± 10 joules/g. for the heat of combustion of cerium metal in oxygen at 25 atmospheres pressure.

Composition of the Cerium Dioxide.—The cerium oxide formed was brown in color. An X-ray pattern showed only lines of cubical CeO_2.

Heat of Formation of CeO_2.—The heat of combustion reported above gives for the reaction in the bomb a value of $\Delta E_{24°} = -1085.9 \pm 1.4$ kjoules/mole. The correction of this value to 25° is less than the uncertainty in the result. To obtain the heat of formation it is necessary to correct for the deviation of oxygen from the perfect gas law and to convert from ΔE to ΔH. Using Rossini and Frandsen's[7] value of $(\partial \Delta E/\partial P)_{301°K.} = -6.51$ joules/atm./mole for oxygen and, taking $\Delta H = \Delta E + \Delta(PV)$, we have for the heat of formation of CeO_2, $\Delta H_{25°} = -1088.6 \pm 1.4$ kjoules/mole. In defined calories this is -260.18 ± 0.33 kcal./mole. This value differs by about 6.8% from the value of -243.6 kcal./mole obtained by Hirsch[8] which has been accepted by Brewer[8] as being the most reliable. It differs by 11.7% from the value of -233 kcal./mole selected by the National Bureau of Standards,[9] evidently from the work of Moose and Parr.[5]

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They also are very appreciative of the courtesy of Dr. F. H. Spedding of Ames Laboratory, A. E. C., through whom the cerium metal was obtained.

[7] F. D. Rossini and M. Frandsen, *J. Research Natl. Bur. Standards*, **9**, 733 (1932).

[8] L. Brewer, "The Thermodynamics of the Rare Earths," UCRL-1931, Sept., 1952.

[9] "Selected Values of Chemical Thermodynamic Properties," N. B. S. Circular 500, 1952, p. 348.

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Ion Exchange as a Separation Method. VI. Column Studies of the Relative Efficiencies of Various Complexing Agents for the Separation of Lighter Rare Earths

BY S. W. MAYER AND E. C. FREILING

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Using columns of Dowex-50 cation-exchange resin at 87°, Sm–Eu and Eu–Tb separation factors have been determined for a number of complexing agents under dynamic conditions. A comparison of the separation factors thus obtained yields the following order of selectivity for the complexing agents studied: EDTA > lactate = glycolate > malate ≥ citrate. EDTA (ethylenediaminetetraacetate) has the disadvantage of low solubility in the *p*H range most suitable for good separations.

Introduction

Until now, buffered solutions of citric acid have been used almost exclusively in the separation of rare earths by cation-exchange chromatography. Although it has been shown that improved separations are obtained in a given time by the use of elevated temperatures,[1,2] no effects of varying the conditions of the eluting agent at the convenient temperature of 87° have been reported. In attempting to achieve an improved separation of the lighter rare earths in a relatively short period of time, we have made a number of column studies at 87° using Dowex-50 cation-exchange resin. These studies involved (1) variation of the *p*H and concentration of citric acid and (2) extension of the equilibrium studies of Tompkins and Mayer[3] to dynamic conditions and to include other complexing agents. Data have been obtained for the relative efficiencies of citric, lactic,[4] malic, glycolic and ethylenediaminetetraacetic (EDTA) acids.

The results of other investigations have indicated that Eu and Sm offer a convenient pair of difficultly separable rare earths. In our studies, the efficiencies of eluting conditions were determined by comparing the purity of Eu and Sm obtained, as well as that of Y and Tb which likewise are difficult to separate.

We have been primarily interested in seeking column conditions which would give the maximum purification of the lighter rare earths within a reasonable period of time. For this reason, conditions were always chosen in an effort to obtain a residence time of approximately 8 hr. for Sm. Such a procedure required the simultaneous alteration of more than one variable.

Experimental

Materials.—Commercial 250–500 mesh Dowex-50 cation-exchange resin was graded to obtain that portion which settled through 6 in. of water in from 2 to 15 min. This portion was washed with 6 *N* HCl to remove Fe, converted to the ammonium form with concentrated NH_4OH and finally washed with distilled water.

The β-emitting isotopes Sm^{153}, $Eu^{152,154}$, Tb^{160} and Y^{91} were used to trace the elution histories of the various runs.

