

Adsorption of a Number of Elements from HNO_3 -HF and H_2SO_4 -HF Solutions by Cation and Anion Exchange

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Cation and anion exchange data are given for 27 metal ions in mixed acid solutions containing hydrofluoric acid (0.1 and 1.0 N) and either nitric acid or sulphuric acid (0.1 and 1.0 N). Comparisons are made with results obtained earlier for the pure acids involved and for systems containing hydrochloric acid. Some of the possible separations of metals of interest in the analysis of metallurgical products are pointed out. Cation exchange of Fe(III) and Cr(III) was studied in some detail. Difficulties in elution of Cr(III) were observed and these are discussed.

The use of hydrofluoric acid in combination with strong inorganic acids for ion exchange separations of metals offers several advantages. Hydrofluoric acid forms complexes with many metals which could be used for separation purposes and in some cases hydrolytic precipitation is prevented. Solutions of pure hydrofluoric acid seem to be less suitable than some mixed acid systems because of solubility difficulties. The components are normally used for dissolving metallic samples, they are readily volatilized if necessary and they are available or may easily be obtained in a high grade of purity.

Until recently nearly all systematic investigations have been confined to adsorption by *anion exchange* from mixtures of HCl and 0.5 or 1 N HF.^{1,2} Some data have also been reported in connection with studies of certain separation problems by several workers, *e.g.* Dixon and Headridge,³ Boni,⁴ Wilkins,⁵ Hague *et al.*,^{6,7} Freund and Miner,⁸ and Wish.⁹ When this work had been in progress for more than a year Huff¹⁰ reported anion exchange data for 19 elements in mixtures of HNO_3 (1–12 N) and HF (0.2–5 N).

Although *cation exchange* from mixed acid systems containing HF could be versatile at least for separation of metals into groups, very few data are available. Only Headridge and Dixon² extended their investigation to include cation exchange of some elements.

This paper presents adsorption data in some HNO_3 -HF and H_2SO_4 -HF solutions by cation and anion exchange for 27 metal ions of interest in the

analysis of metallurgical products. The aim has been to give a general survey of the separation possibilities rather than to examine all elements in detail. Two concentrations of HF (0.1 and 1.0 N) have been used in combination with the same two concentrations of either HNO_3 or H_2SO_4 . The acidity has been kept low for two reasons: separation by cation exchange is more effective in this range and adsorption of anionic fluoride complexes from HF solutions seems to increase with decreasing concentration of HF.¹¹

EXPERIMENTAL

Experimental details and methods used for determination and calculation of weight distribution coefficients, D , have been described in an earlier paper.¹²

Resins. In the batch experiments the cation exchange resin Dowex 50WX8, 100–200 mesh, was used in the hydrogen form and the anion exchange resin Dowex 1X8, 100–200 mesh, in the nitrate and sulphate forms. Before use the resins were treated in the normal manner and dried at 52 % rel. humidity as earlier. The following water contents were found: Dowex 50W, 26.0 % (range ± 0.5 %), Dowex 1 nitrate form, 10.0 % (range ± 0.3 %) and sulphate form, 21.3 % (range ± 0.3 %). The capacities for the dry resins, free of water, were: Dowex 50W (hydrogen form), 4.95 mequiv./g and Dowex 1 (chloride form), 3.40 mequiv./g determined in the usual way.

In the elution experiments particles of size between 200 and 400 mesh were used with the following capacities: 5.00 mequiv./g dry resin (Dowex 50WX8 in the hydrogen form) and 3.20 mequiv./g dry resin (Dowex 1X8 in the chloride form).

Reagents and solutions. Reagent grade chemicals were used. Standard solutions of metals were prepared from metals, oxides, and in some cases from nitrates, sulphates, fluorides, and alkali salts of the corresponding acids.¹²

Procedure. In the batch method plastic ware (polyethylene and polystyrene) was used and the solutions were filtered through filter paper (Munktell 00H) or plastic wool (Dynel Wool, Union Carbide Corp.). Solutions containing hydrofluoric acid were measured using polypropylene pipettes. All such operations were controlled by weighing. Solutions containing 5×10^{-3} M of the metals were used except for Bi(III) and Pb(II) in mixed acids containing 0.1 N HNO_3 , where 10^{-3} M solutions were used.

In the elution experiments acrylic plastic columns (internal diameter 0.95 cm) were used, containing 3–4 g (dry weight) of resin equilibrated with the appropriate acid mixture. The flow rate varied between 0.2 and 0.4 cm/min. In some experiments a RadiRac automatic fraction collector equipped with drop counter was used.

