691. *The Cation Exchange Separation of Zirconium and Hafnium.*

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An investigation has been made of the possibility of separating zirconium and hafnium by elution from a cation-exchange column with sulphuric, hydrochloric, nitric, perchloric, and oxalic acids. A method has been developed depending on sulphuric acid elution whereby gram quantities of the two elements, in their naturally occurring proportions, can be separated by one passage through the column. The method is believed to be the simplest and most satisfactory at present available for the separation of zirconium and hafnium on a laboratory scale.

During the last two years several papers have appeared dealing with the separation of zirconium and hafnium by ion-exchange methods. Street and Seaborg (*J. Amer. Chem. Soc.*, 1948, **70**, 4268) showed that separation on a cation column was possible, and details of a run with 6N-hydrochloric acid as eluant were published. This was followed by two papers dealing with separation by anion exchange. Kraus and Moore (*ibid.*, 1949, **71**, 3263), using a column of Dowex 1, obtained some separation of tracer concentrations of zirconium and 0·2 mg. of hafnium by elution with a mixture of 0·5M-hydrofluoric acid and 1·0M-hydrochloric acid. Huffman and Lilly (*ibid.*, p. 4147) absorbed the ions on Amberlite IRA—400 from dilute hydrofluoric acid solution and then slowly eluted the fluoro-salts with 0·2M- and 0·01M-hydrochloric acid. By all these three methods the hafnium is eluted first from the column. However, from the point of view of an economic purification of zirconium, it is very much more favourable to elute the large quantity of zirconium and retain on the column the very much smaller hafnium impurity. Such a method has been developed by Hansen *et al.* (*ibid.*, 1950, **72**, 5043), who found that silica gel absorbs hafnium with strong preference from a dry methanol solution of the tetrachlorides. For the present work it was decided to start with the two elements in their naturally occurring proportions and to make use of the differences in the solution complexes of zirconium and hafnium in acid solutions combined with cation exchange to attempt to effect a removal of the small hafnium impurity.

Experimental.

Materials.—Zirconium oxide. "Specpure" oxide from Johnson Matthey Ltd. was used in which no purification from hafnium had been made. Analysis of the hafnium content by optical spectrographic methods and by radiochemical absorption analysis showed 1·5—2% of HfO_2.

Zirconium oxychloride. This was prepared from "Specpure" oxide by dissolution in a mixture of sulphuric and hydrofluoric acids, evaporation to dryness, dissolution of the sulphate in hydrochloric acid, precipitation of the hydroxide with ammonia solution, and redissolution in and crystallisation from hydrochloric acid.

Zirconium nitrate. Samples from different commercial sources showed very wide differences in ease of solubility, although spectrographic analysis for trace impurities and gravimetric analysis for zirconium and nitrate showed them to be very similar. [Analysis of a sample from Hopkin and Williams Ltd.: Zr, 33·5; NO_3, 45·4%; Zr : NO_3 = 0·736. Calc. for $ZrO(NO_3)_2,2H_2O$: Zr, 34·1; NO_3, 46·5%; Zr : NO_3 = 0·736.]

General reagents. All were of "AnalaR" grade.

Apparatus and Technique.—It was decided to measure the overall elution curves radiochemically and to analyse certain of the mixed fractions by optical spectrography. The starting materials were irradiated for periods of up to 4 weeks in the Harwell pile, the important reactions being

$$^{94}\text{Zr}\,(n;\ \gamma)\,^{95}\text{Zr} \xrightarrow[t_{1/2}=65\text{ d.}]{-\beta} {}^{95}\text{Nb} \xrightarrow[t_{1/2}=35\text{ d.}]{-\beta} {}^{95}\text{Mo}$$

$$^{96}\text{Zr}\,(n;\ \gamma)\,^{97}\text{Zr} \xrightarrow[t_{1/2}=17\text{ hr.}]{-\beta} {}^{97}\text{Nb} \xrightarrow[t_{1/2}=75\text{ min.}]{-\beta} {}^{97}\text{Mo}$$

$$^{180}\text{Hf}\,(n;\ \gamma)\,^{181}\text{Hf} \xrightarrow[t_{1/2}=45\text{ d.}]{-\beta} {}^{181}\text{Ta}$$

It was found that the activity produced by the 65-day zirconium isotope (^{95}Zr) was too low and, consequently, in most of the separation experiments described, use has been made of the 17-hr. ^{97}Zr activity which has a higher β-particle energy and requires shorter irradiation periods in the pile.