Eluting agents were prepared with boiled distilled water; toluene was added as a preservative. The *p*H of these solutions was adjusted with C.P. NH_4OH and measured on a Beckman Model G *p*H meter.

Apparatus and Procedure.—The columns were made from thick-walled capillary tubing (1.6 mm. i.d.). A 10-mm. Pyrex tubing, sealed to the upper end of the column, served as a preheating reservoir for the eluting agents. By packing these columns with freshly boiled resin while they were maintained at 87°, bubble formation was almost entirely eliminated as long as the columns were kept hot and the *p*H of the eluting agent was kept below 3.5.

Before beginning a run, each column was preconditioned with the appropriate eluting agent and then washed with about 2 ml. of boiled distilled water. Next active solutions were added and allowed to pass through the column. These were followed immediately by the eluting agent.

[1] B. H. Ketelle and G. E. Boyd, THIS JOURNAL, **69**, 2800 (1947).

[2] S. G. Thompson, B. B. Cunningham and G. T. Seaborg, *ibid.*, **72**, 2798 (1950).

[3] E. R. Tompkins and S. W. Mayer, *ibid.*, **69**, 2859 (1947).

[4] Before we had completed any of the column runs with lactate solutions, we received a private communication from H. Petrow to the effect that lactate solutions appeared to be more effective than citrate for the praseodymium–neodymium separation on ion-exchange columns operated at room temperature.

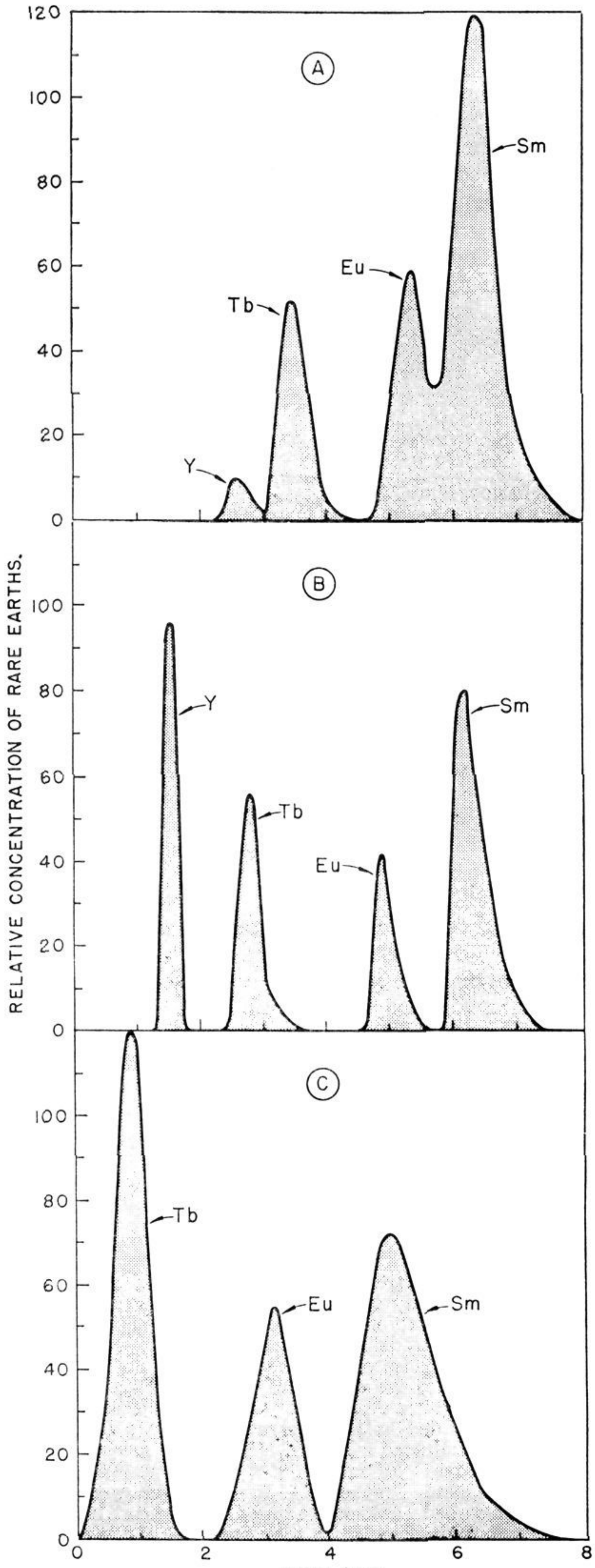

Fig. 1.—Elution history curves: (a) 0.50 *M* citrate, *p*H 3.04, 0.52 ml./hr.; (b) 0.24 *M* lactate, *p*H 5.00, 4.5 ml./hr.; (c) 0.26 *M* EDTA, *p*H 3.62, 0.50 ml./hr.