In the cation elution experiments the interstitial volume was determined as described by Rieman and Breyer.¹³ The interstices of the column were filled with 0.01 N HNO_3 , the column was washed free of acid and the total amount of acid was determined. In the anion elution experiments the interstitial volume was calculated from elution curves of the element that showed the most rapid elution (Ni or Mg).

Analytical methods. Well established colorimetric and titrimetric methods were used as earlier.¹² Hydrofluoric acid was removed prior to the determinations by fuming the solutions with added sulphuric acid in platinum or Teflon beakers. Nitric acid was added beforehand if necessary to destroy organic material.

With a few exceptions (Mg and Al) all solutions were also analysed by X-ray spectrography without preceding treatment. Aliquotes of 2 ml were taken from the original volume of 20 ml. A Philips' automatic instrument PW 1210 with scintillation and flow counters was used. For the determination of tungsten a chromium target was employed, otherwise a tungsten target. In the elution studies this method was widely used.

The determination of Mg and Al and, in the case of large values of D , also of Mn, Ni, and Pb was made by optical emission spectrography. A method developed by Carlsson¹⁴ based upon evaporation of small amounts of solution to dryness on carbon electrodes was applied.

All spectrographic analyses were carried out at the spectrographic laboratory of the Swedish Institute for Metal Research under the supervision of Mr. G. Carlsson. Mr. R. Blom and Mrs. Ingrid Eklöf performed the determinations.

The analytical methods applied in this investigation were controlled by analysis of known quantities of metals, in many cases after dilution with the acid mixture in question to approximately the same level as in the equilibrated solutions. The amount of metal in the initial solutions was determined using the same analytical method. In the batch method differences between duplicate determinations less than 3 % of the amount present were obtained except when D was very large. In these cases, especially when optical emission spectrography was used, lower precision was obtained, but the differences exceeded 10 % only in a few cases.

RESULTS AND DISCUSSION

General remarks

Ringbom¹⁵ has shown that useful distribution coefficients can be calculated from cation exchange constants determined for some metals by Bonner *et al.*^{16,17} However, recent experimental data by Strelow¹⁸ and Nelson *et al.*¹⁹ have revealed differences in adsorbability for metals in various acids that could not easily be predicted or calculated. Theoretical treatment of anion exchange in the same way is at present more difficult. There is a lack of exchange constants and complete stability constants for metal complexes.

Contrary to the batch procedure the elution method could be used easily for the desired acid concentrations after proper equilibration. In the batch method certain concentration changes necessarily occurred. Results obtained for Dowex 1 in the nitrate and sulphate forms using the ordinary batch procedure for acid mixtures free of metal are shown in Table 1. For control purposes one quantity that could be calculated was determined in most cases.

The resin loaded with nitrate remained essentially in its nitrate form while the sulphate resin was converted into its hydrogen sulphate form accompanied by a decrease in the acid concentration as reported earlier.¹² The concentration changes of fluoride found were generally moderate but were remarkably large in the presence of 1 N HF, especially in H_2SO_4 -HF mixtures compared with available data.²⁰ A detailed interpretation of the adsorption

Table 1. Normalities of acids before and after equilibration of 20 ml of mixed acid solution with 1 g of Dowex 1X8 in the batch procedure. c = calculated value.

Before equil.			After equil.		
N HF	N HNO ₃	N(HF + HNO ₃)	N HF	N HNO ₃	N(HF + HNO ₃)
0.100	0.102	0.202	0.096	0.101	0.197
0.100	1.025c	1.125	0.095	1.015c	1.110
0.998	0.104	1.106	0.960	0.110	1.061
1.017	1.023c	2.040	0.966	1.007c	1.973
N HF	N H ₂ SO ₄	N(HF + H ₂ SO ₄)	N HF	N H ₂ SO ₄	N(HF + H ₂ SO ₄)
0.100	0.100	0.200	0.081	0.060	0.143
0.100	1.000	1.104	0.093	0.893	0.989
1.00	0.100	1.102	0.89	0.090	0.973
1.00	1.000	1.996	0.91	0.914	1.840

of fluoride in H_2SO_4 -HF solutions based on Table 1 is not possible. Further studies are needed to evaluate the amount of the different anions present, SO_4^{2-} , HSO_4^- , F^- , and HF_2^- , and the degree of penetration into the resin of the different acids.

