan Project, but also to obtain pure fractions to determine optimum conditions for their separation.

It follows that the conditions used in these studies were not optimum. There is no doubt that, under better conditions, less solution will be required, separation per passage will be more effective and the time of operation will be materially reduced. It is also likely that automatic features can be installed which will greatly decrease the hours of labor required. All of these factors are being studied and will be presented in subsequent papers.

I. The Light Rare Earths (Cerium Group)

1. **Effect of Concentration of Citrate.**—Three 1.00-g. samples of crude Nd_2O_3 were dissolved in a slight excess of hydrochloric acid. The *p*H was adjusted to 1.8 and each solution adsorbed on Amberlite IR-100 beds 28 inches in height and 16 mm. in diameter. The samples were eluted with 5.0, 0.5 and 0.05% citrate solutions at a *p*H of 5.0. The 5% solution eluted the sample rapidly but the break-through with the 0.05% eluant was much too slow for practical purposes; the 0.5% citrate solution eluted the sample at a somewhat slower rate than did the 5% solution but the results were sufficiently promising to warrant detailed studies of the effect of *p*H. The break-through represents the total volume of eluant at which the presence of the given element is first evidenced by precipitation as the oxalate.

2. **Effect of *p*H.**—Samples consisting of 35% Sm_2O_3 and 65% Nd_2O_3, weighing 0.9 g., were treated with hydro-

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(1) This work was supported, in part, by a grant from The Manhattan District, U. S. Corps of Engineers.

(2) F. H. Spedding, A. F. Voigt, E. M. Gladrow and N. R. Sleight, THIS JOURNAL, **69**, 2777 (1947).

(3) F. H. Spedding, A. F. Voigt, E. M. Gladrow, N. R. Sleight, J. E. Powell, J. M. Wright, T. A. Butler and P. Figard, *ibid.*, **69**, 2786 (1947).

(4) The term % refers to the grams of citric acid monohydrate per 100 ml. of original solution. The *p*H is adjusted by the addition of concentrated ammonia; the *p*H values are accurate to 0.02 *p*H unit.