The eluate from the column flowed through a thin walled plastic tube (1 mm. o.d.), about 1 cm. of which was exposed to an end window Geiger–Mueller counter. The activity of eluate was indicated on an automatic recorder connected to a counting rate meter.

It was found advantageous to add I^{131} as iodide ion to the first drop of eluting agent. The appearance of I^{131} in the eluate then coincided with that of the complexing agent.

Results and Discussion

The experimental data are summarized in Table I. Here the symbol C_{Sm} denotes the volume of eluting agent which has flowed through the resin bed when the concentration of Sm in the eluate has reached its maximum. The residence time of Sm in any run can be obtained by dividing C_{Sm} by the flow rate.

TABLE I

COMPARISON OF COMPLEXING AGENTS

Eluting agent	*p*H	$\frac{C_{Sm}}{C_{Eu}}$	$\frac{C_{Eu}}{C_{Tb}}$	Flow, ml./hr.	C_{Sm}, ml.
0.25 *M* Citrate	3.50	1.15	1.7	0.70	4.6
.25 *M* Citrate	3.25	1.21	1.5	0.66	12.0
.30 *M* Citrate	3.25	1.16	1.7	1.2	5.5
.50 *M* Citrate	3.04	1.19	1.6	0.52	3.3
1.00 *M* Citrate	2.46	1.13	1.2[a]	.51	19.7
0.026 *M* EDTA	3.62	1.60	3.5	.50	2.6
.017 *M* EDTA	3.62	1.46	3.8[b]	.71	8.6
.20 *M* Lactate	6.00	1.28	1.8	4.5	40.7
.24 *M* Lactate	5.00	1.28	1.7	4.5	27.7
.32 *M* Lactate	5.00	1.25	1.9	2.3	6.0
.40 *M* Lactate	4.10	1.28	2.0	2.0	7.4
.30 *M* Lactate	4.00	1.31	2.1	4.0	42.6
1.33 *M* Lactate	3.08	1.32	2.1	0.63	2.9
1.00 *M* Lactate	3.00	1.23	1.9	2.5	27.0
0.30 *M* Glycolate	4.00	1.28	2.0	2.5	2.8
.50 *M* Malate	3.25	1.15	1.5	1.2[a]	5.2
.70 *M* Malate	2.99	1.23	1.5	1.2	17.1

[a] Estimated. [b] The peaks of the elution curve were flat-topped which caused the estimation of the *C* value to be uncertain.

Among the citrate solutions tested, the 0.50 *M* citrate solution at *p*H 3.04 gave the best separation within the allotted time although considerable cross-contamination occurred. A graph of the elution history of this run is presented in Fig. 1, together with similar graphs of the best separations obtained with lactate and EDTA eluting agents.

For a column run made under equilibrium conditions, the *C* value of an ion (expressed in free column volumes) is equal to the distribution coefficient of that ion between the resin and liquid phases.[5] The ratio of *C* values of any two ions, therefore, is equal to the separation factor. The significance of the *C* ratios obtained in these studies

TABLE II

THEORETICAL PERCENTAGE OF Eu RECOVERABLE IN DESIRED PURITY FROM A 400-PLATE COLUMN WHEN C_{Sm} IS FOUR FREE COLUMN VOLUMES

$\frac{C_{Sm}}{C_{Eu}}$	Percentage Eu recoverable	
	99% Purity	99.99% Purity
1.15	50.0	5.8
1.20	80.9	30.9
1.25	93.7	43.4
1.30	99.8	69.5
1.35	99.9	88.5
1.50	100.0	99.9

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(5) S. W. Mayer and E. R. Tompkins, THIS JOURNAL, **69**, 2866 (1947).

is illustrated by Table II which lists the theoretical percentage of Eu recoverable in 99 and 99.99% purity from a column run in which C_{Sm} is four free column volumes and the number of theoretical plates is 400.

