[Contribution from the Department of Chemistry and Laboratory for Nuclear Science, Massachusetts Institute of Technology]

Distribution of Zirconium and Hafnium between Cation-exchange Resin and Acid Solutions. The Column Separation with Nitric Acid–Citric Acid Mixture[*]

By Joseph T. Benedict, Walter C. Schumb and Charles D. Coryell

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A survey has been made, using radioactive tracers, of the distribution of zirconium and hafnium between solutions containing varying concentrations of sulfuric, hydrochloric or nitric acids and the cation-exchange resin Dowex-50. Since the differences in behavior of the two elements were not great, attention was also given to the effects of varying concentrations of oxalic, tartaric and citric acids in nitric acid. These data cast light on the chemical behavior of the elements in acid solution. A gross difference in the distribution coefficient in a solution 0.45 *M* in nitric acid and 0.09 *M* in citric acid was exploited by using this solution as elutriant for the elements from an ion-exchange column; the column separation was very effective in removing the zirconium from the more slowly eluted hafnium.

Introduction

The problem of separation of zirconium and hafnium compounds has presented a challenge because of the close similarity in the chemical behavior of these elements. The present study was undertaken to explore the chemical behavior of the ions of these two elements in solution of mineral acids, and to search for systematic differences that might lead to effective separation on cation-exchange columns. Following analogies from the ion-exchange properties of the rare earth elements, attention was also given to differences in the complexing properties of oxalic, tartaric and citric acid. These studies showed that the hydroxy acids magnify the differences in resin affinities between zirconium and hafnium salts; and conditions were outlined for a decisive separation by an ion-exchange column using as an eluant 0.09 *M* citric acid in 0.45 *M* nitric acid. In this separation, zirconium precedes hafnium in travel down the column by having a distribution constant favoring solution phase. This is an advantage for procedures designed to purify zirconium, as those, for instance, of general interest in nuclear chemistry.

While this study was in progress, a report by Street and Seaborg[1] appeared showing fairly successful separation by elution from cation-exchange resin with 6 *M* hydrochloric acid, whereby hafnium precedes zirconium in elution. Lister[2] has made a study of practical aspects of column behavior of the two elements with various mineral acids, demonstrating good separation of zirconium (faster moving) from hafnium by elution with 0.5 *M* H_2SO_4. The present study provides more detailed information on the partitions between cation-exchange resins and solutions and leads to a sharper separation. In addition Kraus and Moore[3] and Huffman and co-workers[4,5] have used elution from anion-exchange resins by hydrofluoric acid–hydrochloric acid mixtures. These systems furnish chemical information of quite a different nature. The separations are fairly good, and zirconium precedes hafnium in the elution operation, but the reverse is true[5] in the absence of hydrofluoric acid. A recent study[6] of citrate elution of mixtures of zirconium, titanium and thorium casts some light on the nature of the citrate complexes of quadrivalent metal ions.

At the start of this work, considerable effort was spent developing techniques to avoid difficulties with hydrolysis and colloid formation of the two elements. The techniques were also partly conditioned by radiochemical requirements for removing the niobium daughter activity (35d Nb^{95}) of the zirconium tracer used. The procedures and evaluations of their success are recorded below.

Experimental

The Cation-exchange Resin.—The cation-exchange resin was Dowex-50 furnished by courtesy of the Dow Chemical Company. It was pre-treated by washing four times with 6 *M* hydrochloric acid alternated with washings with 6 *M* ammonium hydroxide. The resin in the hydrogen form was then washed exhaustively with distilled water, air dried and stored in a desiccator above 50% sulfuric acid. The capacity was determined by adding weighed 0.5-g. portions to 10 ml. of 0.6 *N* sodium chloride solution and titrating the hydrogen ion released with standard sodium hydroxide. The capacity was redetermined several times over a period of months and was found to remain constant at the value 3.87 ± 0.04 meq. per gram of air-dried resin.

