to about one-half to one-quarter of its original value. The data in the series 6, 7 and 8, 9, 10 indicate some exchange of activity between ClO_2 and hypochlorite. In the series 11, 12, 13, the exchange was followed by noting appearance of activity in ClO_2, rather than the loss from this substance. These data also indicate a slight exchange. The extent of the exchange appears to increase as the extent of the net change in the system increases. Work on this exchange is being continued by H. C. D. and discussion of the mechanism by which exchange takes place is deferred for the present.

Acknowledgment.—The cyclotron was operated with the aid of funds from the Office of Naval Research (N60NR-20, Task, Order III).

Summary

A rapid exchange between ClO_2 and ClO_2^- takes place in acid and neutral solution (aqueous solutions). At high dilutions (concentrations about 10^{-4} M) the rate of exchange is slow enough to be measurable.

ClO_2 does not exchange at an appreciable rate with ClO_4^-, ClO_3^-, Cl_2 or Cl^-. In the presence of HOCl, the oxidation of ClO_2 to ClO_3^- takes place fairly rapidly. In addition to this net chemical change, a slow exchange between HOCl and ClO_2 takes place.

RECEIVED NOVEMBER 26, 1948

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

A Study of the Effect of a Number of Column Variables[1]

BY E. R. TOMPKINS, D. H. HARRIS AND J. X. KHYM

Introduction

In the course of the development of an ion exchange column apparatus for separating and purifying fission products, it became necessary to investigate the effect of a number of operating variables on the efficiency of the column for separating solutes as well as for volume reduction. At the end of the separation step, each fission product is contained in a rather large volume of citrate solution. In most cases it is desirable that the fission product be shipped in hydrochloric acid solution or some other acid which can be removed by distillation. Therefore, it was necessary that this column apparatus not only separate and purify each fission product, but also that one or more volume reduction steps be accomplished and that a metathesis be made so that the final product would be contained in the desired solvent.

In a previous publication of Cohn, Parker and Tompkins,[1a] the principles of the separation and the volume reduction and metathesis steps are discussed. Also shown in this article is a separation column apparatus which was installed in a concrete cell for separating the fission products obtained by exposing uranium in the chain-reacting pile. As pointed out in this publication, the volume reduction and metathesis steps were carried on in a shielded hood after the separation step. Because of the large quantities of fission products which were desired when general distribution of radioisotopes were announced, it was necessary to construct an apparatus which would carry out all of the separation and volume reduction and metathesis steps within the concrete cell, so that it would not be necessary to remove any radioactive substance until the product was removed for shipment.

A tentative engineering design for the apparatus was drawn up, but before the best size and shape for each of the various columns could be decided, it was necessary to determine the factors affecting their efficiencies. It was decided that hydrostatic pressure should be used exclusively to avoid complicating the apparatus. Due to space considerations in the shielded cell in which the equipment was to be built, short columns of large diameter were indicated, in order that the flow rate would not be excessively low. On the other hand, previous experiments[2,3] had shown that the separation efficiency and the volume reduction factor per stage were functions of column length. In determining the geometry of the various columns, it was necessary, therefore, to compromise between the desire for more efficient operation and faster flow rate, since the over-all hydrostatic head for the necessary four stages was limited by the size of the cell in which the apparatus was to be constructed. For this reason the hydrodynamics of column flow and a number of factors determining column efficiency had to be studied so that a reasonable compromise could be made. The first of these studies, made by M. B. Hawkins and R. E. Garber, was described in an Oak Ridge National Laboratory report. The results of the second study are reported here. Also included are the results of a few experiments to test the effect of carrier, both isotopic and non-isotopic, on the efficiency of separations of two similar elements.

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(1) This work was done at Clinton Laboratories (renamed Oak Ridge National Laboratory), a part of the Plutonium Project, during 1945–1946, and was done under Contract W-35-058-eng-71 for the Atomic Energy Project.

(1a) W. E. Cohn, G. W. Parker and E. R. Tompkins, *Nucleonics*, **3**, 22 (1948).

(2) F. H. Spedding, *et al.*, THIS JOURNAL, **69**, 2786 (1947).

(3) J. X. Khym, E. R. Tompkins and W. E. Cohn, unpublished work.