In these experiments fluoride was determined colorimetrically²¹ in solutions containing H_2SO_4 , otherwise volumetrically, essentially according to Ellestad as given by Kolthoff and Sandell,²² nitrate by titration after reduction with Devarda's alloy and sulphate gravimetrically as barium sulphate after volatilization of HF with perchloric acid.

In similar experiments with the Dowex 50W resin the initial concentrations changed slightly, usually less than 1 %, showing only weak penetration of acid into the resin. However, when the adsorption of metal takes place an equivalent amount of hydrogen ions is transferred into the external solution thus increasing the acidity. In this study this increase was limited to 0.01 N for divalent metal ions. Strelow^{23,18} partly compensated for this effect of a high degree of loading by using a large external volume, but calculations indicate that acid concentrations of 0.10 N in many cases increased to 0.12 N for divalent metal ions. To take advantage of a low degree of loading in this and other respects it seems necessary to use inconveniently large volumes of solution if extremely sensitive methods of analysis are not available.

Presentation of the results

The ion exchange data in this paper are presented schematically. Differences in adsorbability sufficiently large to permit separation by simple ion exchange procedures are by this means easily surveyed. For column chromatography more detailed investigations of the systems involved are generally necessary, since changes in degree of loading, ionic strength and factors concerning the column operation will have a marked effect.

Distribution coefficients were determined for 27 elements including different valency states in mixtures of HF (0.1 and 1.0 N) and either HNO_3 or H_2SO_4 (0.1 and 1.0 N). Elements known to form compounds which are almost insoluble in the acids used were omitted as well as metal ions very sensitive to reduction or oxidation. Bismuth(III) and Pb(II) were studied only in HNO_3 -HF, Fe(II) and V(IV) only in H_2SO_4 -HF.

The weight distribution coefficients, D , are given in Figs. 1, 2, 5, and 6. Figs. 1 and 2 refer to the cation exchange resin Dowex 50WX8 and Figs. 5 and 6 to the anion exchange resin Dowex 1X8. Figs. 1 and 5 cover acid mixtures with 0.1 N HNO_3 and 0.1 N H_2SO_4 and the other figures mixtures with 1.0 N HNO_3 and 1.0 N H_2SO_4 . The elements are arranged in alphabetical order. All results obtained with the elution method are distinctly denoted (○). Exact values of D below 1 are given only for the elution method, $D \leq 1$ from the batch results is indicated. In many cases these values are certainly close to zero, but the batch method did not permit an accurate determination. The sign ● indicates $D < 1$ or $D \leq 0.1$ according to its position in the scheme. For practical reasons the initial acid concentrations are recorded in the presentation of the results.

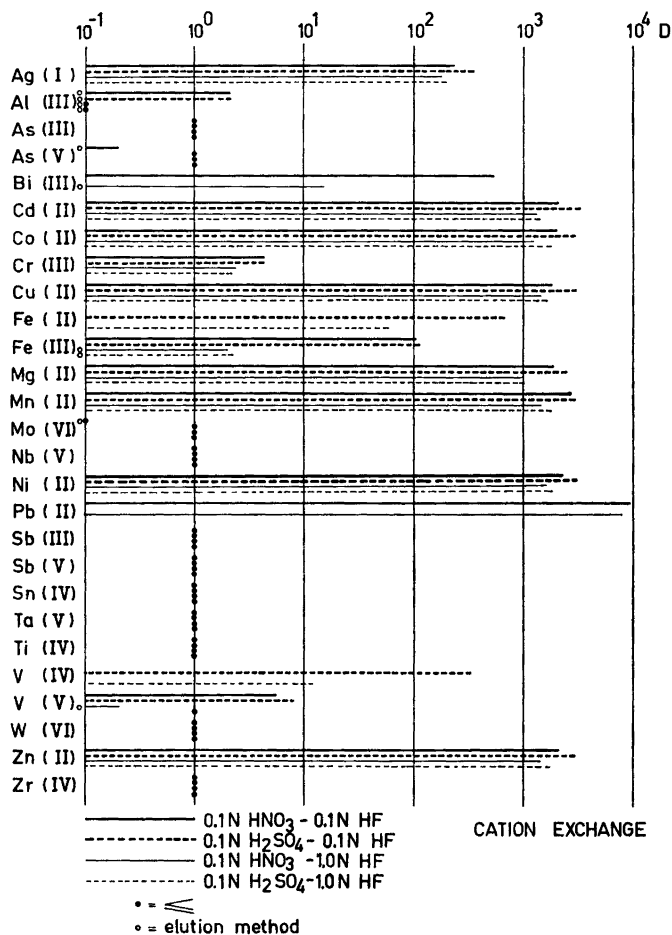


Fig. 1. Distribution coefficients in 0.1 N HNO₃-HF (0.1 and 1 N) and 0.1 N H₂SO₄-HF (0.1 and 1 N). Resin: Dowex 50WX8. Cf. text.