Zirconium Stock Solution with Tracer.—Commercial C.P. zirconium oxychloride was recrystallized from concd. hydrochloric acid as $ZrOCl_2 \cdot 8H_2O$.[7] Zirconium analyses were generally made radiometrically (γ-activity) with the aid of 65d Zr^{95} obtained as hafnium-free fission product activity from the Isotopes Division of the U.S. Atomic Energy Commission, Oak Ridge, Tennessee. Tracer and carrier were brought to chemical equivalence (interchange) by refluxing the mixture in 12 *M* sulfuric acid for a period of 6 hr. This procedure was considered effective because 12 *M* sulfuric acid dissolves in even less time zirconium dioxide that has been ignited to 600° for 9 hr. The tagged zirconium was then precipitated with ammonia as hydroxide and redissolved immediately in 0.1 *M* oxalic acid solution. The oxalic acid solution was kept as stock solution of known total zirconium concentration.

Removal of Niobium Daughter Activity.—The zirconium tracer (65d Zr^{95}) produces in its decay[8] 35d Nb^{95} and in 2% of the decays 90h Nb^{95m} is formed as an intermediate species. The rate of growth per day (in activity) of these radiochemical contaminants is thus 2 and 0.4%. To avoid error

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[*] This work was performed in partial fulfillment of the requirements for the Ph.D. degree by J. T. Benedict; and was also presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society Meeting in Chicago, Ill., Sept. 6, 1950.

(1) K. Street, Jr., and G. T. Seaborg, This Journal, **70**, 4268 (1948); see also I. E. Newman *ibid.*, **73**, 5899 (1951).

(2) B. A. J. Lister, *J. Chem. Soc.*, 3123 (1951).

(3) K. A. Kraus and G. E. Moore, This Journal, **71**, 3263 (1949).

(4) E. H. Huffman and R. C. Lilly, *ibid.*, **71**, 4147 (1949); *ibid.*, **73**, 2902 (1951).

(5) E. H. Huffman, G. M. Iddings and R. C. Lilly, *ibid.*, **73**, 4474 (1951).

(6) W. E. Brown and W. Riemann, III, *ibid.*, **74**, 1278 (1952).

(7) R. C. Young and A. Arch, "Inorganic Syntheses," Vol. 2, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 121.

(8) K. Way, L. Fano, M. R. Scott and K. Thew, "Nuclear Data." National Bureau of Standards Circular 499 and Supplements 1 and 2, U. S. Government Printing Office, Washington, 1950 and 1951.

from the γ-rays of 35d Nb^{95}, niobium activities must be removed chemically less than 12 hours before counting is carried out. This was done by an adaptation of the procedure of Gest and Glendenin[9] which uses hydrous manganese dioxide as specific carrier for niobium without appreciable loss of zirconium. The oxalic acid stock solution of zirconium carrier was made 10 M in nitric acid and the oxalic acid was destroyed by adding 40% hydrogen peroxide dropwise at 80–90°. Manganese dioxide was then formed by the addition of two to five drops of 0.1 M potassium permanganate solution, and removed by centrifugation. Two more precipitations were made to ensure complete removal of niobium activity. Zirconium hydroxide was then precipitated, centrifuged down, washed and immediately dissolved in the acid to be used for study.

Hafnium Solutions.—Hafnium oxide was obtained from A. D. Mackay Co., New York; analyses showed approximately 5.4% zirconia. All analyses were made radiochemically (γ-activity) using hafnium activity produced in pile irradiation and furnished by the Isotopes Division of the U. S. Atomic Energy Commission in Oak Ridge. This tracer contains[8] comparable amounts of 70d Hf^{175} decaying by electron capture and γ-emission and 46d Hf^{181} decaying by β- and γ-emission; cross-sections[8] preclude the presence of significant amounts of 65d Zr^{95} even if very impure hafnium had been exposed in the pile. Carrier and tracer were brought to interchange in 12 M sulfuric acid, and transformed to oxalic acid stock solution in procedures identical with those described above for zirconium. The oxalate was destroyed by hydrogen peroxide in 10 M nitric acid; three manganese dioxide precipitations were made to ensure complete destruction of oxalate and to make the treatment fully parallel to that for zirconium, the hafnium was precipitated as hydroxide, and immediately dissolved in the acid system used for study.