Experimental

Materials and Apparatus.—In most of the experiments reported here the exchanger Amberlite IR-1 was used. A single large lot of this exchanger, having a particle size of 40–60 mesh, was obtained for the series. Since previous experiments[3] had established the behavior of strontium and barium, the experiments described below were limited to a study of the rare earth type elements, with cerium being used in most of them and yttrium in the remainder. The elutrient solution used in most of the experiments was made by dissolving 50 g. of citric acid monohydrate in water, adjusting the solution to the desired *p*H with ammonia and then diluting it to a liter. Hydrochloric acid was used to adjust the *p*H of eluates in the volume reduction experiments. The apparatus for all experiments consisted of Pyrex glass columns (of varying dimensions) with sintered-glass discs on which the resin beds rested, similar to that described by Harris and Tompkins.[4]

Methods.—In most of the experiments the radioactive tracer was adsorbed on the top section of the column of exchanger from a solution of its chloride in 0.1–0.2 *M* hydrochloric acid, and subsequently eluted with the citrate solution, the eluate being collected in fractions and analyzed by counting the radioisotopes. In the experiments designed to determine the volume reduction factor, the *p*H's of the eluates were adjusted by addition of hydrochloric acid, after which they were passed through much smaller columns and the break-through of the radioisotope determined in the effluent solutions. In a few column runs an automatic recording device was used to plot the elution curves.

The widths of the elution curves were used as a criterion in comparing the effects of a number of variables on the efficiency of elution. This criterion was chosen since it is an indication both of the degree of separation of two elements and the volume reduction factor which can be obtained. Since it was not possible to determine accurately the total width of the elution curve because of the difficulty of locating the beginning and the final points, the widths of the portions of the elution curves between the points of 10 and 90% elution of the tracer were arbitrarily chosen for comparative purposes.

Results

Determination of Approximate Volume Reduction Factors for Cerium and Yttrium Radioisotopes.—In order to simulate actual operating conditions the original tracer was adsorbed on an IR-1 column whose bed volume was about six liters (72 sq. cm. in area and 84 cm. high). It was then eluted with *p*H 3.5 citrate at a rate of about 1 ml./sq. cm./min., the eluate being collected in fractions of 0.2 column volumes[5] (1200 ml.). Aliquots of the fractions of eluate containing activity were counted. These fractions were combined (total volume = 9000 ml.) and the *p*H of this solution was adjusted to 1.4, after which it was passed through another column with a bed volume of 50 ml. at an over-all rate of about 30 ml./min. and the eluate from this column again collected in fractions and analyzed by counting. The break-through of activity was plotted as concentration in eluate/concentration in influent (C/C_0) *versus* volume of eluate in column volumes. From this it was possible to calculate the per cent. recovery for any volume reduction factor up to 120. Two runs were made on yttrium and one with cerium tracer. The approximate volume reduction factors that were obtained with various recoveries are shown in Table I.

TABLE I

VOLUME REDUCTION FACTORS FOR VARIOUS RECOVERIES OF YTTRIUM AND CERIUM

	98%	95%	93%	90%
Y	65	100	109	120
Ce	120	120	120	120

From the results in this table it can be seen that yttrium is the limiting case for the trivalent fission products. (Other rare earths, *i. e.*, neodymium, phraseodymium, and 61, fall between yttrium and cerium.) Thus, if the columns are designed for a certain percentage of yttrium recovery, the loss of the other rare earth radioisotopes will be lower. Due to the "tailing out" of the element when it is being eluted at the flow rate used above, there is a loss of 1–2% per volume reduction step which is unavoidable if large volume reduction factors are needed. These experiments indicate that it should be possible to obtain a volume reduction factor of 60 in one stage for the trivalents without any appreciable loss.

Effect of Column Geometry on Elution Curves.—The chief criterion which determines the volume reduction factor that can be obtained, as well as of separation of two elements being eluted from a column, is the width of the elution band. This width is affected by a number of factors, including the geometry of the columns. Two series of experiments were undertaken to determine the variation of the band width with (1) area, and (2) length of a column.

Column Area.—Experiments similar to those described here, which were performed concurrently by Spedding and associates,[2] indicated that the band width (as measured by the degree of separation of two rare earths) of the elution curves is independent of the diameter of the column from which the elements are eluted. In this study the band width was measured directly. Two runs each were made on columns of 1.24, 15 and 72 sq. cm. area and 80 cm. length, all other factors being held constant. The widths of the integral elution curves, obtained by plotting the percentage eluted *versus* the volume of eluate, were measured, as described above, between the points of 10 and 90% elution. The results of these runs are shown in Table II and the average values for each column are plotted in Fig. 1.