Cation exchange (Figs. 1 and 2)

When classified by their adsorption characteristics most of the elements can be placed in either of two groups. **A**, Strongly adsorbed from all solutions investigated, involving no or only slight influence of HF; **B**, Weak or no adsorption at all concentrations. Some elements which do not fit well into either of these groups are treated under **C**. Comparisons are made with the comprehensive lists of distribution coefficients of cations in HCl, HNO₃, and H₂SO₄ solutions given by Strelow.^{23,18}

A. Strong adsorption. This group contains Ag, Cd, Co, Cu, Mg, Mn, Ni, Pb, and Zn. Some of these elements form positively charged complex ions with

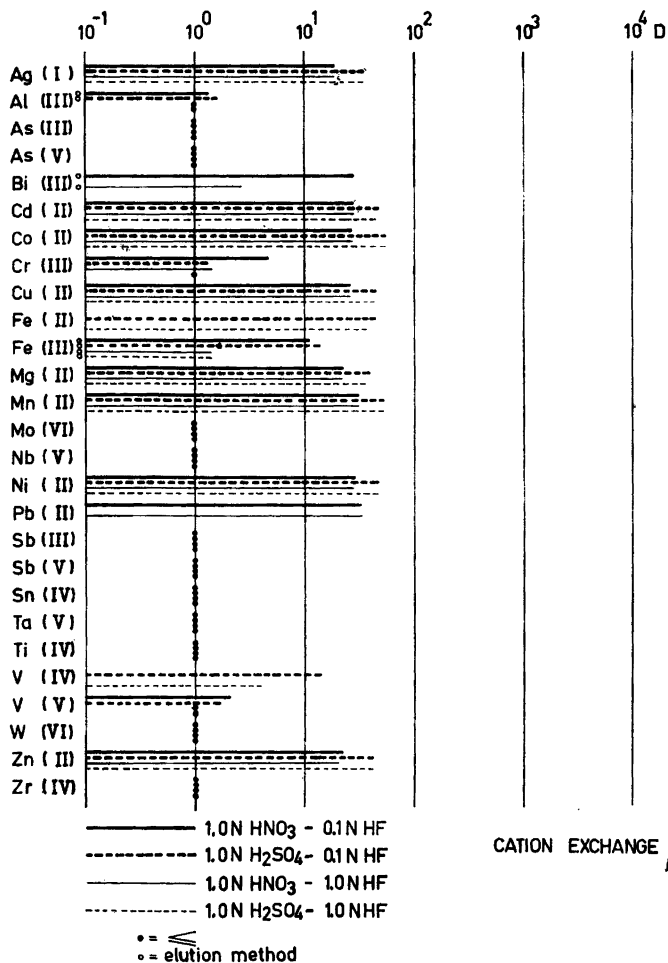


Fig. 2. Distribution coefficients in 1 N HNO₃-HF (0.1 and 1 N) and 1 N H₂SO₄-HF (0.1 and 1 N). Resin: Dowex 50WX8. Cf. text.

fluoride,²⁴ but no obvious effect on adsorption was found in the solutions investigated.

The adsorption decreased with the acidity essentially following the relationship $D_{Me} = \text{const}_{Me} \times c_{H^+}^{-n}$, where n is the charge of the particular metal ion (Me). Thus for divalent ions in 1 N HNO₃-1 N HF the distribution coefficients amounted to approximately 1 % of the values in 0.1 N HNO₃-0.1 N HF (20–30 and 2000–2500, resp.). In most cases the relatively weak acid HF affected the acidity only slightly. The results are in good agreement with those given by Strelow for HNO₃ and H₂SO₄ solutions. The higher values reported here in 0.1 N HNO₃ and H₂SO₄ solutions may be explained by the lower degree of loading used.

The nature of the anions present does not seem to have any effect on the distribution coefficient. The stronger adsorption in solutions containing H_2SO_4 is due to the lower acidity compared with HNO_3 solutions. In HCl-HF solutions somewhat lower values for Cd and Zn may be expected, since these elements are adsorbed less strongly in pure HCl solutions.

The reported results indicate that it should be possible to separate by a simple cation exchange procedure elements in this group from those in group B and under certain circumstances, also from elements listed under C.

