The Analysis of Complex Alloys, with Particular Reference to Niobium, Tantalum and Tungsten

The Distribution of Metallic Ions between Ion-exchange Resins and Hydrochloric - Hydrofluoric Acid Solutions

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The distribution coefficients of aluminium, titanium[IV], zirconium, vanadium[IV] and vanadium[V], niobium[V], tantalum, chromium[III], molybdenum[VI], tungsten[VI], manganese[II], iron[III], cobalt[II], nickel and copper[II] between the ion-exchange resins De-Acidite FF and Zeo-Karb 225 and up to 10 M hydrochloric acid (and mixtures 1 M in hydrofluoric acid and up to 10 M in hydrochloric acid) have been determined. From a study of the results, a scheme is proposed for the separation of these elements into more manageable groups.

THE wet-chemical quantitative determination of niobium, tantalum and tungsten in complex alloys has always been a lengthy procedure, partly owing to the ease with which salts of these metals are hydrolysed in acid solution and partly because of the similarity between their chemical properties. In the procedure often used, niobium and tantalum are completely precipitated as their hydrated oxides; most of the tungsten is co-precipitated as tungstic acid,[1,2] and the remainder is removed from the solution as its insoluble complex with rhodamine B.[1] In this way, these elements can be separated from most of the other constituents of the alloy. However, clean-cut separation is difficult to achieve, and the ignited precipitate usually contains almost all of the silicon and small amounts of certain other oxides, such as titanium dioxide and molybdenum trioxide. Silicon can be readily removed by treatment with hydrofluoric and sulphuric acids, but the presence of small amounts of the other oxides must be allowed for in the subsequent analysis of the ignited precipitate for niobium, tantalum and tungsten. Satisfactory analysis of this ignited precipitate usually necessitates further separation into individual constituents. Niobium and tantalum can be separated from tungsten by fusion of the oxides in potassium carbonate and precipitation of the niobium and tantalum by magnesium sulphate and ammonium chloride,[2,3] but the separation of niobium from tantalum by precipitation reactions has, until recently, been time-consuming. These elements can be more readily separated on columns of cellulose[4] or ion-exchange resins[5] or by solvent extraction.[6,7] (Recently, however, the use of N-benzoyl-N-phenyl-hydroxylamine for precipitating niobium, tantalum and titanium substantially free from almost all other elements, including tungsten, and for the separation by consecutive precipitation under different conditions of niobium, tantalum and titanium has been described[8,9]; this technique appears to show promise, but no results seem to have been published for the determination of niobium and tantalum in complex alloys by means of this reagent.)

The combination of precipitation and separation does, however, after many hours' work, produce the correct results for the niobium, tantalum and tungsten contents of an alloy. For example, Hague and Machlan[10] have satisfactorily determined niobium, tantalum, titanium and zirconium (but not tungsten) in steels by precipitating these elements from solution with cupferron, igniting the precipitate to give the mixed oxides and separating the constituents of the solution of mixed oxides on a column of ion-exchange resin.

The time taken for an analysis would be greatly decreased if its first stage, the precipitation of niobium, tantalum and tungsten, could be by-passed, and we decided to examine the possibility of analysing alloys containing niobium and tantalum or niobium, tantalum and tungsten entirely by the use of ion-exchange resins. These elements only remain dissolved in dilute acid in the presence of certain complexing agents, and solutions of hydrofluoric acid in hydrochloric acid were used for this purpose. Wilkins[11] has described the separation and determination of nickel, chromium, cobalt, iron, titanium, tungsten, molybdenum, niobium and tantalum by a method not involving initial precipitation and in which fluoride

solutions and ion-exchange resins were used; so far, however, no results for the application of his scheme to alloys containing widely different amounts of these elements have been published. Wetlesen[12] has also reported a satisfactory method for the analysis of mixtures of titanium, niobium and tantalum; he used hydrochloric - hydrofluoric acid solutions and a column of the anion-exchange resin Amberlite IRA-400, but did not examine the effects of other metals on the separation.

So that the desired separations might be achieved in a reasonable time, we have used resins of mesh size 52 to 100; much work on ion-exchange separation has been carried out by American investigators with 200-mesh resin, but it was thought that the rate of flow through resin of this size would be too slow for our purposes. The resins chosen for this work were De-Acidite FF (type SRA 70) and Zeo-Karb 225 (type SRC 14), obtainable from the Permutit Co. Ltd., London. In order to devise the best possible scheme for solutions of alloys, it was necessary to determine the distribution coefficients of niobium, tantalum, tungsten, etc., between the hydrochloric - hydrofluoric acid solutions and the cation- and anion-exchange resins; in this paper, the results of these studies are reported.