Batch Equilibrations.—A series of known masses of the air-dried Dowex-50 resin in the hydrogen form, weighed to 1%, was distributed in cylindrical vials, 10-ml. portions of standard acid (perchloric, sulfuric, hydrochloric or nitric acid, or the latter with additions of oxalic, tartaric or citric acid) were added, and then 1-ml. aliquots of the tagged zirconium or hafnium carrier prepared (as described) in the corresponding mineral acid solution. The initial molarity in zirconium or hafnium was computed from the titer and aliquot of the oxalate stock solution taken, and the volume of the mineral acid used to dissolve the hydroxide in the last step. Duplicate radiometric analyses of evaporated 1-ml. aliquots gave the activity C_0 corresponding to the initial molarity. The vials were closed and shaken vigorously at room temperature for 2 hr., after which the resin was allowed to settle and two or more 1-ml. aliquots were taken of each supernatant solution. On drying these were counted to give the equilibrium activities C_f corresponding to the different systems in each vial.

Detailed studies of the time dependence of C_f with 4.04×10^{-3} M and 4.04×10^{-5} M hafnium solution in 2.08 M perchloric acid solution showed that 100 C_f/C_0 became constant at 70 in less than 1 hr., and spot checks gave assurance of completion of reaction in other systems.

For most purposes it is sufficient for a given quantity of resin to consider the value 100 C_f/C_0, the percentage of the ion unabsorbed, as the first interest lies in gross changes in this percentage and substantial difference for a given medium between its values for zirconium and hafnium. For some purposes, however, there is an interest in the effective distribution constant K'_d of the metal between the resin and the solution, which is under conditions of negligible mole fraction of resin involved in binding the metal ion

$$K'_d = \frac{C_0 - C_f}{M_{HR}}\frac{V}{C_f} = \frac{V}{M_{HR}}\left(\frac{C_0}{C_f} - 1\right) \qquad (1)$$

where M_{HR} is the number of grams of resin HR and V is the volume of the solution in milliliters. K'_d represents the ratio of concentration of metal ion per gram of resin to that per milliliter of solution.

Column Separation.—The column studies on zirconium and hafnium were carried out with a resin bed 2.1 cm. in diameter and 16 cm. deep. The ground resin had been wet-screened to pass a 100-mesh screen, separated from fines by levigation, and conditioned by acid-base cycles. It was finally washed thoroughly with the elution solution (0.091 M citric acid in 0.45 M nitric acid). Zirconium or zirconium-hafnium mixture in 0.8 M sulfuric acid was adsorbed completely by the use of successive 0.4-ml. charges of resin in the acid form, and the charges were mixed and slurried on top of the resin column. The elution rate was held at 0.06 ml./cm.²/min. until the zirconium peak had passed, after which it was increased to 0.21 mg./cm.²/min.

Activity was determined by counting γ-rays from 25-ml. samples of the eluate with a brass-walled Geiger–Mueller counter.

A rapid semiquantitative procedure was developed for zirconium analysis, depending on measuring in a calibrated conical centrifuge tube the volume of hydrous zirconium phosphate precipitate obtained in 40 minutes of centrifugation from samples of the eluant containing 1 ml. of 85% phosphoric acid for each 10 ml. The quantity of precipitate was found to be linear with the zirconium content with a ratio of 0.20 ml. of precipitate per milligram of zirconium dioxide present.

Results and Discussion

The first tests were made of the stability of the solutions under investigation. This problem seemed important because of the difficulties encountered by many workers in obtaining reproducibility, which were ascribed to various stages of hydrolysis beginning with "polymerization" and colloid formation.[10] Indeed, Ayres[11] made use of the colloidal properties of zirconium to prevent its retention on cation-resin columns in an early study of zirconium in ion-exchange systems.