Fritz *et al.*²⁵ reported that Cd(II) was eluted with 0.1 M HF from a column of Dowex 50WX8 loaded with hydrogen ions and that rapid elution was obtained with 1.0 M HF also for Mn(II) and Zn(II). No values of D were given. Since these results did not appear to agree with those given in this paper, even though different conditions were used, some further experiments were carried out.

In the first experiment 0.45 mmole of Mn and Ni, as nitrates, in 25 ml of water were adsorbed on the top of a resin bed of Dowex 50WX8 (H^+ -form, 100–200 mesh), height 11 cm and diameter 10 mm, in a column of acrylic plastics. Elution with 100 ml of 1 N HF was applied, using a flow rate of 1–2 ml/min. In the effluent Mn could not be detected colorimetrically or by X-ray spectrography. Both Mn and Ni were stripped quantitatively with 2 N HNO_3 .

In the second experiment 25 ml of a solution containing 0.45 mmole each of Cd, Zn, and Cu nitrates were added to the same column. Elution with 200 ml of 0.1 N HF, 120 ml of 1 N HF and 120 ml of 2 N HNO_3 was applied. The different eluates were collected and analysed by X-ray spectrography. The first two fractions (0.1 and 1 N HF) contained no Cd, Zn, or Cu. The elements were stripped with 2 N HNO_3 . Both these experiments were made in duplicate.

Fritz reported quantitative separation of these elements using approximately the same amount of Dowex 50WX8, 100–200 mesh (bed height 8 cm, diameter 12 mm).

B. Weak or no adsorption. Aluminium(III), As(III), As(V), Mo(VI), Nb(V), Sb(III), Sb(V), Sn(IV), Ta(V), Ti(IV), W(VI), and Zr(IV) were not appreciably adsorbed from any of the solutions studied.

Even in the absence of HF As(III) and As(V) are not adsorbed, while slight adsorption of Nb(V) and Mo(VI) has been reported by Strelow. Many of the elements in this group including Nb, Sb, Sn, Ta, and W are not easily studied in solutions of HCl , HNO_3 or H_2SO_4 alone, because of their tendency to polymerize and precipitate and a suitable complexing agent is almost indispensable. For this reason comparable data for these elements in strong inorganic acids are not available.

Aluminium(III), Zr(IV), and Ti(IV) are very strongly adsorbed in 0.1 N HNO_3 , whilst D_{Ti} and D_{Zr} are lower in 0.1 N H_2SO_4 due to complexation but still 400–600. These elements are known to form strong complexes with fluoride, and addition of 0.1 N HF is sufficient to prevent adsorption of Ti and Zr completely and to reduce the adsorption of Al enough to permit rapid elution.

C. Bi(III), Cr(III), Fe(II), Fe(III), V(IV), and V(V). For these elements 0.1 N HF is not sufficient to eliminate adsorption and some of the elements are also adsorbed in the presence of 1 N HF but a considerable decrease

takes place. In Table 2 a comparison is made between solutions with and without HF.

Table 2. Distribution coefficients (D) in 0.1 N HNO_3 and 0.1 N H_2SO_4 with and without HF. Resin: Dowex 50WX8. D in the absence of HF from Strelow.¹⁸

Element	D					
	0.1 N HNO_3	0.1 N HNO_3 - 0.1 N HF	0.1 N HNO_3 - 1.0 N HF	0.1 N H_2SO_4	0.1 N H_2SO_4 - 0.1 N HF	0.1 N H_2SO_4 - 1.0 N HF
Bi(III)	893	500	15			
Fe(II)				1600	680	58
Fe(III)	$> 10^4$	102	2	$> 10^4$	110	2
V(IV)				1230	320	12
V(V)	20	5	0.2	27	8	< 1

In 1 N HNO_3 there was no obvious effect of 0.1 N HF on the adsorption of Bi(III), but in 1 N HNO_3 - 1 N HF $D = 2.6$ was found compared with $D = 25$ in 1 N HNO_3 . The adsorption of Fe(II) in 1 N H_2SO_4 was very little influenced even in the presence of 1 N HF (Fig. 2). The small decrease in adsorption found was possibly due to slight oxidation of Fe(II) to Fe(III), but this oxidation effect was not studied.