TABLE II

RELATIONSHIP BETWEEN COLUMN AREA AND ELUTION CURVE BAND WIDTH

		Area of column, sq. cm.		
		1.24	15	72
Band width	1	0.717	0.837	0.947
	2	.672	.883	.982
	Av.	.695	.860	.963

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[4] D. H. Harris and E. R. Tompkins, THIS JOURNAL, **69**, 2792 (1947).

[5] This use of the volume of the column as a unit facilitated the comparisons between columns of various sizes, particularly in the calculation of volume reduction factors.

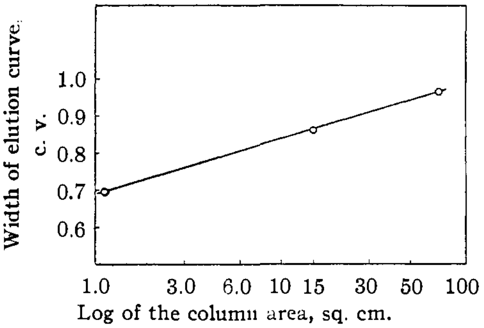

Fig. 1.—The variation of elution curve width with column area.

It will be seen that the width of the curve varied directly with the log of the column area. These data indicate that increasing the diameter of a column decreases its efficiency both in a volume reduction and separations capacity. The reason for this dependence is not clear. Quantitative data have not been obtained at other flow rates, citrate concentrations, *p*H's, etc., nor with other resins.

Column Length.—Experiments performed by F. H. Spedding, *et al.*,[2] during this period showed that rare earth separations are increased by using longer columns. The study reported here was made on columns 15 sq. cm. in area and varying in length from 20 to 180 cm. As in previous experiments radioactive cerium was adsorbed near the top of the column and then eluted with citrate buffer at a *p*H of 3.5. The flow rate was held constant at 1.0 ml./sq. cm./min. for all but two of these runs in which the rate decreased during the experiment due to the clogging of the sintered-glass disc on which the resin bed rested. The data summarizing the results of these columns runs are shown in Table III. In addition, the results of two runs with a 6-liter column (72 sq. cm. × 84 cm.) are given. Figure 2 shows a plot of the log of column length *versus* the log of the width of the elution curve. According to either the mass transfer[6] or the plate[7] theory the width of the elution curve should vary with the square root of the column length, and thus a log plot of the curve width *versus* the column length (as shown in Fig. 2) should give a straight line with a slope of 0.5. A straight line may be drawn through the points (in Fig. 2) but its slope is greater than 0.5. The explanation for this discrepancy is not clear. It is interesting to note that the difference between the experimental and theoretical curves is a constant value which could be explained by assuming that the initial band width of the adsorbed tracer (before elution) was 3 cm.

Table III

The Effect of Column Length on the Width of the Elution Curve

Column length	Column volume (C. V.)	Width of curve in C. V. for 10–90%	Width in C. V. corrected for original adsorption band of 3 cm.
20	300	1.92	1.58
20	300	1.84	
40	600	1.28	1.18
60	900	1.05	1.00
80	1200	0.84	0.83
80	1200	.88	
100	1500	.76	0.73
120	1800	.59[a]	..
140	2100	.50[a]	..
160	2400	.57	0.56
180	2700	.55	0.55
84 × 72 sq. cm.	6000	.95	0.83[b]
84 × 72 sq. cm.	6000	.98	

[a] Low value due to decrease in rate during the run. [b] Corrected also for effect of diameter (see Fig. 1).

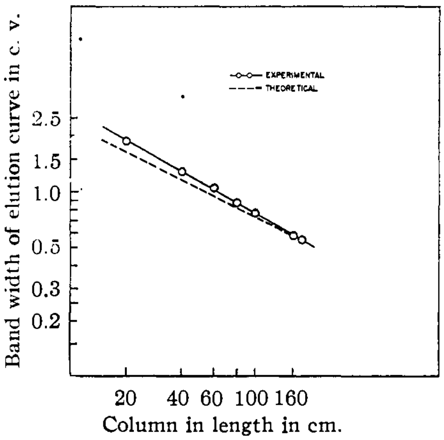

Fig. 2.—The relationship between column length and the width of the elution curve.