In seven tests spread over a period of a month, duplicate samples of the oxalic stock solution of hafnium (0.01 M) were converted to 1.5 M nitric acid solution (see above) and equilibrated with 0.40 g. of resin. All gave the same fraction adsorbed (87% within the experimental error of 3%) irrespective of the time of analysis. Correspondingly, a freshly prepared solution of hafnium in 1.5 M nitric acid was tested seven times over a period of nine hours and found to give the same fraction adsorbed. It is expected that these findings are also valid for zirconium because of the great similarities between the chemistry of these two elements. It is concluded that no problem occurs over indefinite time due to instability of the oxalate stock solutions, and that the stability of dilute acid solutions of zirconium and hafnium is at least adequate for working studies of resin adsorption.

Tests were also made to explore the stoichiometry of the ion-exchange process. Measurements were made of the uptake of zirconium on a small column (10 g.) of Dowex-50 when a slightly acid zirconium oxychloride solution was passed through until the effluent Zr:Cl ratio became equal to the original ratio (0.810 M/2.81 M). The resin was washed quickly and all of the zirconium was removed from the resin by elution with 6 M hydrochloric acid. It was found that the washed resin had contained 0.96 millimole of zirconium per gram of air-dried resin. This figure corresponds essentially to complete conversion of 3.87 millimoles of resin HR to the ortho-zirconium salt, ZrR_4. Ayres[11] had found under his conditions of study (solutions near neutrality) an uptake of colloidal zirconium

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[9] H. Gest and L. E. Glendenin, "National Nuclear Energy Series," Paper 254, Vol. 9, Div. IV, McGraw-Hill Book Co., New York, 1951, p. 1529.

[10] R. E. Connick and W. H. Reas, U. S. Atomic Energy Commission Document AECD-2491, March, 1949.

[11] J. A. Ayres, THIS JOURNAL, **69**, 2879 (1947).

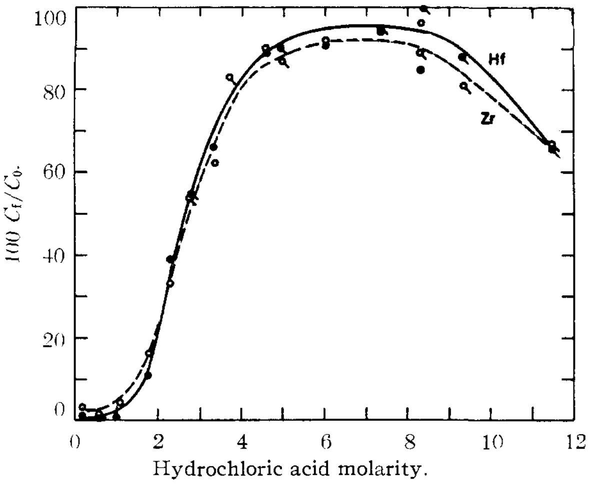

Fig. 1.—Percentage zirconium or hafnium unabsorbed by 0.40 g. of resin from 11.0 ml. of hydrochloric acid solution: circles, $C_0 = 9.8 \times 10^{-4}$ *M*; circles with tails, $C_0 = 4.5 \times 10^{-5}$ *M*; open circles and broken curve, zirconium; filled circles and solid curve, hafnium.

by Amberlite IR-100 resin lower by a factor of approximately one hundred.

If the zirconium is in monodisperse form in acid solution, but in unspecified degree of partial hydrolysis and anion complex formation, the equilibrium equation is predicted to be

$$[Zr(OH)_xCl_y]^{4-x-y} + 4HR = ZrR_4 + (4 - x)H^+ + yCl^- + xH_2O \quad (2)$$

The mass action constant K'_d at fixed hydrochloric acid concentration would be given by eq. 1 for low metal ion concentration, and it would fall with increasing activity product $[H^+]^{4-x}[Cl^-]^y$. Experiments at several different acid concentrations showed the constancy of K'_d within the experimental reproducibility of ±4% for each of these as the quantity of resin taken was varied over the range 0.12 to 1.6 g. K'_d falls from 520 to 2.7 as the hydrochloric acid is increased from 1.1 to 5.3 *M* corresponding to a rather large value of the sum of the exponents $4 - x + y$ for the activity product. Connick and McVey[12] give evidence that x is near 1 in 1 *M* acid solutions, and that y is near 1 in 1 *M* chloride solutions. Lack of knowledge of solute activity coefficients prevents closer correlation.