The apparatus consisted essentially of a reservoir at the head of a glass column packed with cation-exchange material, shown in Fig. 1. The outlet at the base of the column led through a radioactivity-counting assembly with recorder, and finally to an automatic eluate sampler. Three columns were used in the separation experiments : (1) 60 cm. × 0·8 cm. diameter holding *ca.* 20 g. of resin (mesh size 200—250); (2) 60 cm. × 1 cm. diameter holding *ca.* 30 g. of resin (mesh size 60—100); (3) for later larger-scale runs, the column size was increased to 120 cm. long and 2·5 cm. diameter to hold about 350 g. of resin (particle size about 0·5 mm. diameter).

FIG. 1.

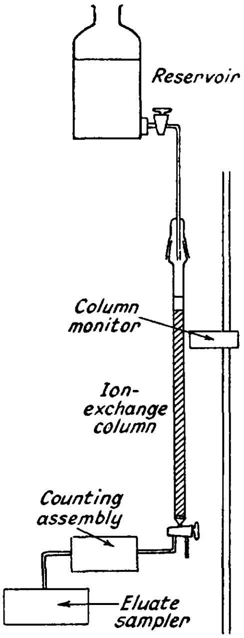
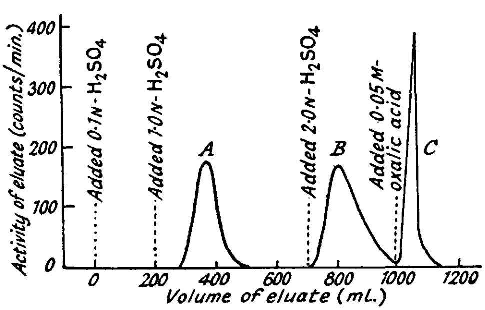


Diagram of separation apparatus.

FIG. 2.



Elution with 0·1, 1·0, *and* 2·0N-H_2SO_4 : *load* ca. 15 *mg. of* ZrO_2.

To enable the weak-energy β-particles to be counted, a thin window liquid-flow counter was needed. A suitable cell was constructed by making a shallow zig-zag channel (*ca.* 0·02″ deep) in a Perspex block and covering this with a thin Distrene sheet (thickness 2 mg./cm.^{2}) cemented on to the block with a very thin layer of black wax. The groove, which had a total length of 24 cm. and held about 0·2 ml. of liquid, was centred beneath an end-window type Geiger–Müller counter and a suitable filter interposed to remove the weak niobium activity (a daughter product of ^{95}Zr). The whole was enclosed within a 2″ lead-walled castle.

Output pulses from the counter were passed *via* a pre-amplifier into a rate-meter circuit coupled to a four-pen recorder and a relay control unit. The rate-meter circuit consisted of three separate linear rate-meters whose ranges were 0—10, 0—100, and 0—1000 pulses per second, respectively. Each was coupled to a separate pen on the recorder, and readings of the activity could be made from the most convenient trace. The fourth pen on the recorder gave information on bottle changes. Complete details of the counting and liquid sampling mechanism will be published soon (Bennett and Whyard).

The activity at points along the column was determined by using a brass-screened end-window counter (connected to a scaling system) designed to receive a collimated beam of activity and able to move up and down a vertically calibrated bar. Activity–column position curves constructed from such measurements have been termed " profile " curves and are a very valuable guide to the progress down the column of the uneluted portion of the activity.