Values of distribution coefficients can be applied directly to work on columns by means of the following equation[13]—

$$V_{max.} = D_v + i$$

provided that the total amount of cation or anion is less than about 3 per cent. of the total capacity of the column.[14] In this equation, $V_{max.}$ is the volume (in column volumes) eluted when the maximum concentration of metal ion is observed in the effluent, D_v is the volume-distribution coefficient of the element between the resin and the solution and i, a fraction, is the interstitial volume of the column of resin. The value of D_v is found by batch-equilibration experiments and is defined by the expression—

$$\frac{\text{Amount of element on resin/volume of resin (in litres)}}{\text{Amount of element in solution/volume of solution (in litres)}}.$$

The value of D_v varies with the loading of the resin, decreasing as the loading increases, but generally does not alter appreciably for loadings less than 3 per cent. of the total capacity. Since, in subsequent work with columns, we intended to keep the total column loading to less than 3 per cent. for ions appreciably adsorbed, it was thought that the values of D_v found with a resin loading of never more than 3 per cent. could be used with reasonable exactness to predict the positions of band maxima in elution studies.

Kraus and his co-workers have determined distribution coefficients for most metals between the anion-exchange resin Dowex 1-X10 (i.e., Dowex 1 containing 10 per cent. of divinylbenzene) of 170 to 220 mesh and hydrochloric acid[15] and hydrochloric - hydrofluoric acid media.[16] However, their results for niobium, tantalum and zirconium refer to 0·5 M hydrofluoric acid with different concentrations of hydrochloric acid, and our investigation was made entirely with 1 M hydrofluoric acid and different concentrations of hydrochloric acid. The resin De-Acidite FF was also expected to show some difference in affinities for certain elements when compared with Dowex 1 under the same experimental conditions. Recently,[17] distribution coefficients have been determined for some fifty elements between 200-mesh Dowex 1-X10 resin and pure hydrofluoric acid solutions. That work indicated, however, that hydrofluoric acid was less versatile a reagent than hydrochloric - hydrofluoric acid mixture.

The distribution coefficients of many elements between the cation-exchange resin Zeo-Karb 225 and hydrochloric - hydrofluoric acid media are also reported in this paper. Little work has so far been carried out on distribution coefficients with cation-exchange resins. Strelow[18] determined the distribution coefficients of forty-three cations between 100- to 200-mesh AG50W-X8 resin (prepared from Dowex 50) and hydrochloric acid, but he used rather a high column loading (40 per cent.). Mann and Swanson[19] have also recently determined the distribution coefficients of manganese, iron[II], iron[III], nickel, copper[II], zinc, cadmium and mercury[II] between 0·5 to 12 M hydrochloric acid and 100- to 200-mesh Dowex 50W resin containing 2, 4, 8, 12 or 16 per cent. of divinylbenzene.

In our work, it was more convenient to determine weight-distribution coefficients for elements between the solutions and resins, but these can be readily converted to volume-distribution coefficients by means of the relationship—

$$D_v = D\rho$$

in which D is the weight-distribution coefficient and ρ is the density of the resin bed in kilograms per litre (the value of ρ is 0·41 for De-Acidite FF resin, type SRA 70, and 0·43 for Zeo-Karb 225 resin, type SRC 14). The weight-distribution coefficient is given by the expression—

$$\frac{\text{Amount of element on resin/weight of resin (in kilograms)}}{\text{Amount of element in solution/volume of solution (in litres)}}.$$

In determining weight-distribution coefficients by batch-equilibration experiments, it was convenient to shake a few grams of resin with a few millilitres of solution in small polythene bottles. Distribution coefficients were calculated from the final concentration of an element in the solution and from the decrease in concentration of the solution after it had been shaken with the resin. As the total resin loading was at no time to exceed 3 per cent., solutions containing metals in low concentration had to be used, and the concentrations of elements in the solution before and after being shaken with the resin were determined by sensitive colorimetric procedures.

EXPERIMENTAL

APPARATUS—

Polythene ware—For determining distribution coefficients, solutions and resins were shaken in polythene 1-oz bottles fitted with polythene screw-caps. Solutions containing hydrofluoric acid were kept in polythene bottles and vessels.

Shaker—A mechanical shaker was constructed to accommodate twelve polythene bottles. The speed of shaking could be altered by means of a rheostat, but the motor on the shaker was generally operated at about 500 cycles per minute.

Spectrophotometer—A Unicam SP600 instrument was used in the colorimetric determinations of metals in solution.

pH meter—A Pye universal pH meter was used when necessary.

RESINS—

Zeo-Karb 225—Type SRC 14 was used; it contained 8 per cent. of divinylbenzene and consisted of particles of size between 52 and 100 mesh. Before use, the resin was thoroughly washed in a column, first with 2 N hydrochloric acid to convert it from the sodium form (as supplied) into the hydrogen form and then with distilled water until the effluent was free from chloride. Finally, it was dried over anhydrone *in vacuo* at 60° C.