Effect of Flow Rate on Elution Curves.—A number of column runs were made to determine the effect of flow rate on the width of the elution curve. The criterion used in these experiments was the curve width between the points of 10 and 90% elution of the cerium tracer,

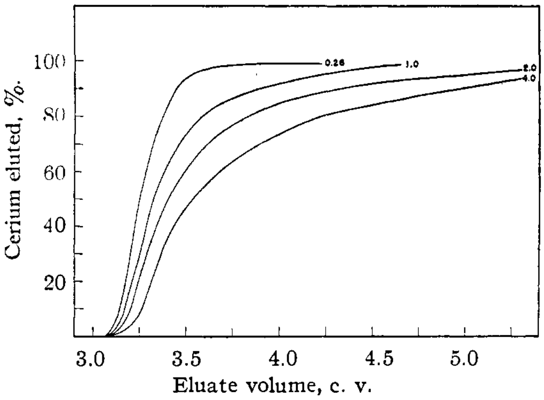

Fig. 3.—The effect of flow rate on the shape of the elution curve.

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(6) G. E. Boyd, L. S. Myers, Jr., and A. W. Adamson, This Journal, **69**, 2849 (1947).

(7) S. W. Mayer and E. R. Tompkins, *ibid.*, **69**, 2866 (1947).

as described above. Several typical curves are shown in Fig. 3, in which the percentage of cerium eluted is plotted against the eluate volume. From these curves the importance of flow rate on the band width is evident. The results of twelve runs on the same column at various flow rates, other conditions being held constant, are shown in Table IV and Fig. 4.

TABLE IV

THE EFFECT OF FLOW RATE ON THE WIDTH OF THE ELUTION CURVE

Flow rate (ml./sq. cm./min.)	Band width in C. V., 10-90%	Relative efficiency
0.10	0.295	1.00
.10	.310	0.95
.26	.310	.95
.50	.320	.92
.75	.640	.46
1.00	.72	.41
2.00	1.17	.25
2.00	1.12	.26
2.50	1.38	.21
3.00	1.70	.17
4.00	1.60	.18
4.00	1.70	.17

At rates below 0.5 ml./sq. cm./min. the band width is nearly independent of the flow rate, for rates in the range 0.75 to 2.5 ml./sq. cm./min. there is apparently a linear relation between flow rate and band width while there appears to be a second zone of independence above 3.0 ml./sq. cm./min.

These experiments indicate that, under these elution conditions, a great deal can be gained in efficiency, both as to separations and volume reduction, by operating the columns at a rate not in excess of 0.5 ml./sq. cm./min. If time is an important factor it may be advisable to increase the flow rate above this value. The total time for an elution includes the period during which the solute is developed down the column, while only the time that it is being eluted from the column is involved in the plot in Fig. 4. The volume of elutrient which must be passed through a column before the solute appears first in the eluate is largely independent of the flow rate, as may be seen in Fig. 3. The time required to develop the solute down the column is always several times longer than the time required to remove it. However, the loss in efficiency is not linear with the over-all time required for an elution. Table V shows the relationship between flow rate, time required for a run and efficiency of operation.

TABLE V

RELATIONSHIP BETWEEN FLOW RATE, EFFICIENCY AND TIME REQUIRED FOR ELUTION OF CERIUM

Flow rate, ml./sq. cm./min.	Time required, minutes for recovery 90%	Time required, minutes for recovery 98%	Comparative volume reduction factor for recovery 90%	Comparative volume reduction factor for recovery 98%
0.1	2700	2850	2.00	2.55
0.5	545	620	2.00	1.55
1.0	310	360	1.00	1.00
2.0	160	192	0.80	0.78
4.0	100	125	0.42	0.45

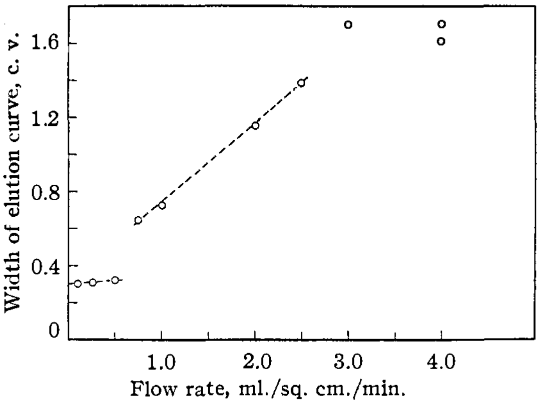

Fig. 4.—The variation of the width of the elution curve with flow rate.