Principle of the Method.—Ion-exchange materials can be used in two ways to effect separation: (*a*) the specificity of the exchange resin for one or other of the ions can be utilised, or (*b*) the resin can merely act as a second phase, and the main factor in the separation is the difference in the solution equilibria. In the present case, the second of these alternatives is being employed and the type of cation-exchange resin used is in no way specific for the separation.

Impregnation Procedure.—As a starting point in the separation experiments it was decided to use Street and Seaborg's impregnation method (*loc. cit.*) although this was later modified. 50 mg. of pile-irradiated " Specpure " zirconium oxide were dissolved with gentle warming in a mixture of 15 ml. of sulphuric acid and 15 ml. of 40% hydrofluoric acid. The solution were evaporated to dryness and the crystalline sulphate produced was dissolved with warming in 5 ml. of concentrated hydrochloric acid. After precipitation with ammonia solution, the hydroxide was centrifuged off, washed several times with water, and redissolved in hydrochloric acid. The oxychloride was crystallised from this solution. The product was dissolved in 5 ml. of 2N-perchloric acid, and the solution was slowly added (15 minutes) to an air-agitated suspension of 1 g. of Dowex 50 in 25 ml. of 2N-perchloric acid. When the addition was complete, the slurry was transferred to the top of a 60-cm. column of Dowex 50, the resin allowed to settle, the supernatant liquor removed as completely as possible, and the elution started. According to Street and Seaborg, absorption from 2N-perchloric acid overcomes difficulties due to polymerisation of the zirconium species and the uptake is about 80% complete (in the author's experience the uptake is not quite as high as this).

This procedure was later modified, the active zirconium-containing solution being fed slowly through a small subsidiary column of Dowex 50. After this column had been washed with N/2-perchloric acid, its content was transferred as a slurry to the top of the main column.

In the later stages of the work, it was found that absorption of zirconium from 2N-nitric acid solution was more efficient than from perchloric acid, and the impregnation procedure was altered accordingly.

Results.—Although other acid eluants have been used, namely, hydrochloric, nitric, perchloric, and oxalic acids of varying concentrations, by far the most satisfactory method for the separation of zirconium and hafnium depends on elution with sulphuric acid.

Sulphuric acid eluant. According to Connick and McVey (*J. Amer. Chem. Soc.*, 1949, **71**, 3182), sulphuric acid forms complexes quite strongly with zirconium (anion complexes are known to be formed) and one would expect a more rapid rate of elution than with other strong acids. A run was made in the 30-g. column in which the concentration of sulphuric acid eluant was increased stepwise from 0·1 to 1·0N., and then to 2·0N., the flow rate being kept constant at 40 ml./hour. With 0·1N-acid no movement of the zirconium–hafnium band (containing *ca.* 14 mg. of oxide) was observed after 200 ml. At this point, N-acid was added and a breakthrough of activity was observed after 90 ml. The activity, after rising sharply, had again reached a background level after a further 200 ml. and remained there until 500 ml. of the 1N-acid had been passed (Fraction A). Profile measurements showed that substantial activity still remained on the column, and the eluant was changed to 2N-sulphuric acid. A rapid increase in activity of the eluate was observed and, after a maximum had been passed, a near background level was again reached after 300 ml. of eluate had been collected (Fraction B). At this point 0·05M-oxalic acid solution (which forms very strong complexes with zirconium and hafnium) was passed through the column and all residual activity was rapidly removed (Fraction C). The complete elution curve is shown in Fig. 2. Precipitation with ammonia solution followed by ignition yielded 12·4 mg. of oxides from Fraction A (containing $<0·1\%$ of hafnium); no visible precipitate was obtained by addition of ammonia solution to Fractions B and C, in spite of their considerable radioactivity, obviously due to hafnium. Thus an apparently complete separation of the two elements had been achieved with a very wide gap between the hafnium and the zirconium fractions. It is noteworthy that the order of separation is in the desired direction, the reverse of that obtained by Street and Seaborg's hydrochloric acid elution method and by the two published anion-exchange methods.