The adsorption of vanadium (V) from acid solutions is generally attributed to a partial reduction to V(IV) in contact with the resin.²⁶ In solutions containing 0.1 N HF the adsorption seems to decrease slightly and in the presence

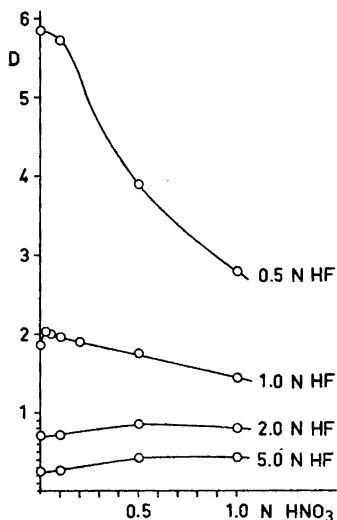


Fig. 3. Adsorption of Fe(III) by Dowex 50WX8 at different concentrations of HNO_3 and HF. Elution method.

of 1 N HF rapid elution is achieved. Vanadium(IV) is known to form complexes with fluoride and a marked effect of HF is seen in Table 2, but D does not decrease below 1 even at the highest acid concentrations studied (Fig. 2).

Iron(III) was studied in more detail due to plans to use these acid mixtures in the analysis of iron and steel. Fig. 3 shows results from elution experiments with varying concentrations of HNO_3 and HF. It is obvious that, at the lowest concentrations of HNO_3 which must be used to adsorb elements in group A strongly, a rather high concentration of HF is needed to elute Fe(III) rapidly. Some experiments with mixtures of H_2SO_4 (0.1–1 N) and HF (1–2 N) indicated only minor differences between these systems in this range. Headridge and Dixon² obtained similar results for HCl-1 M HF using Zeo-Karb 225.

Chromium(III) has earlier been reported to be held firmly by Dowex 50WX8 in 1 N HF²⁵ but also to be only slightly adsorbed by Zeo-Karb 225 in 1 N HF ($D = 1$), the values of D decreasing further on addition of HCl.² The results in Table 3 for HNO_3 -HF and H_2SO_4 -HF solutions might give an

Table 3. Apparent values of D for Cr(III). Resin: Dowex 50WX8. I = solution prepared without heating, II preheated solution. (Cf. text).

0.1 N HNO_3 –0.1 N HF		0.1 N HNO_3 –1 N HF	
I	II	I	II
2.2×10^3	4.2	6.0×10^2	2.4
1 N HNO_3 –0.1 N HF		1 N HNO_3 –1 N HF	
I	II	I	II
87	4.7	63	1.4
0.1 N H_2SO_4 –0.1 N HF		0.1 N H_2SO_4 –1 N HF	
I	II	I	II
45	4.1	21	2.2
1 N H_2SO_4 –0.1 N HF		1 N H_2SO_4 –1 N HF	
I	II	I	II
21	1.3	15	<1

explanation. The solutions under I were prepared from chromium nitrate and sulphate without heating, while the solutions under II were prepared from chromium metal, dissolved by heating in conc. HF, the solution taken to dryness, the residue then dissolved by warming in the proper acid mixture.

In the presence of HF the values of D decrease even if the solutions have not been heated but it can easily be understood that elution of chromium will be difficult at low acidities. Headridge and Dixon² on the other hand used conditions similar to those under II, Table 3.

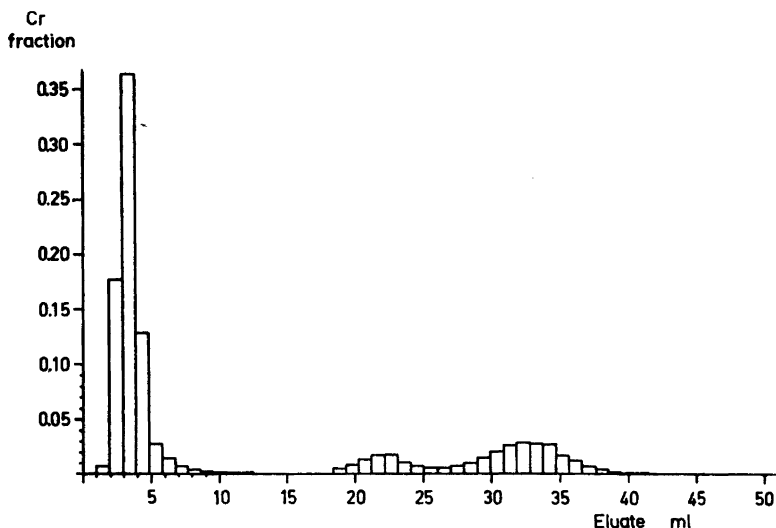


Fig. 4. Elution of Cr(III) from Dowex 50WX8 cation exchange column with 0.1 N HNO_3 -1 N HF, showing presence of inert complexes.