The efficiency is based on the volume reduction factor compared to that at a flow rate of 1.0 ml./sq. cm./min. This factor determines the sizes of the columns in a volume reduction apparatus. Thus it can be seen that by operating the columns at 0.5 rather than at 1.0 ml./sq. cm./min. the volume reduction factor for 98% recovery can be increased by a factor of 1.55 and thus the column on which the eluate is re-adsorbed need be only about two-thirds as large as when the rate is 1.0 ml./sq. cm./min. Increasing the rate to 2.0 ml./sq. cm./min. necessitates an increase in the size of the adsorption column to 1.25 times that of the column used for a flow rate of 1.0 ml./sq. cm./min., while a rate of 4.00 ml./sq. cm./min. requires a column about 2.2 to 2.5 times as large.

The Effect of a *p*H Boundary on the Width of the Elution Curve

It has been pointed out earlier[8] that when a solute is being eluted from a column of hydrogen form resin by complex formation, its movement may be limited by a *p*H boundary. This will occur if the stability of the complex is *p*H dependent (*e. g.*, citrate complexes) and if it tends to move down the column faster than the *p*H boundary which results from the exchange between HR and NH_4^+. The higher the *p*H of the elutrient solution the more pronounced is this effect, since the rate of movement of the solute is approximately dependent upon the product of the third power of the (NH_4^+) concentration times the third power of the (H_2Cit^-) concentration, while the movement of the *p*H boundary depends upon the first power of the NH_4^+ concentration. Doubling the (NH_4^+) the rate of movement of the *p*H boundary should increase by a factor of two while the solute's rate of movement should be increased by a factor of

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

64.[9] Thus, for *p*H's at which the solute moves faster than the *p*H boundary it tends to concentrate in a narrow zone and so is much more concentrated in the eluate than if it had been eluted from a column of resin in the NH_4R form.

Because of the much greater capacity of Dowex 50 resin this effect is more pronounced than when IR-1 exchanger is used. The elution curves (1) and (2) in Fig. 5 show this concentrating effect when Y^{91} is eluted from Dowex 50 with citrate at *p*H 3.0.[10] It will be seen that about 98% of the Y^{91} may be recovered from the column of resin in the hydrogen form in a volume of about one-fourth that required to remove it from a column in the ammonium form. It is interesting to note that despite the zone of concentration shown in elution curve (1), the trailing portions of the two curves coincide. The effect of *p*H on the width of the elution curve may be seen by a comparison of curves (1), (3) and (4), Fig. 5. The higher the *p*H the narrower the elution band, and thus the smaller volume of eluate required to remove any given percentage of solute. Thus to obtain the largest volume reduction factor, the solute should be removed from the column of hydrogen form resin at a relatively high *p*H.

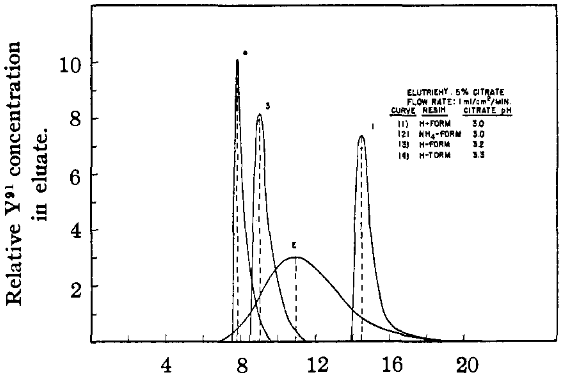

Fig. 5.—Elution of Y^{91} from a column of Dowex 50 (40–60 mesh) 0.5 sq. cm. × 28 cm.

In the separation step it may be desirable to have the resin in the NH_4^+ form. For instance, if two very similar solutes are being separated at a *p*H such that their rate of movement is faster than the rate of the *p*H boundary, they will both concentrate at the *p*H boundary and thus the separation will be less complete than when they are eluted from resin in the ammonium form.