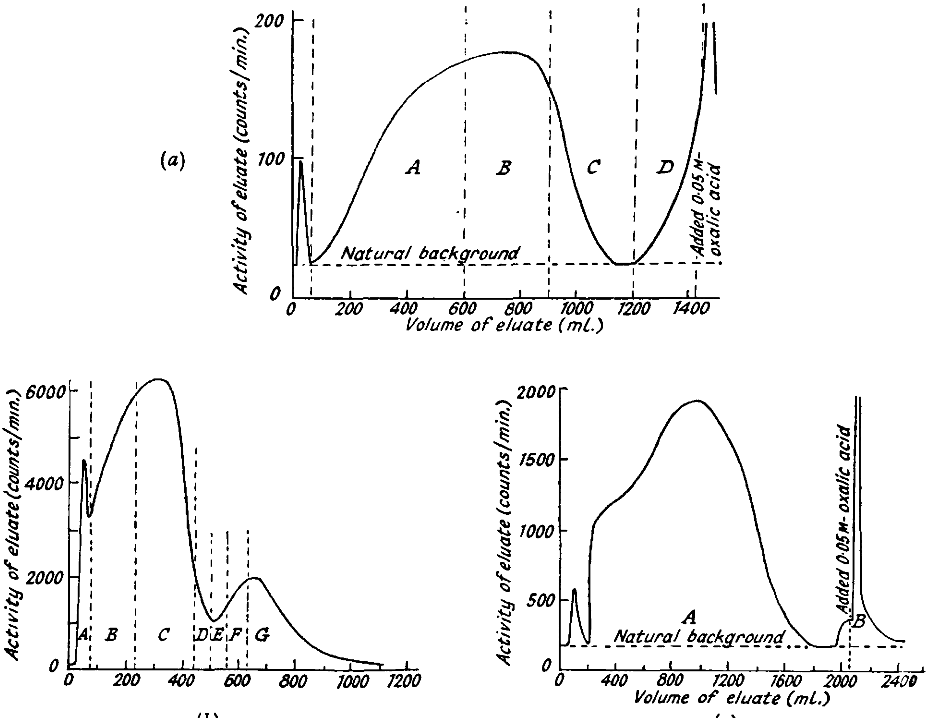
Experiments were made to find the maximum load which could be successfully treated on this column (containing 30 g. of Dowex 50) by elution with N-sulphuric acid. The practical limit was reached with a loading of 900 mg. of oxides. As shown in Fig. 3(*a*), the breakthrough point was 90 ml., and a background level of activity lasting for 30—40 ml. was reached after 1150 ml. The oxide precipitated from the eluate up to 1150 ml. was shown to contain $<0·01\%$ of hafnium.

The uptake of zirconium from sulphuric acid solution by a cation exchanger has been shown to fall off rapidly with increase in acid concentration above 0·2N., and to be negligible above 1·5N. Thus small variations in acid concentration would probably cause considerable differences in the rate of elution from the column. The same column conditions being used as had been found just to give complete separation with N-acid, *i.e.*, a load of 900 mg. of oxide on the 30-g. column and a flow rate of 60 ml./hour, runs were made with 1·2N- and 0·8N-sulphuric acid eluant. With the stronger acid, as expected, a considerably more rapid elution was achieved but the separation was not quite complete. As shown in Fig. 3(*b*), activity between the two peaks was a minimum at about 500 ml. (compared with 1200 ml. with N-acid). An examination of the profile curves showed that the ratio of the volumes of the two acids required to cause the same movement of the hafnium peak was about 3 : 1. It is apparent that a complete separation could be achieved with a comparatively small decrease in loading. Such alteration of the conditions might possibly be advantageous to the rate of production of hafnium-free zirconium, but a greater number of runs would be necessary. The run with 0·8N-acid showed a much smaller rate of elution but with complete separation [see Fig. 3(*c*)].

An initial small peak has often been noticed before the main zirconium peak is eluted. This may be due to the rapid removal of adsorbed polymerised material as distinct from zirconium held on the resin by an exchange mechanism.