De-Acidite FF—Type SRA 70 was used; its cross-linking was approximately 7 to 9 per cent., and it consisted of particles of size between 52 and 100 mesh. It was supplied in the chloride form, but, before use, was treated with hydrochloric acid and washed and dried as described above for Zeo-Karb 225.

STANDARD SOLUTIONS OF METALS—

These were prepared from Specpure metals or oxides obtained from Johnson, Matthey and Co. Ltd.

For work with hydrochloric - hydrofluoric acid solutions—Standard solutions of aluminium, titanium[IV], zirconium, vanadium[V], niobium[V], tantalum, chromium[III], molybdenum[VI], manganese[II], iron[III], cobalt[II], nickel and cerium[IV] were prepared by dissolving in 40 per cent. w/w hydrofluoric acid, with heating when necessary, weighed amounts of the following materials: aluminium rod, titanium sponge, zirconium oxide, vanadium pentoxide, niobium pentoxide, tantalum pentoxide, chromium pellets, molybdenum trioxide, manganese flake, iron sponge, cobalt sponge, nickel sponge and ceric oxide. Iron and titanium sponge dissolved in the hydrofluoric acid with the formation of iron[II] and titanium[III], respectively. Iron[II] was oxidised to iron[III] by hydrogen peroxide, excess of which was destroyed by boiling. Titanium[III] was oxidised to titanium[IV] by adding concentrated nitric acid dropwise to the boiling solution.

A standard solution of copper[II] was prepared by dissolving powdered copper in the hydrofluoric acid, with the addition of hydrogen peroxide; excess of hydrogen peroxide was destroyed by boiling.

A standard solution of tungsten[VI] was prepared by dissolving tungsten trioxide in ammonia solution, sp.gr. 0·880, evaporating the solution to dryness and dissolving the residue in the hydrofluoric acid.

The concentration of residual hydrofluoric acid in these solutions was adjusted to about 5 M and accurately determined by titration with standard alkali. The concentrations of metals in the solutions varied from 0·4 to 4 mg per g.

Standard vanadium[IV] solution was prepared by bubbling sulphur dioxide for 15 minutes through a solution of vanadium pentoxide (about 50 mg) in 50 ml of 10 M hydrofluoric acid, removing the excess of sulphur dioxide by boiling and then diluting with water until the concentration of vanadium[IV] was approximately 0·5 mg per g.

For the solution of cerium[IV], the metal content was determined by adding a suitable volume of standard iron[II] solution to an aliquot of the cerium[IV] solution and then determining the excess of iron[II] colorimetrically with bipyridyl[20]; this was necessary because it could not be assumed that Specpure ceric oxide contained 100 per cent. of CeO_2.

For work with hydrochloric acid containing no hydrofluoric acid—Standard solutions of aluminium, vanadium[V], chromium[III], manganese[II], iron[III], cobalt[II] and nickel were prepared by dissolving about 100 mg of the Specpure metal or oxide in 10 to 20 ml of water containing the minimum amount of concentrated hydrochloric acid and diluting with water until the concentration of metal was approximately 1 mg per g. With iron[III], hydrogen peroxide was added to the solution to oxidise iron[II], and the excess of peroxide was destroyed by boiling.

A standard solution of copper[II] was prepared by dissolving powdered copper in the minimum volume of a mixture of hydrochloric acid and 30 per cent. w/v hydrogen peroxide solution, destroying the excess of peroxide by boiling and diluting with water until the concentration of copper[II] was about 1 mg per g.

Residual hydrochloric acid in these solutions was determined by titration with standard alkali.

OTHER REAGENTS—

Hydrochloric, hydrofluoric and sulphuric acids—These were of analytical-reagent grade.

Reagents and solutions for colorimetric determinations—These were of the purest grade available.

DETERMINATION OF DISTRIBUTION COEFFICIENTS

PROCEDURE FOR ZEO-KARB 225 OR DE-ACIDITE FF AND HYDROCHLORIC - HYDROFLUORIC ACID SOLUTIONS—

An aliquot (1 to 2 ml) of the standard solution of the metal in hydrofluoric acid was placed in a tared 1-oz polythene bottle and accurately weighed; from the density of the solution, the exact volume of the aliquot was determined. Calculated volumes of concentrated hydrochloric acid and water were then added from burettes to adjust the concentration of hydrofluoric acid to 1 M and that of hydrochloric acid to the required value. The bottle and its contents were then weighed to ascertain the total weight of solution. A 0·5- to 1·0-g portion of dried resin was placed in the bottle, and the exact amount used was found by weighing the bottle and contents; this amount was such as to give a total resin loading of less than 3 per cent. The bottle, together with eleven others containing resin and solutions having different ratios of hydrochloric to hydrofluoric acid, but prepared in a similar way, was shaken mechanically for a minimum of 16 hours. (With Zeo-Karb 225 and solutions 7 M or more in hydrochloric acid, the time of shaking was only 30 minutes, as the resin was slowly attacked by the acid at these concentrations.)