The Effect of Carrier on the Separation of Solutes

Although the use of carriers in the ion-exchange fission product separation process was unnecessary, it appeared that some information concerning their effect on the degree of separation of two or more solutes was desirable. In addition, the separation of other elements in greater than trace concentrations was of interest. Previous results[8]

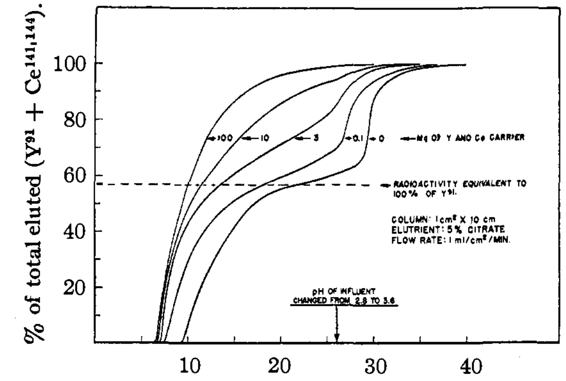

Fig. 6.—Effect of Y and Ce carrier on their elution from amberlite IR-1, H-form.

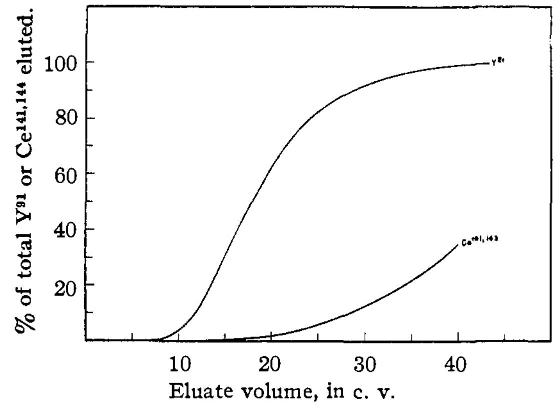

Fig. 7.—The effect of Y carrier on Y^{91} and $Ce^{141,144}$ elution: column, 1 sq. cm. × 10 cm.; resin, IR-1, 40, 60 mesh, H-form; elutrient, 5% citrate, *p*H 2.42 + 0.01 *M* Y; flow rate, 2 ml./sq. cm./min.

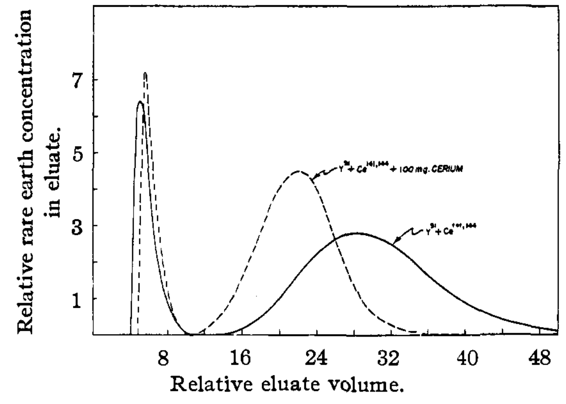

Fig. 8.—Effect of cerium carrier on the elution of Y^{91} and $Ce^{141,144}$ tracers: column, 0.5 sq. cm. × 28 cm.; resin, Dowex 50, 40–60 mesh, H-form; elutrient, 5% citrate, *p*H 3.2; flow rate, 1 ml./sq. cm./min.

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[9] This is true only if the (NH_4^+) is added to the citric acid as NH_4OH. In this case (NH_4^+) ≅ (H_2Cit^-) and thus the increase in rate ≅ $2^3 \times 2^3/1^3 \times 1^3 = 64$.

[10] The quantity of tracer used in number (2) was twice that used for number (1), as may be seen from the relative areas under the two curves.

TABLE VI

THE EFFECT OF Y AND Ce CARRIER ON THE SEPARATIONS OF Y^{91} AND $Ce^{141,144}$

Column: 1 sq. cm. × 10 cm. of Amberlite IR-1, 40–60 mesh. Elutrient: 5% citrate, *p*H 2.8, fractions 1–11; *p*H 3.6, fractions 12–18. Flow Rate: 1 ml./sq.cm./min. Analysis was by differential counting of the Y^{91} and $Ce^{141,144}$ tracers.