To investigate the possibility of treating larger amounts of material, a new column was constructed 120 cm. long and 2·5 cm. in diameter to hold about 10 times as much resin. Several changes in procedure were made. Dowex 50 resin was replaced by Zeokarb 225 (*ex* Permutit Co. Ltd.) which had been shown to be very similar to Dowex 50 in respect of both its capacity and its general exchange behaviour. The resin particle size was increased to about 0·5 mm. diameter to enable a higher flow rate to be used. To avoid disturbing the column, a simplified impregnation procedure was adopted whereby the zirconium solution was allowed to percolate very slowly through the main column, the activity being absorbed on the top section. The use of zirconyl nitrate instead of chloride enabled irradiated material to be used directly in the impregnating solution without the need for disposing of radioactive chlorine daughter products in this "*in situ*" impregnation method. Further, it was shown that the absorption of zirconium on a resin column from 2N-nitric acid was rather more efficient than from 2N-perchloric acid, and an alteration in this direction was made. For the higher flow rates needed in this column, the thin window counting assembly was replaced by a more robust internal spiral liquid-flow counter with a glass wall thickness of *ca.* 40 mg./cm.^{2}

FIG. 3.



(*b*) (*c*)

Elution with sulphuric acid: (*a*) 1·0N, (*b*) 1·2N, (*c*) 0·8N. *Load* ca. 900 *mg. of* ZrO_2.

Thus a solution of 20 g. of zirconyl nitrate (containing 1 g. of neutron-irradiated "Specpure" zirconyl nitrate) in 1 l. of 2N-nitric acid was allowed to percolate very slowly through the column, and the absorbed material was eluted with N-sulphuric acid at a flow rate of 100 ml./hour. The profile curves of the hafnium activity are shown in Fig. 4. Hafnium started to appear in the eluate after about 9 l. of eluant had been passed, and spectrographic analysis of the oxide products obtained before this point showed <0·01% of hafnium. About 95—98% of the zirconium was recovered with this purity.

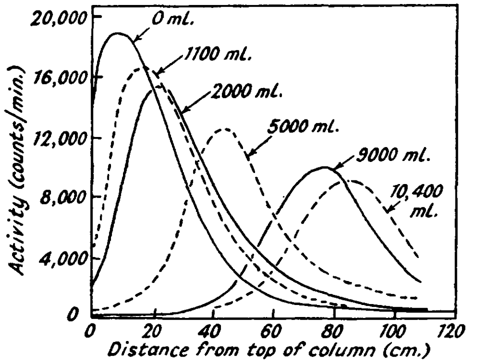
Breakthrough Technique.—A disadvantage of the elution chromatography technique is the number of stages involved. A more useful separation method is the "breakthrough" technique whereby the mixture to be separated, dissolved in a suitable solvent, is passed through a column of resin, the mixture being continually fed in as the run proceeds. This method cuts out the impregnation step and so considerably simplifies the procedure.

The possibility of using the "breakthrough" technique in the present case was investigated by passing through the large (350-g.) column a solution containing 2·5 g. of zirconyl nitrate per l. of N-sulphuric acid at a flow rate of about 200 ml./hour. Fractions of the effluent from the column were collected, the hydroxides precipitated and ignited, and the oxides examined spectrographically for hafnium. It is seen from Fig. 5 that a small quantity of zirconium and hafnium leak through into the effluent almost immediately, this concentration remaining approximately constant until the main zirconium breakthrough point at about 9 l. Over this initial portion the hafnium–zirconium ratio remains quite high at about the value of the in-going solution. The concentration of hafnium in the effluent remains sensibly constant until it begins to rise rapidly at about 18 l. (*i.e.*, when 10 g. of mixed oxides have passed through the column). Up to this point the oxides precipitated from the effluent contained overall *ca.* 0·1% of HfO_2. The first 8·2 g. of oxides had an overall HfO_2 content of 0·047%. The drop in zirconium content towards the end of the run is probably due to a fall in the flow rate. The slow uptake of zirconium was indicated by the decrease in effluent concentration noted at two points in the run after the flow had been stopped for some hours.