Extraction by Strong Acids.—A systematic study was made of the differences in the extraction of zirconium and hafnium from the resin by hydrochloric acid as a function of the concentration from 0.2 to 11.5 *M*. Batch tests were made with the elements at 4.5×10^{-5} and 9.8×10^{-4} *M* in 11.0 ml. of hydrochloric acid solution equilibrated with charges of 0.40 g. of Dowex-50. The data are plotted in Fig. 1 as 100 C_f/C_0 *versus* the molarity of the hydrochloric acid. All points were made in duplicate, the average deviation in the pairs being about 5%.

The data show that zirconium is eluted more easily than hafnium below 2 *M* hydrochloric acid, the K'_d values being lower by a factor of about three at 1 *M*. An inversion occurs above 2 *M*, with greater extractability of hafnium[2,3] persisting to very high acidity, although the scatter of the experimental data obscures the results somewhat. The increase of adsorption for both elements above 8 *M* acid is unexpected and remarkable. It may be that complexes that are nearly electroneutral are salted out from the aqueous phase into the resin phase, which is less polar under these circumstances.

When 100 C_f/C_0 reaches 90 in these experiments, K'_d has fallen to 3, which would correspond to rather prompt elution of material from an ion-exchange column. According to the treatment of Mayer and Tompkins,[13] the maximum of the elution curve comes through at the elution volume $K'_d\,m/v$ where m is the mass of resin in the column, and v is the free volume of the packed column; such low K'_d values are not conducive to good elution peaks. The curves of Fig. 1 indicate that hydrochloric acid is not too attractive a prospect to be an eluting agent for separating zirconium and hafnium because of the small differences in distribution and because of low K'_d values for both above 3 *M* concentration.

A completely analogous study was made of the extractability of zirconium and hafnium by nitric acid over the concentration range 0.5 to 14.8 *M*, as shown by the data plotted in Fig. 2. The zirconium curve up to 3 *M* nitric acid is practically superposable on the corresponding curve for hydrochloric acid (Fig. 1), in agreement with the findings of Connick and McVey[12] of equal complexing in 1.2 or 2.0 *M* solutions of nitric and hydrochloric

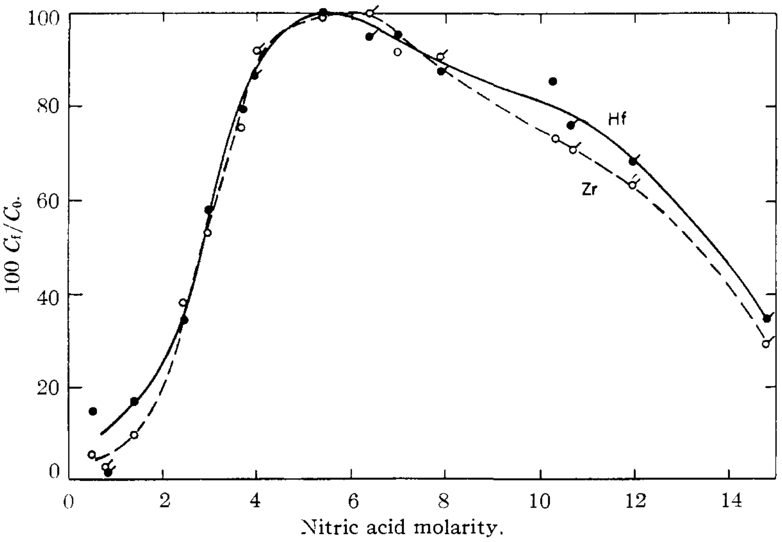

Fig. 2.—Percentage zirconium and hafnium unabsorbed by 0.40 g. of resin from 11.0 ml. of nitric acid solution: circles, $C_0 = 9.8 \times 10^{-4}$ *M*; circles with tails, $C_0 = 8.9 \times 10^{-5}$ *M*; open circles and broken curve, zirconium; filled circles and solid curve, hafnium.