Fraction		% Composition of fractions with varying quantities of carrier (Y and Ce)											
		0 mg.		0.1 mg.		1 mg.		3 mg.		10 mg.		100 mg.	
Number	Volume in C. V.	% Y	% Ce	% Y	% Ce	% Y	% Ce	% Y	% Ce	% Y	% Ce	% Y	% Ce
1	6	...	...	...	...	...	..	...	...	...	..	..	..
2	2	...	...	100	0	100	0	100	0	100	0	95	5
3	2	100	0	100	0	100	0	100	0	93	7	81	19
4	2	100	0	100	0	95	5	90	10	63	37	32	68
5	2	100	0	99	1	79	21	50	50	30	70	15	85
6	2	100	0	82	18	47	53	28	72	16	84	8	92
7	2	96	4	58	42	16	84	16	84	8	92	15	85
8	2	88	12	38	62	18	82	8	92	9	91	17	83
9	2	80	20	22	78	17	83	6	94	7	93	18	82
10	2	59	41	15	85	9	91	13	87	8	92	17	83
11	2	43	57	1	99	13	87	11	89	10	90	23	77
12	2	14	86	0	100	7	93	16	84	9	91	24	76
13	2	0	100	0	100	4	96	11	89	5	95	42	58
14	2	0	100	9	91	2	98	36	64	2	97	..	..
15	2	0	100	18	82	13	87	13	87	21	79	..	..
16	2	0	100	20	80	39	61	0	100	44	56	..	..
17	2	0	100	26	74	50	50	0	100	67	33	..	..
18	2	0	100	46	56	37	63	...	...	...	..	..	..

obtained in our studies had indicated that the presence of carrier decreases the degree of separation. However, F. H. Spedding, *et al.*,[11] have reported evidence of increased separation of Y^{91} and $Ce^{141,144}$ when carriers were present.

The first series of experiments on the effect of carrier, the results of which are shown in Figs. 6 and 7, were done with short columns of Amberlite IR-1 resin. In the second series, shown in Fig. 8, Dowex 50 resin was used.

The results of the series of experiments with IR-1, shown in Figs. 6 and 7 and in Tables VI and VII, clearly demonstrate the deleterious effect of carrier on the separation when yttrium and cerium are eluted from IR-1 under the conditions shown. While it is possible that carrier may enhance the separation under certain conditions, in all of our experience we have never noted any case where this occurred. In Table VI the degree of separation, when varying quantities of carrier have been added, is shown. It can be seen that the number of fractions of pure yttrium or cerium decreases sharply as the mass of carrier is increased. However, the carrier also affects the rates of elution of these solutes, as may be seen in Fig. 6. Thus the quantity of solute in the early fractions also increases as the mass of carrier is increased. The percentage of the first of two solutes which can be obtained pure does not decrease as rapidly as that of the second, as may be seen in Table VII. For instance, when as little as 1 mg. of each carrier was added, a negligible amount of pure cerium was recovered, while the percentage of pure yttrium obtained was still about 86% of that obtained when no carriers were used. When 100 mg. of each element was added, no pure yttrium or cerium was obtained.

TABLE VII

THE RECOVERY OF PURE Y^{91} AND $Ce^{141,144}$ BY COLUMN SEPARATION AS A FUNCTION OF THE MASS OF Y AND Ce CARRIER, IR-1 RESIN

Mass of Y and Ce (mg.)	% Y^{91} Pure	% $Ce^{141,144}$ pure
$<10^{-5}$	81	86
0.1	79	54
1.0	70	0
3.0	75	<1
10.0[a]	33	0
100.0	0	0

[a] When Y and Ce tracer were eluted with 10 mg. of Y carrier, no Y was obtained pure but 30% of the Ce was pure.

Other experiments in which only yttrium carrier was used showed that it affected the elution of both the Y^{91} and $Ce^{141,144}$ tracers, although the effect on the Y^{91} was the greater. The data shown graphically in Fig. 7 represent the results of one of these experiments. In this case the two tracers were adsorbed at the top of the column and eluted with citrate containing yttrium in a concentration of about 0.01 *M*. This solution eluted the Y^{91} very rapidly but the separation was still far from complete.

In the second series of experiments on the effect of carrier, Dowex 50 resin was used. It was found that the separation of yttrium and cerium when eluted from a Dowex 50 column with citrate at a *p*H of 2.8 was so great that the effect of the carrier could not be ascertained. A series of experiments in which these tracers were eluted at *p*H's 2.8, 3.0, 3.2 and 3.3 showed that as the *p*H was increased the separation decreased. The highest *p*H which would just give complete separation of trace quantities of these elements on the column chosen was 3.2. Thus, this *p*H was chosen for the

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[11] F. H. Spedding, *et al.*, THIS JOURNAL, **69**, 2777 (1947).

experiments designed to test the effect of carrier on the separation.