Some of the hydrochloric - hydrofluoric acid solution was then filtered through a dry 5·5-cm Whatman No. 42 filter-paper supported in a 1½-inch polythene funnel, collected in a weighed tall 100-ml beaker and weighed. The concentration of residual metal in the solution was determined by one of the methods outlined below.

PROCEDURE FOR ZEO-KARB 225 OR DE-ACIDITE FF AND HYDROCHLORIC ACID—

The procedure was similar to that described above, but the aliquot of filtered solution was collected in a small calibrated flask before being weighed.

TREATMENT OF SOLUTIONS BEFORE COLORIMETRIC DETERMINATION—

As most of the colorimetric determinations were carried out in acid solution, it was necessary to remove hydrofluoric acid from the weighed aliquots of hydrochloric - hydrofluoric acid solutions to prevent the glass cells from being attacked. If it was known that the colorimetric method was subject to no interference from the presence in the solution of

silicon, boron or aluminium, 2 ml of concentrated sulphuric acid were added to each hydro-chloric - hydrofluoric acid solution, and the mixture was evaporated in a Pyrex-glass beaker until fumes of sulphur trioxide were evolved.   When interference from silicon, boron or aluminium was expected, concentrated hydrochloric acid was added, and the solution was evaporated to dryness in a polytetrafluoroethylene beaker; this evaporation served to free the solution from hydrofluoric acid.   With weighed aliquots of solutions containing only hydrochloric acid, evaporation with concentrated sulphuric acid was not necessary.
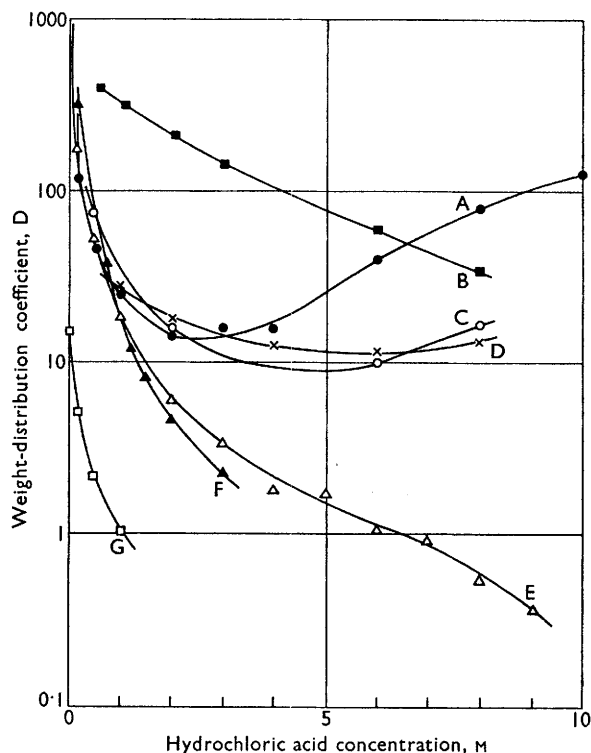
Fig. 1.   Weight-distribution curves between De-Acidite FF resin and solutions 1M in hydrofluoric acid and contain-ing different concentrations of hydrochloric acid: curve A, molybdenum^{VI}; curve B, tantalum; curve C, niobium^{V}; curve D, tungsten^{VI}; curve E, titanium^{IV}; curve F, zirconium; curve G, vanadium^{V}

COLORIMETRIC DETERMINATIONS OF METALS—

The concentrations of metal ions in the solutions were determined as outlined below, all or only part of the solution being used, depending on the amount of metal present and the sensitivity of the colorimetric procedure.

Aluminium—This was determined as its complex with Solochrome cyanine R in a solution buffered at pH 6·0 with pyridine and hydrochloric acid; optical-density measurements were made at 537 mμ.[21]

Titanium^{IV}—This was determined as its complex with chromotropic acid in a solution buffered at pH 4·0 with acetic acid and sodium acetate; optical-density measurements were made at 438 mμ.[22]

Zirconium—This was determined as its complex with xylenol orange in 0·2 N sulphuric acid; optical-density measurements were made at 535 mμ.[23]

Vanadium—Vanadium^{IV} was determined as its complex with catechol in ammoniacal solution (pH 8 to 9),[24] and vanadium^{V}, after reduction by sulphite,[24] was similarly determined; optical-density measurements were made at 585 mμ.