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[12] R. E. Connick and W. H. McVey, This Journal, **71**, 3182 (1949).

[13] W. M. Mayer and E. R. Tompkins, *ibid.*, **69**, 2866 (1947).

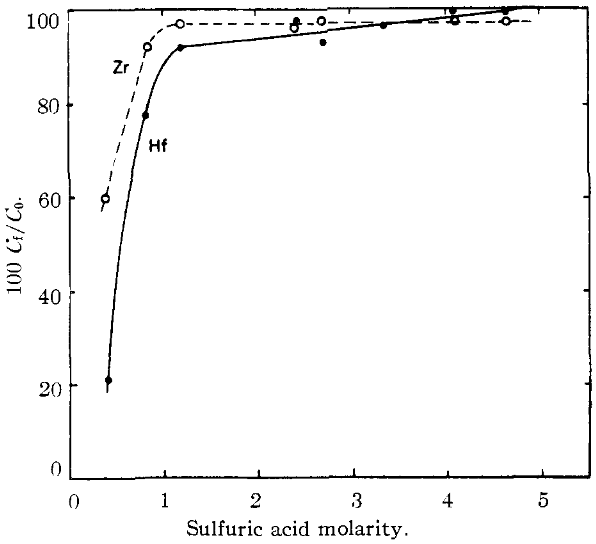

Fig. 3.—Percentage zirconium and hafnium unabsorbed by 0.70 g. of resin from 11.0 ml. of sulfuric acid.

acids. In the next region up to 7 *M* the higher position of the curve suggests that complex formation is more pronounced with nitric acid. The fall of the curve in very strong acid sets in sooner with nitric acid. Very little difference can be seen in the hafnium and zirconium curves for nitric acid concentrations from 2 to 8 *M*. Below and above this concentration region, hafnium seems to be more extractable than zirconium, but there is some inconsistency in the low-acid points for hafnium. Nitric acid does not seem to offer much prospect as a separating agent, particularly at 3 *M* which gives no separation at all according to Lister.[2]

An analogous study with sulfuric acid solutions 0.39 to 4.7 *M*, using 0.70 g. of resin is presented in Fig. 3. Both zirconium and hafnium are extracted to a considerably greater extent, presumably due to the appreciable formation of sulfate complexes, and the zirconium curve lies appreciably above the hafnium curve in the low sulfuric acid region. In 0.4 *M* sulfuric acid K'_d for zirconium is 10.6, whereas the value for 0.4 *M* hydrochloric or nitric acid is approximately 880 (for 3% unabsorbed); this corresponds to the diminution in free zirconium ion at roughly the same hydrogen ion concentration and ionic strength by about the factor 80. This effect is caused by the sulfate ion of activity approximately 0.01 *M* in 0.4 *M* sulfuric acid solution. This effect is smaller by about a factor of 3 than that predicted with the constants of Connick and McVey[12] for the formation of chloride and sulfate complexes, as determined by chelate extraction from 2 *M* perchloric acid. The agreement is satisfactory in view of the approximations on both sides.

Since the search was directed toward better zirconium–hafnium separation even than that offered by dilute sulfuric acid, no column run was made with this system. The data of Fig. 3 indicate a K'_d of 63 for hafnium in 0.39 *M* sulfuric acid, which would correspond[13] to an elution peak for hafnium at a volume 6.0 times that of zirconium. Lister[2] independently explored elution of zirconium–hafnium mixtures by 0.4 *M* sulfuric acid and found experimentally a ratio of 4.8 in the column mobilities, which are directly comparable to the peak volumes. As predictable by Fig. 3, he found a falling off of separation efficiency but an increase in elution efficiency with increasing sulfuric acid concentration.

Extraction by Organic Acids.—Tests with 11.0 ml. of oxalic acid at concentrations as low as 9.1×10^{-4} *M* in 0.9 *M* nitric acid showed retention in the solution phase of more than 85% of the zirconium or hafnium at 3.6×10^{-4} *M* when 0.65 g. of the resin was taken. The complexing power of oxalic acid is too great for the acid to be useful as an agent in the elution separation of the two elements. It is, however, very effective in stripping both of the elements from a cation-exchange column.