Those eluting agents prepared from monobasic acids present a system which is much simpler to deal with theoretically than eluting agents prepared from polybasic acids. Consider the case of an eluting agent which contains only one species capable of complexing the rare earth ions and which forms with each rare earth ion only one major complex species. The *C* ratio or separation factor of any two rare earths is then equal to the ratio of the equilibrium constants for the respective adsorption reactions

$$MX_3 + 3NH_4R \rightleftharpoons MR_3 + 3X^- + 3NH_4^+$$

where M is the bound rare earth, X^- the complexing anion and R refers to the resin. Therefore, for runs made under conditions approaching equilibrium, one would expect the *C* ratios to be independent of the *p*H and concentration of eluting agent. Since lactate solutions satisfy these conditions, the *C* ratios obtained in the lactate runs should be a function only of the flow rate. Mayer and Tompkins[5] have pointed out that *C* ratios of two rare earths would not be expected to vary greatly with flow rate. They have demonstrated that with colloidal agglomerates of Dowex-50 at room temperature no significant variation occurs at flow rates as high as 1.152 ml./sq. cm./min. According to our results at 87°, the *C* ratios remain essentially constant up to a flow rate of 3.73 ml./sq. cm./min. From these considerations, it becomes apparent that, in the case of a monobasic acid, only one run may be necessary to judge its value as a candidate for an eluting agent.

In agreement with the plate theory of Mayer and Tompkins,[5] cross-contamination was found to be greater with those lactate solutions which eluted the rare earths in a relatively small volume of eluate. Higher flow rates were employed to utilize the weaker lactate solutions and maintain the desired residence time for Sm. These were achieved by applying pressure of N_2 up to 10 p.s.i. to the reservoir of eluting agent. At first this technique seemed highly successful, but subsequent investigations have indicated that a detailed investigation of the tailing involved must be completed before the method can be fully recommended.

The greater selectivity obtained with lactic acid, relative to citrate, agrees with the equilibrium results obtained by Tompkins and Mayer.[3] Its adjacent homolog, glycolic acid, has essentially the same selectivity, together with the added advantage of being a stronger complexing agent.

From the standpoint of selectivity, EDTA was by far the best eluting agent tested. Because of the low solubility of EDTA within the useful *p*H range, the consequently low solution capacity makes it especially important that (1) the column be preconditioned with eluant until the *p*H of the eluate is the same as that of the eluting agent and (2) the loading of rare earth be not excessive. Thus with a charge of 6 mg. of Sm_2O_3 per sq. cm., lowering the EDTA concentration from 0.026 to 0.017 *M* resulted in an elution curve with broad, flat-topped peaks. These peaks were similar to those which Spedding and his co-workers[6,7] obtained with low capacity citrate solutions. Cross-contamination, however, remained low. As was to be expected, eluting agents of lower *p*H and EDTA concentration showed the flat-topped peaks to a greater extent and were relatively slow in their eluting action.

The data obtained for malic acid are not sufficiently extensive to fix unequivocally the position of its selectivity relative to the other eluting agents tested. However, in view of the separations obtained with lactic acid and EDTA, the results with malic acid did not seem sufficiently promising to merit further investigation at this time.

A rough rule of thumb has been found useful in predicting the *C* value of Sm from the *C* values of Eu and Tb: namely, that $(C_{\text{Sm}}/C_{\text{Eu}})^{2.7} = C_{\text{Eu}}/C_{\text{Tb}}$. This relationship seems to hold remarkably well considering the variety of eluting agents tested and the experimental error involved. However, more accurate and extensive data will be required before it will be possible to attribute any degree of quantitativity or theoretical significance to this and similar relationships. Such investigations are now in progress.

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[6] F. H. Spedding, E. I. Fulmer, J. E. Powell and T. A. Butler, THIS JOURNAL, **72**, 2354 (1950).

[7] F. H. Spedding, E. I. Fulmer, J. E. Powell. T. A. Butler and I. S. Yaffe, *ibid.*, **72**, 4840 (1951).