The data plotted in Fig. 8 are representative of the results of this series of experiments. As in the IR-1 experiments, the separation is decreased by the presence of carrier. However, the effect is much less pronounced in this case. It was the results of these experiments which led to the use of Dowex 50 for rare earth separation.[4] Not only is the degree of separation obtained by its use with trace quantities of rare earths many times greater than that obtained with IR-1, but also the effect of carrier is much less than the effect with IR-1, as may be seen by comparing the results of these two series of experiments. The column used in the Dowex 50 series was longer (although it had only a slightly larger volume) than that used with IR-1, so that quantitative comparison of the two series is not possible; however, the qualitative difference is obvious. The results of many subsequent experiments on gram quantities of rare earths have amply demonstrated the superiority of Dowex 50.

Summary

The effects of several variables on the efficiency of an ion-exchange column for the applications of volume reduction and separation of several cationic fission products have been studied.

When the flow rate per unit area was held constant at 1.0 ml./sq. cm./min., the column area was found to affect the width of the elution curve. The effect of column length on the width of the elution curve differed slightly from that predicted from theoretical considerations. Flow rate was an important factor in both volume reduction and separations column applications. The original form of the resin was found to be important. For obtaining the maximum volume reduction factor, it should be in the hydrogen form initially, and the elution of rare earths should be made with citrate at a *p*H of 3.3–3.5. These conditions are not optimum for separations. For this purpose it is preferable to elute the mixture of rare earths from a column of resin in the ammonium form using citrate at a lower *p*H. Addition of carrier had a deleterious effect on the separation of solutes. This was very pronounced when amberlite IR-1 was used, but was much less pronounced when Dowex 50 was employed.

The results of this investigation, together with data obtained previously, were used as a basis for the design of an ion-exchange column apparatus for separating and purifying fission products. The principles involved in this apparatus are applicable for the separation of other substances. The results of these experiments aid in the interpretation of the theory of ion-exchange column operation.

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RECEIVED JULY 24, 1948

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

Chemistry of Aqueous Uranium(V) Solutions. I. Preparation and Properties. Analogy between Uranium(V), Neptunium(V) and Plutonium(V)[1]

BY KURT A. KRAUS, FREDERICK NELSON AND GORDON L. JOHNSON

1. Introduction

On the basis of rather detailed polarographic studies of uranium(VI) it has been concluded recently[2,3,4] that uranium(VI) can be reduced to uranium(V) at the dropping mercury electrode and that the electrode reaction for the first reduction wave (which occurs at about −0.180 v. *vs.* the S. C. E.) is

$$UO_2^{++} + e^- \longrightarrow UO_2^+ \tag{1}$$

The formula UO_2^+ for the uranium(V) ion in acid solutions was deduced from the acid independence of the U(V)/(VI) half-wave potential assuming UO_2^{++} as the formula of uranium(VI). Reaction (1) was shown to be reversible at the d. m. e. since $\log i/(i_t - i)$ changes linearly with E (where i_t is the diffusion current and i the current at voltage E) and since the line has a slope of close to the theoretical value 0.059 for an electrode reaction involving a one-electron change.

Harris and Kolthoff,[2] and Heal,[3] felt that UO_2^+ exists only as a transient species which is too rapidly destroyed through the disproportionation reaction

$$2U(V) \longrightarrow U(IV) + U(VI). \tag{2}$$

to permit preparation of uranium(V) solutions of reasonable concentration.

Approximately simultaneously with this work on uranium(V) the +5 oxidation states of the elements neptunium and plutonium had been observed, and it had been concluded that these ions exist also as the species XO_2^+ in acidic solu-

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(1) This document is based on work performed under Contract Number W-7405 eng 26 for the Atomic Energy Project at Oak Ridge National Laboratory. Part of this work has previously been published in the project reports Mon N-161 (August, 1946), Mon N-176 (September, 1946) and Mon N-194 (October, 1946). This paper was presented in part at the Meeting of the American Chemical Society, March 28, 1949.

(2) W. E. Harris and I. M. Kolthoff, THIS JOURNAL, **67**, 1484 (1945).

(3) H. G. Heal, Report MC-95, October, 1944, *Nature*, **157**, 225 (1946).

(4) For summary of the polarographic work on uranium see references (1) and (2).