Similar tests with tartaric acid in nitric acid solution showed that complex formation is appreciable for both elements, but more so for zirconium. More pronounced differences in K'_d values occurred at 0.9 *M* nitric acid at low tartaric acid concentrations (below 0.01 *M*). Comparative studies with citric acid showed the same qualitative behavior but still greater differences caused by this complexing agent at more easily controlled concentrations.

A representative picture of the data obtained at moderate concentrations of citric acid is given in

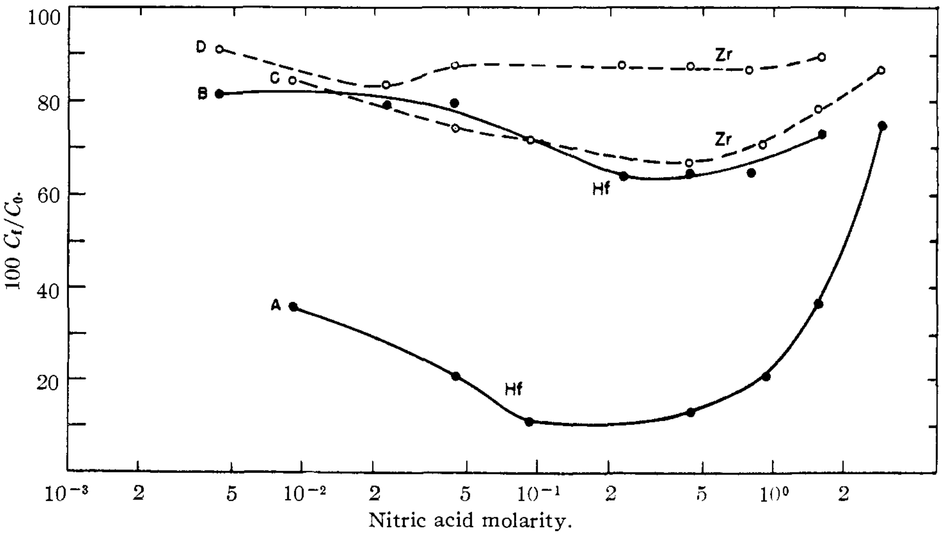

Fig. 4.—Percentage of zirconium and hafnium unabsorbed from 11.0 ml. of nitric acid–citric acid mixtures by 0.70 g. of resin as a function of nitric acid concentration: A, Hf in 0.091 *M* citric acid; B, Hf in 0.455 *M* citric acid; C, Zr in 0.091 *M* citric acid; D, Zr in 0.455 *M* citric acid.