The reason for this behaviour of Cr(III) is that equilibration between the different ions present is not rapidly established. The preheated solutions contain a larger amount of non-adsorbable or weakly adsorbable complexes but these also seem to be inert and are eluted separately (Fig. 4). The distribution coefficients given in Figs. 1 and 2 and Table 3, II are thus mixed values of D for several complexes. Elution experiments gave two or more distinct peaks for all eight solutions studied, with the exception of 1 N H_2SO_4 - 1 N HF. In all these cases, however, the main fraction of Cr(III), generally 65–80 %, was eluted rapidly. More than one band was observed also in elution with 1 N HF and using Zeo-Karb 225 in elution of Cr with 0.1 N HNO_3 -1 N HF.

Fig. 4 shows the fractions of the total amount of Cr that were found in different fractions of the eluate, when using 0.1 N HNO_3 -1 N HF. The Cr(III) solution was prepared by heating chromium metal in concentrated HF as described above. *Ca.* 72 % belonged to the first elution band with D close to zero, *ca.* 7 % to a second band with $D = 6.3$, *ca.* 21 % to a third band with $D = 9.8$ and a very small amount, probably much less than 1 %, was eluted with 4 N HNO_3 when 50 ml of 0.1 N HNO_3 -1 N HF had passed the column. No efforts were made to identify the different species but this method might be useful for the separation of some chromium complexes.

Application of these acid systems to metal analysis is rendered difficult by the behaviour of chromium. Further studies will show if elution at higher temperatures or the use of higher concentrations of fluoride will lead to complete and rapid elution of Cr(III).

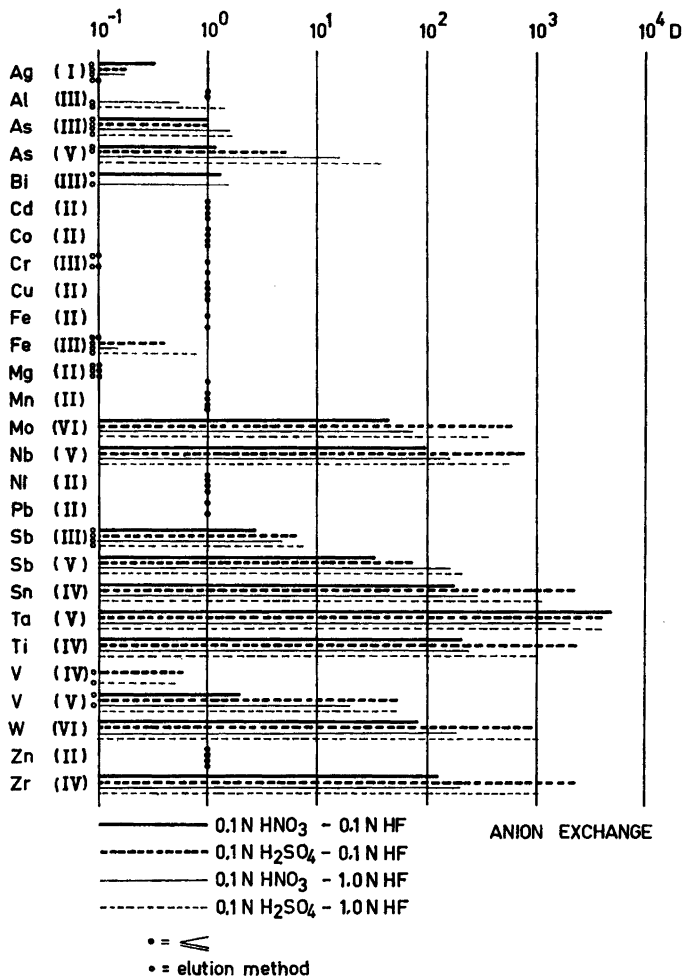


Fig. 5. Distribution coefficients in 0.1 N HNO₃-HF (0.1 and 1 N) and 0.1 N H₂SO₄-HF (0.1 and 1 N). Resin: Dowex 1X8. Cf. text.