Niobium[V]—This was determined by extraction into ether of its complex **with** potassium thiocyanate and subsequent measurement of optical density at 385 mμ.[25]

Tantalum—This was determined with pyrogallol, optical-density measurements being made at 365 mμ.[26]

Chromium[III]—This, after oxidation to the sexavalent state, was determined as its complex with diphenylcarbazide in a dilute solution of orthophosphoric acid; optical-density measurements were made at 540 mμ.[27]

Molybdenum[VI]—This was determined as its complex with toluene-3,4-dithiol in an aqueous solution containing 30 per cent. v/v of butyl alcohol and 5 M in hydrochloric acid; optical-density measurements were made at 680 mμ.[28]

Tungsten[VI]—This was determined after extraction of its complex with toluene-3,4-dithiol into carbon tetrachloride; optical-density measurements were made at 635 mμ.[29]
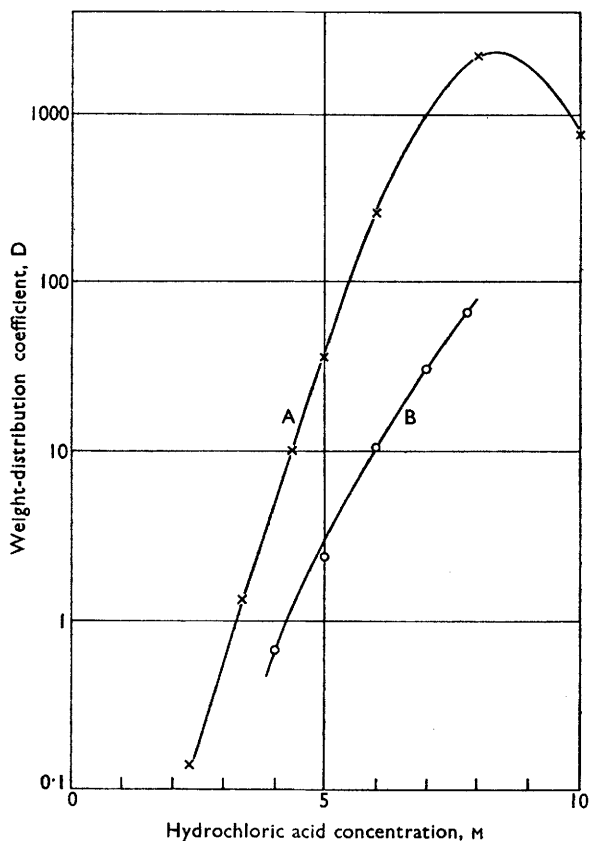

Fig. 2.   Weight-distribution curves for iron and cobalt
(conditions as in Fig. 1): curve A, iron[III]; curve B, cobalt[II]

Manganese[II]—This was determined, after oxidation by periodate, as **permanganate**, optical-density measurements being made at 525 mμ.[30]

Iron[III]—This was determined, after reduction by hydroxylamine, as its complex **with** bipyridyl; optical-density measurements were made at 522 mμ.[20]

Cobalt[II]—This was determined as its complex with nitroso-R salt, optical-density measurements being made at 530 mμ.[31]

Nickel—This was determined as its complex with dimethylglyoxime, after oxidation by bromine; optical-density measurements were made at 465 mμ.[32]

Copper[II]—This was determined by extraction into carbon tetrachloride of its complex with sodium diethyldithiocarbamate, optical-density measurements being made at 435 mμ.[33]

Cerium[IV]—This was determined by adding an excess of standard iron[II] solution and then determining the unreacted iron with bipyridyl, optical-density measurements being made at 522 mμ.[20]

RESULTS FOR DE-ACIDITE FF RESIN

Fig. 1 shows graphs of weight-distribution coefficient, D, against concentration of hydrochloric acid for titanium[IV], zirconium, vanadium[V], niobium[V], tantalum, molybdenum[VI] and tungsten[VI] in solutions 1 M in hydrofluoric acid; D is plotted on a logarithmic scale. Similar graphs for iron[III] and cobalt[II] are shown in Fig. 2, and individual results for a few other elements are listed in Table I.

TABLE I

WEIGHT-DISTRIBUTION COEFFICIENTS FOR VARIOUS ELEMENTS ON DE-ACIDITE FF RESIN

Element	Solution	Value of D
Aluminium		<0·5
Vanadium[IV]	Hydrochloric acid, 8 M	1·5
Chromium[III]		<0·5
Nickel		<0·5
Aluminium		<0·5
Vanadium[IV]	Hydrofluoric acid, 1 M	0·7
Chromium[III]		<0·5