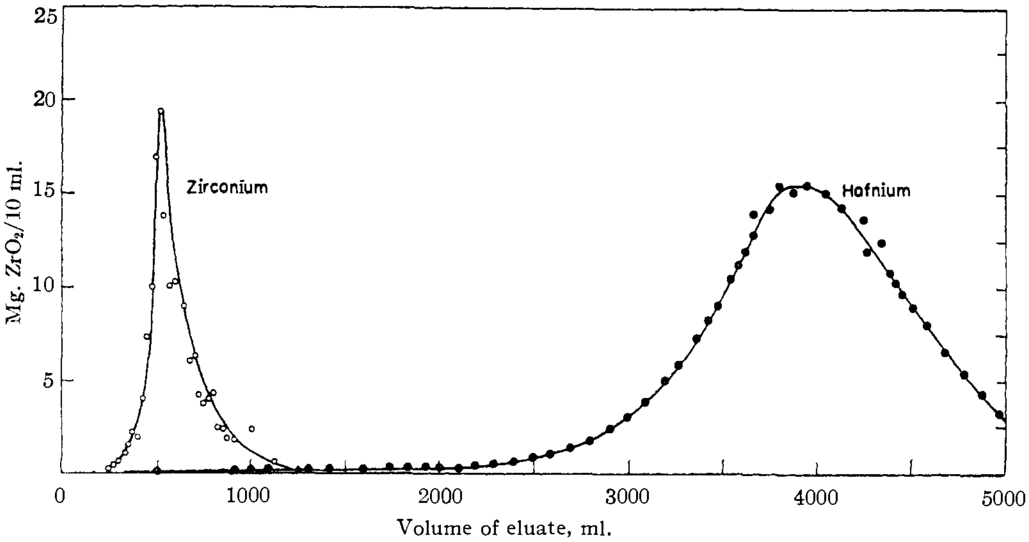

Fig. 5.—The elution curve of zirconium and hafnium: 1.6 mmoles of Zr, 0.71 mmole of Hf; eluant, 0.45 M nitric–0.091 M citric acid.

Fig. 4. Batch equilibrations were made with 0.70 g. of resin and 11.0 ml. of solutions either 0.091 or 0.45 M in citric acid at nitric acid concentrations varying from 0.005 to 3.2 M (with logarithmic scale in Fig. 4). The initial zirconium or hafnium concentration was 4.7×10^{-4} M.

It is seen from the more sensitive hafnium curves that K'_d rises (extractability falls) with increasing nitric acid concentration up to the region about 0.2 M, although the total extractability is much higher than in the absence of citric acid. The effect is due to suppression of the ionization of citric acid, the fall in extractability indicating that more protons are required to break up the average citrate complex, forming citric acid, than are released by resin exchange. The rise in the region above 1 M corresponds to acid citrate complexes requiring less acid than is released by resin exchange. The higher concentration of citric acid (0.45 M) moves K'_d values into a range too low for good elution. From consideration of Fig. 4 and of other tests at lower citric acid concentration, it was concluded that a favorable region for the eluant for ion-exchange column separation was 0.091 M in citric acid and 0.45 M in nitric acid. Under these conditions the K'_d values for zirconium and hafnium are 8 and 100, respectively.

It is interesting to note that the K'_d ratio for hafnium to zirconium under these conditions is about the square root of the same ratio for titanium to zirconium reported by Brown and Riemann[6] for acid citrate solutions of 0.052 M.

Column Elutions.—The ion-exchange column was loaded with 5 mg. of zirconium and tracer, and subjected to elution with 0.091 M citric acid in 0.45 M nitric acid. Zirconium activity began to come through at about 480 ml. of elution, reaching a maximum at 625 ml., falling to background before 800 ml., the distribution being a symmetrical bell-shaped curve with a width of 180 ml. at 0.37 of the maximum (1/e width). This peak required a somewhat larger volume of eluant than was expected from the K'_d value in the batch equilibrations.

After several other column tests showing that zirconium and hafnium behaved chemically as expected in the column, detailed analyses were made on a run consisting of charges of 1.60 mmoles of zirconium and 0.710 mmole of hafnium with hafnium activity as tracer. Zirconium analyses were made by volume of phosphate precipitate from duplicate 10-ml. samples, and hafnium analyses were by the activity in 25-ml. samples. The elution curves for the two elements in the run are shown in Fig. 5.

A small fraction, about 3%, of both species came through in the first few column volumes. This is ascribed to colloidal forms held very weakly by the resin which was not completely eliminated in preparing the solutions. Others[2,9,11] also have noted this phenomenon in larger degree.

The first zirconium of the main peak was detectable at 200 ml., and the concentration in the eluate rose to a maximum at 525 ml., then fell off fairly symmetrically to an undetectable level beyond 1500 ml. The main hafnium peak was well separated from the zirconium peak, as less than 1% of the activity came through before 2000 ml., and the highest concentration came at 3830 ml. The cross-contamination of the two elements was small; indeed cutting the zirconium fraction at 1200 ml. would give over 99% yield with negligible contamination. After the zirconium peak had gone, the hafnium peak could be eluted in small volume with oxalic or nitric acid.

The quality of this separation is in agreement with the expectations from the differences in behavior of zirconium and hafnium in the batch tests with nitric acid–citric acid, and exceeds in sharpness that of other ion-exchange separations reported to date. The mixed acid medium is recommended for further use for exhaustive separation of the two elements.

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Cambridge, Massachusetts