of the band progress down the column, the length of the column necessary to reach the fully developed band and the number of liters of citric acid which will have to be passed through the column before the break-through of the rare earths at the bottom of the column is observed.

Experimental results will be presented correlating the shrinkage or expansion of the resins with the form of the resin present: for example, rare earth resin, ammonium resin and hydrogen resin. It has been possible to determine these band fronts much more precisely when neodymium was used since band edges become very clearly visible, due to the characteristic color of the neodymium ions, when the columns are illuminated in the dark with blue light.

Since the over-all change which occurs when a rare earth equilibrium band is being moved down the column is the conversion of the hydrogen resin which precedes the band into the ammonium resin which follows it, the break-through of the rare earth band at the bottom can be calculated with very high precision. While there is of course some hydrogen resin mixed with the ammonium resin which follows the band, the amount of this resin is extremely small as can be readily seen from the fact that the hydrogen ion in solution is so dilute compared to the ammonium ion. Accordingly, one needs only to divide the number of active points in the column occupied by hydrogen below the originally adsorbed rare earth band by the number of ammonium ions which are being put in the top of the column per liter to obtain the break-through volume. For example

$$V_B = \frac{A - B}{C_{NH_4^+}} = \frac{WQ - B}{C_{NH_4^+}}$$

V_B = volume of eluant required for break-through in liters

A = exchange capacity of the resin bed in milliequivalents

B = milliequivalents of rare earth adsorbed on bed

$C_{NH_4^+}$ = milliequivalents of ammonium ion per liter of eluant

W = weight of resin in the column in grams

Q = capacity of the resin in milliequivalents per gram

pH	Rare earth	A meq.	B meq.	$A - B$ meq.	$C_{NH_4^+}$ meq./l.	V_B (calcd.), l.	V_B (obs.), l.
6.4	Pr	852	44.0	808	13.87	58.2	58.0
	Nd	852	44.5	807	13.87	58.1	58.1
6.1	Pr	852	44.0	808	12.90	62.6	62.5
	Nd	852	44.5	807	12.90	62.5	62.4
5.8	Pr	852	44.0	808	11.78	68.6	68.5
	Nd	852	44.5	807	11.78	68.5	68.4
5.5	Pr	852	44.0	808	10.69	75.6	75.4
	Nd	852	44.5	807	10.69	75.5	75.4
7.3	Nd	852	178.0	674	15.38	43.8	43.7
7.6	Nd	852	178.0	674	15.70	42.9	43.0
8.2	Nd	852	178.0	674	16.88	39.9	39.8
5.6	Nd	852	27.0	825	10.99	75.1	75.0
5.9	Nd	852	53.5	798	12.10	65.9	65.5[a]
6.2	Nd	852	89.0	763	13.27	57.5	57.5
6.5	Nd	852	89.0	763	14.05	54.3	54.0
6.8	Nd	852	89.0	763	14.67	52.0	51.8[a]

[a] Extrapolated values obtained from band-front measurements.

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QUANTITATIVE THEORY OF RARE EARTH SEPARATIONS ON ION-EXCHANGE COLUMNS

Sir:

This Laboratory, in a series of papers (THIS JOURNAL, **69**, 2812 (1947); **72**, 2349, 2354 (1950); **73**, 4840 (1951)) has described how the rare earths can be separated from each other on ion-exchange columns. The method consists essentially of adsorbing a mixture of neutral rare earth chlorides on the top of a high-capacity ion-exchange column in the hydrogen cycle. The rare earth band which forms at the top is then moved down the column by eluting it with a solution of citric acid which has been adjusted to a known pH value by the addition of ammonium hydroxide. If the pH range of the eluant is between 5.5 and 7.3 for 0.1% citric acid, it is found that when the elution curves are plotted (concentration of rare earth in the eluate against liters of citric acid passed through the column), flat-topped elution curves are observed.

Shortly we expect to publish detailed experimental results and calculations showing that if the amount of rare earth adsorbed on the column, the concentration of citrate solution which goes in the top of the column and the pH of that solution, or its ammonium equivalent, are known, then it is possible to calculate to better than 5%, and in most cases to better than 1 or 2%, the composition of the eluate coming out the bottom. This includes the ammonium concentration, the rare earth concentration and the pH or hydrogen ion concentration. Some very interesting relations between the data and the activity coefficients of the resin can be observed. These can be deduced as a result of the constraints put upon the system by the fact that the resin has a fixed capacity. In order to make these calculations it is only necessary to use simple thermodynamics involving the ionization constants K_1, K_2, K_3 of citric acid, the equilibrium constant of the rare earth complex, the conservation conditions of the electrical neutrality of the solution and the fixed capacity of the resin.

It has been found that the predominating and only important rare earth complex formed in this pH range is (RE $cit_2^\equiv$). Experimentally, it has been found that if the ammonium ion of the eluant, the hydrogen total of the eluant H_T (a summation of the hydrogen combined with H_3cit, H_2cit^- and $Hcit^-$ + the H^+ ion), the H_T of the eluate, the ammonium ion of the eluate, and the rare earth total of the eluate are plotted against the H^+ ion of the eluate, that linear curves result. Accordingly, if any pair of these are plotted against each other linear functions are also found. The slopes of these lines can be calculated from theoretical considerations. Furthermore, the instability constant K for the RE $cit_2^\equiv$ complex can be calculated for each of the rare earths.

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