Thus, although the method is convenient and efficient for producing a low hafnium-content zirconium oxide, it does not give the clean separation achieved by the elution method for the same amount of material processed.

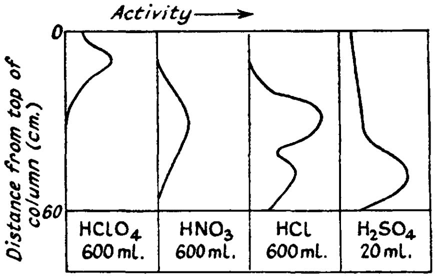
Purification of Hafnium.—A sample of 70 mg. of hafnium oxide was converted into oxychloride and absorbed on the 30-g. column as previously described for zirconium. Spectrographic analysis indicated the presence of about 8% of zirconium oxide and it was hoped, by elution with N-sulphuric acid, to purify the hafnium oxide from this contaminant. Breakthrough of hafnium activity was observed after 675 ml.; 6 mg. of oxides were obtained from the eluate up to this volume, and oxalic acid treatment of the column produced a further 63 mg. of oxide which was shown to be substantially free from zirconium.

FIG. 4.



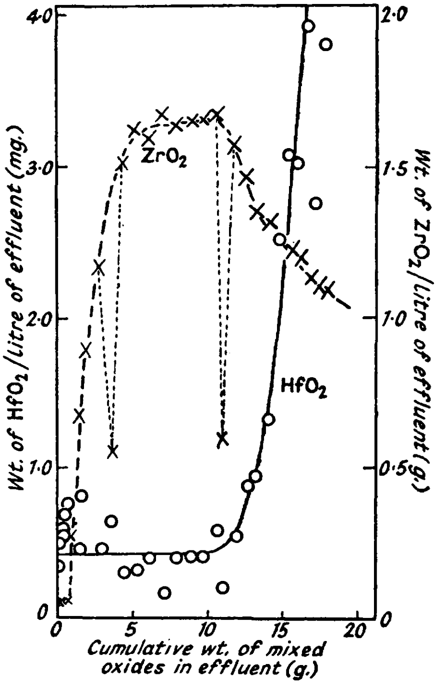
Profile curves of hafnium activity during elution with 1N-H_2SO_4. *Load*: 9 *g. of* ZrO_2 *on* 350-*g. column.*

FIG. 6.



Comparison of profile curves for 3N-*acid eluants.*

FIG. 5.



Effluent curves for "breakthrough" run using 1N-H_2SO_4 *solution.*

Experiments with Other Acids as Eluants.—Other acid eluants were not as satisfactory as sulphuric acid for the separation, but it is interesting to compare the results obtained.

Hydrochloric acid eluant. Under the same conditions as those used by Street and Seaborg, *i.e.*, elution with 6N-hydrochloric acid, some separation was apparent from the elution and profile curves, but the elution was far too rapid for good resolution to be achieved.

A slower rate of elution was found with 3N-hydrochloric acid. The flow rate was maintained constant at 8 ml./hour, and the activity of the eluate started to rise after about 370 ml. After 67 hours the activity was again at background level after having passed through a maximum, and the residual activity on the column was stripped with 0·05M-oxalic acid solution. No hydroxide precipitate was obtained from the solution before oxalic acid treatment, but 10 mg. of oxide (corresponding to the loading of the column) were obtained from the oxalic acid fraction. Spectrographic analysis of this oxide showed a hafnium content of 0·14%.

Similar results were obtained with a 10-fold increase in the loading, the first 10 mg. of oxide precipitated from the eluate having an increased hafnium content of 3·1%.