The distribution coefficients for manganese[II], iron[III] and copper[II] between the resin and hydrochloric acid are shown in Fig. 3.
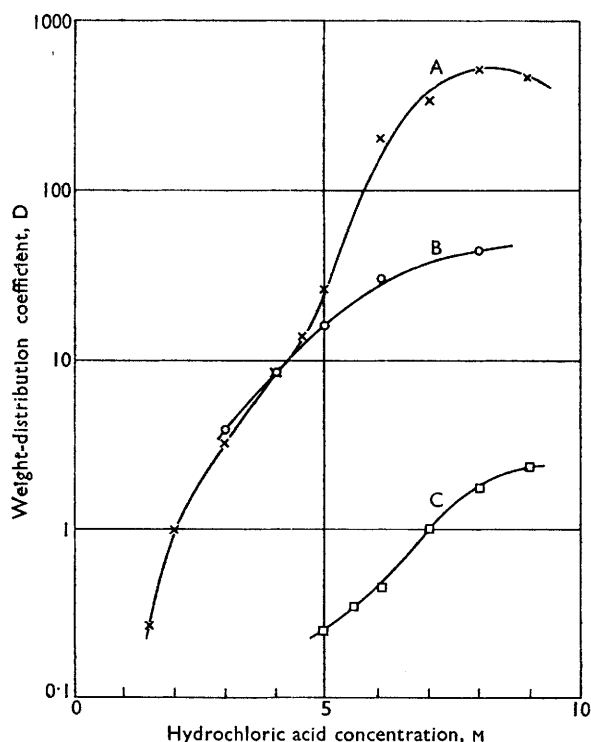

Fig. 3.   Weight-distribution curves between De-Acidite FF resin and hydrochloric acid: curve A, iron[III]; curve B, copper[II]; curve C, manganese[II]

RESULTS FOR ZEO-KARB 225 RESIN

Fig. 4 shows graphs of weight-distribution coefficient against concentration of hydrochloric acid for vanadium[IV], chromium[III], iron[III] and cobalt[II] in solutions 1 M in hydrofluoric
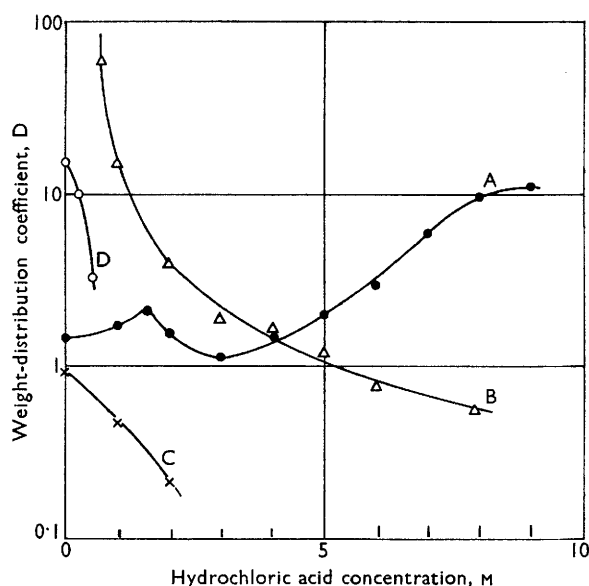
Fig. 4.   Weight-distribution curves between Zeo-Karb 225 resin and solutions 1 M in hydrofluoric acid and containing different concentrations of hydrochloric acid: curve A, iron[III]; curve B, cobalt[II]; curve C, chromium[III]; curve D, vanadium[IV]

acid.   Similar graphs for solutions containing no hydrofluoric acid are shown in Fig. 5 for aluminium, vanadium[IV], chromium[III], manganese[II], iron[III], nickel and copper[II].   Other results for some of these elements are listed in Table II.

TABLE II

WEIGHT-DISTRIBUTION COEFFICIENTS FOR VARIOUS ELEMENTS ON ZEO-KARB 225 RESIN

Element	Solution	Value of D
Aluminium	Hydrochloric acid (0 to 1 M) - hydrofluoric acid (1 M)	<0·5
Vanadium[V]	{ Hydrofluoric acid, 1 M	1·2
	{ Hydrochloric acid, 0·06 M	32
Manganese[II]	Hydrofluoric acid, 1 M	>2000
Nickel	Hydrochloric acid (0·1 M) - hydrofluoric acid (1 M)	∼5000
Copper[II]	Hydrofluoric acid, 1 M	>7000

DISCUSSION OF RESULTS

DE-ACIDITE FF RESIN—

As expected, the curves in Fig. 1 for titanium[IV], zirconium, niobium[V], tantalum, molybdenum[VI] and tungsten[VI] were similar in shape to those obtained by Nelson, Rush and Kraus,[16] who used the anion-exchange resin Dowex 1.   At low concentrations of hydrochloric acid, these elements are strongly adsorbed on the resin, as they form fairly stable anionic complex fluorides that compete favourably with chloride ions for sites on the resin.   Nelson, Rush and Kraus[16] did not study the adsorption of vanadium[V] in detail, but it is evident from Fig. 1 that this element is appreciably adsorbed at low concentrations of hydrochloric acid.   Vanadium[V] is not particularly stable in the presence of De-Acidite FF; in fact, it was rapidly reduced to vanadium[IV] in the presence of 10 M hydrochloric acid.   In 5 M hydrochloric acid, a determination of the ratio of vanadium[V] to vanadium[IV] after being shaken for 30 minutes with the resin showed that 67 per cent. of the vanadium[V] had been reduced. At concentrations of hydrochloric acid less than 1 M, reduction of vanadium[V] appears to be negligible, and the values of D for vanadium[V] in solutions 1 M in hydrofluoric acid and up to 1 M in hydrochloric acid are considered to be reliable.   However, the concentration of

acid at which reduction begins is not known exactly, and no other values of D are therefore reported for vanadium^V.

The curves in Fig. 2 for iron^{III} and cobalt^{II} are also similar in shape to those obtained by Kraus and his co-workers,[15],[16] although they determined the distribution coefficients for cobalt^{II} with only hydrochloric acid (up to 10 M). However, the curves obtained in presence and absence of 1 M hydrofluoric acid will be similar in shape, as cobalt^{II} does not form anionic complexes with fluoride.[34] Likewise, manganese^{II} [34] and copper^{II} [35] show no tendency to form anionic fluoride complexes; graphs for these elements (Fig. 3) were plotted from the results obtained with hydrochloric acid alone instead of mixed with hydrofluoric acid, as results could more speedily be obtained with the former solution. The presence of 1 M hydrofluoric acid will have little or no effect on these curves.
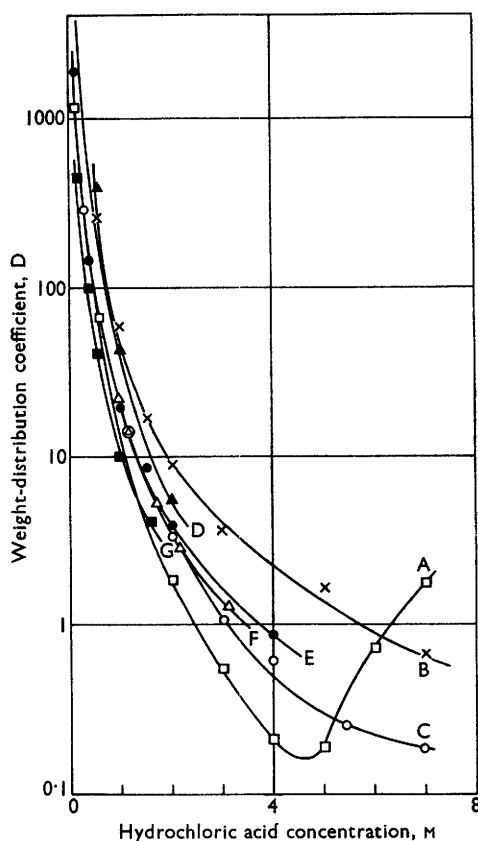

Fig. 5. Weight-distribution curves between Zeo-Karb 225 resin and hydrochloric acid: curve A, iron^{III}; curve B, chromium^{III}; curve C, manganese^{II}; curve D, aluminium; curve E, copper^{II}; curve F, nickel; curve G, vanadium^{IV}

Aluminium, vanadium^{IV}, chromium^{III} and nickel are adsorbed either not at all or only slightly on Dowex 1 from hydrochloric acid of any concentration.[15] If they were to be adsorbed on De-Acidite FF from hydrochloric acid, adsorption would occur only at high concentrations of acid; however, the results in Table I show that there was little or no adsorption of these elements from solutions 8 M in this acid. If aluminium, vanadium^{IV} and chromium^{III} were to be appreciably adsorbed from hydrochloric - hydrofluoric acid solution, such adsorption could occur only at low concentrations of hydrochloric acid, when any anionic fluoride complexes formed could compete favourably with a low concentration of chloride ions for sites on the resin. However, it is evident from Table I that neither aluminium nor chromium^{III} is adsorbed on De-Acidite FF from 1 M hydrofluoric acid and that vanadium^{IV} is adsorbed only slightly.

The distribution coefficients of cerium^{IV} between De-Acidite FF and hydrochloric - hydrofluoric acid solution could not be determined, as, in presence of the resin, cerium^{IV} was rapidly reduced to cerium^{III}.

With solutions containing only hydrofluoric acid (1 M), it could not be assumed that the solution, after being shaken with the resin, contained no chloride ions. However, strongly basic anion-exchange resins have much greater affinity for chloride than for fluoride,[36] and, as the concentration of fluoride as F$^-$ and HF$_2^-$ in 1 M hydrofluoric acid is approximately 0·06 gram-ion per litre, it seemed likely that the concentration of chloride ions would not exceed 0·1 M and would probably be very much less. In an experiment in which 1 g of dry resin was shaken with 5 ml of 1 M hydrofluoric acid, the concentration of chloride ions in the solution after the shaking was 0·015 M.