Oxalic acid eluant. Results obtained while stripping residual activity from the column with oxalic acid indicated that separation might be achieved, with zirconium coming first from the column, by using dilute oxalic acid as eluant. Runs were made with 0·01 and 0·001M-oxalic acid. Spectrographic analysis showed that hafnium was, in fact, held more strongly on the column, but the separation achieved was not as marked as with hydrochloric acid. With both concentrations of oxalic acid, very rapid breakthroughs were obtained at about 30 ml., followed by long " tails " in the elution curves.

Nitric acid eluant. Nitric acid has been reported by Connick and McVey (*loc. cit.*) to have similar complexing properties for zirconium to hydrochloric acid. However, elution with 3N-acid gave no apparent separation, although the single observed activity peak moved at a rate similar to that of the zirconium peak in runs with 3N-hydrochloric acid.

Perchloric acid eluant. Perchloric acid has been assumed to show the least inclination of the strong acids to complex with zirconium; and, indeed, elution with 3N-perchloric acid showed a very much slower rate of movement of the activity peak down the column than with the same concentration of nitric and hydrochloric acids. No separation was noticed.

Comparative profile curves for the four strong acids studied are shown in Fig. 6.

SUMMARY AND DISCUSSION.

The sulphuric acid elution technique provides the simplest and most satisfactory method now available for the separation of zirconium and hafnium on a laboratory scale. The method appears to be equally applicable to the purification of either element and can be used with starting materials of any composition. Although the silica gel adsorption method described by Hansen *et al.* (*loc. cit.*) can apparently deal with larger quantities of material in a shorter time, difficulties may be found in the preparation of the very dry methanol required, and the recovery of zirconium salts from the eluate is not so convenient as in the present ion-exchange method.

The rate E of elution from an ion-exchange column may be defined by the expression $E = dA/V$, where d is the distance (in cm.) a band peak travels after V ml. of eluant have passed through a column of cross-sectional area A cm.^{2}.

In many of the runs made with hafnium and zirconium elution, no separate zirconium peak was noted owing to its low activity. However, in some cases the movement of both bands was observed and the elution constants could be calculated (see table). In other cases the movement of the zirconium was found by repeating the runs, only zirconium tracer being used.

Elution constants for zirconium and hafnium.

Acid	Normality	Column size, g.	Load (mg.)	E_{Zr}	E_{Hf}	$E_{Zr}/E_{Hf} = \bar{E}$
$HClO_4$	3·0	30	*ca.* 15	*ca.* 0·001	*ca.* 0·001	*ca.* 1·0
HCl	3·0	20	,,	0·038	0·067	0·57
	,,	30	*ca.* 200	0·038	0·062	0·62
	4·5	20	*ca.* 15	—	0·34	—
	6·0	,,	,,	0·39	0·52	0·76
HNO_3	3·0	30	,,	0·038	0·038	*ca.* 1·0
H_2SO_4	0·8	,,	*ca.* 900	0·064	0·0133	4·8
	1·0	,,	,,	0·085	0·022	4·1
	1·2	,,	,,	0·181	0·069	2·7

The great difference between the elution constant for 3N-perchloric acid and other acids of the same concentration makes it clear that the elution of zirconium and hafnium ions by nitric, hydrochloric, and sulphuric acids is due to a complex action. The nature of this action has been made clearer by work on the solution chemistry of zirconium to be described in a later communication.

As would be expected, the degree of separation represented by the relationship $E_{Zr}/E_{Hf} = \bar{E}$ increases with decreasing acid concentration both in hydrochloric and in sulphuric acid solution, although the utility of reducing the acid concentration further gets progressively less. For example, with sulphuric acid the ratio of the $\bar{E}$ values between 1·2 and 1·0N. is about 1·5, while between 1·0 and 0·8N. it is only 1·17.

It is of interest that the elution constants for zirconium in 3N-hydrochloric and nitric acid solution are the same; no separation, however, is achieved with the latter while, with the former, $\bar{E} = ca.\ 0{\cdot}6$.

The breakthrough technique, although convenient and efficient for producing a low hafnium-content zirconium oxide, does not give the clean separation achieved by the elution method.

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