ZEO-KARB 225 RESIN—

The curves in Fig. 4 for vanadium^{IV}, chromium^{III} and iron^{III} and the values of D for aluminium in Table II indicate that all of these elements are appreciably complexed with fluoride at low concentrations of hydrochloric acid. Aluminium, chromium^{III} and iron^{III} are scarcely adsorbed on Zeo-Karb 225 in presence of 1 M hydrofluoric acid and at concentrations of hydrochloric acid less than 5 M, and vanadium^{IV} is only adsorbed to a moderate extent. On the other hand, manganese^{II}, cobalt^{II}, nickel and copper^{II} are strongly adsorbed at concentrations of hydrochloric acid less than 0·5 M in presence of 1 M hydrofluoric acid. In fact, a curve for solutions 1 M in hydrofluoric acid and up to 8 M in hydrochloric acid was obtained only for cobalt^{II}, but manganese^{II}[34] and nickel[37] have little tendency to form complexes with fluoride, and the curves obtained for these elements with hydrochloric acid media containing no hydrofluoric acid will not be appreciably changed by the presence of the latter acid. It is evident from Table II that the values of D for manganese^{II} and nickel are scarcely affected by the presence of fluoride ions. Copper^{II} forms the weakly cationic complex CuF$^+$ with fluoride,[35] but this has obviously little effect on the adsorption of copper^{II} on Zeo-Karb 225 from 1 M hydrofluoric acid (see Table II).

Two values of D are shown in Table II for vanadium^V. Distribution coefficients at higher concentrations of acid were not determined, as it was doubtful if they would be reliable. In 3 M hydrochloric acid, about 40 per cent. of the vanadium^V is reduced to vanadium^{IV} after being shaken overnight with Zeo-Karb 225.

The curve for iron^{III} in Fig. 4 has an unusual shape, but the increase in the value of D at concentrations of hydrochloric acid greater than 5 M also occurred in absence of hydrofluoric acid (see Fig. 5); similar results for iron^{III} in hydrochloric acid were found by Kraus, Michelson and Nelson[38] with the cation-exchange resin Dowex 50.

As expected, the values of D for aluminium, vanadium^{IV}, chromium^{III}, manganese^{II}, nickel and copper^{II} in up to 5 M hydrochloric acid decreased rapidly as the concentration of acid increased; these results are in reasonable agreement with those found by Strelow[18] and by Mann and Swanson,[19] who used Dowex 50 resin.

PROPOSED SEPARATION SCHEME

It is evident from the above results that the best medium in which to separate the constituents of a complex alloy is a solution 1 M in hydrofluoric acid and less than 0·1 M in hydrochloric acid. If such a solution, containing vanadium in the quadrivalent state, were passed through a column of De-Acidite FF in the chloride form and the column were washed with a small volume of 1 M hydrofluoric acid - 0·1 M hydrochloric acid mixture, then titanium^{IV}, zirconium, niobium^V, tantalum, molybdenum^{VI} and tungsten^{VI} would be strongly adsorbed on the resin, whereas aluminium, vanadium^{IV}, chromium^{III}, manganese^{II}, iron^{III}, cobalt^{II}, nickel and copper^{II} would pass through.

If the effluent were then passed through a column of Zeo-Karb 225 in the hydrogen form and the column were washed with two volumes of 1 M hydrofluoric acid, vanadium^{IV}, manganese^{II}, cobalt^{II}, nickel and copper^{II} would be retained by the resin, and aluminium, chromium^{III} and iron^{III} would appear in the effluent. Vanadium^{IV} could then be rapidly removed by washing the Zeo-Karb resin with 1 M hydrofluoric - 0·5 M hydrochloric acid mixture.

Treatment of the De-Acidite FF resin with 1 M hydrofluoric acid - 6 M hydrochloric acid mixture would rapidly remove titanium^{IV} and zirconium from the column. Separation

of the four remaining elements into niobium^{V} *plus* tungsten^{VI}, and molybdenum^{VI}, leaving tantalum on the column, should be possible by eluting with 6 M hydrochloric acid - 1 M hydrofluoric acid mixture and then with 2 M hydrochloric acid - 1 M hydrofluoric acid mixture, but it seems likely that these elements would be more readily separated by eluting with solutions of hydrofluoric acid mixed with either ammonium chloride or ammonium fluoride *plus* ammonium chloride.   Work on the determination of distribution coefficients for these four elements in such media and on the separation of prepared mixtures and alloy solutions by means of the proposed scheme is in progress.

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