Anion exchange (Figs. 5 and 6)

The elements are divided into 4 groups A—D, the adsorbed elements somewhat arbitrarily divided, B containing elements moderately adsorbed, C elements adsorbed very strongly in H₂SO₄-HF solutions, and D strongly adsorbed elements, that are not easily studied in solutions not containing HF. When not otherwise stated the results compared with refer to: HCl: Kraus and Nelson,²⁷ HNO₃: Faris and Buchanan,²⁸ H₂SO₄: Danielsson,¹² HF: Faris,¹¹ and HCl-HF: Nelson, Rush and Kraus.¹ All these authors used Dowex 1X10 except Danielsson who used Dowex 1X8. A higher degree of cross-linking generally involves larger distribution coefficients.^{29,30}

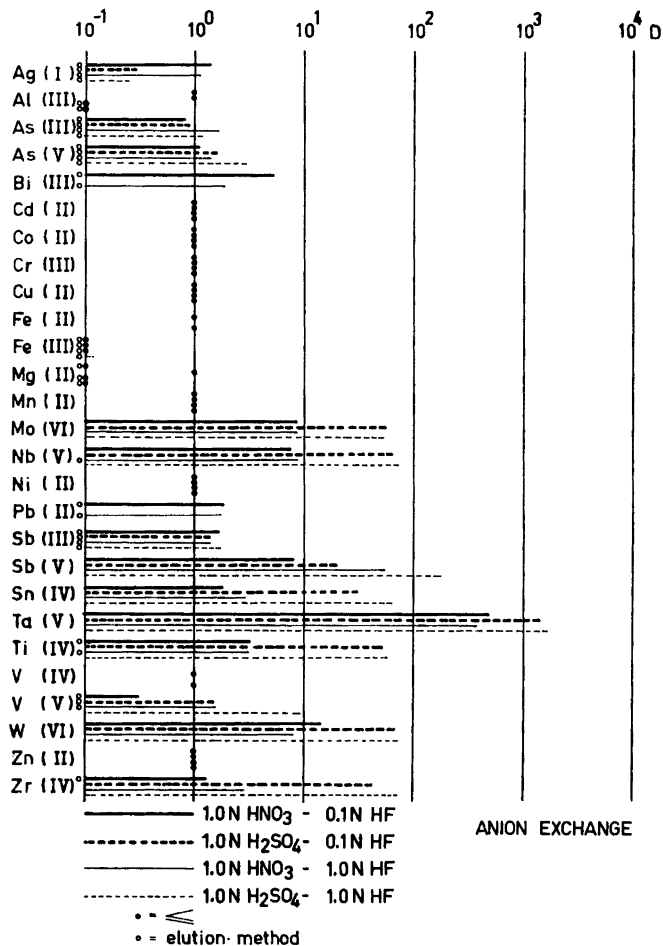


Fig. 6. Distribution coefficients in 1 N HNO₃-HF (0.1 and 1 N) and 1 N H₂SO₄-HF (0.1 and 1 N). Resin: Dowex 1X8. Cf. text.

A. Weak or no adsorption. This group consists of Ag(I), Al(III), As(III), Bi(III), Cd(II), Co(II), Cr(III), Cu(II), Fe(II), Fe(III), Mg(II), Mn(II), Ni(II), Pb(II), V(IV), and Zn(II). It includes the elements that are held strongly by the cation exchange resin Dowex 50W and in addition nearly all elements that are placed in the cation exchange group C, the only exception being V(V). Aluminium(III) and arsenic(III) were weakly adsorbed by cation as well as by anion exchange in all solutions studied.

Iron(III) that showed adsorption from H₂SO₄ solutions in a previous investigation was very weakly adsorbed in H₂SO₄-HF solutions. A special study in 0.1 N HNO₃ with varying amounts of HF showed increasing adsorption of Fe(III) with increasing concentration of HF, but even in 0.1 N HNO₃-5 N HF *D* did not exceed 0.6.

An increase of the concentration of HNO_3 gave slightly higher values of D for Bi and Pb, as would be expected from adsorption data in HNO_3 solutions,³¹ but also to a minor extent for Ag.

Some of the elements in this group are adsorbed in dilute HF namely Al, Fe(II), Fe(III), Cr, and possibly also V(IV) and Mg. A slight adsorption of Al in 0.1 N H_2SO_4 -1 N HF indicates presence of negatively charged fluoride complexes.

In HCl-1 N HF solutions several of these elements are adsorbed, some of them strongly, due to formation of chloride complexes. The presence of HF lowers the values of D in some cases, but Bi, Zn and Pb are adsorbed and probably also Cd and Ag that have not been studied in HCl-HF. At higher concentrations of HCl containing 1 N HF Fe(III) is adsorbed strongly. A similar effect of increasing the HNO_3 or H_2SO_4 concentration is most unlikely.

B. As(V), Sb(III), Sb(V), and V(V). These elements were adsorbed to a limited extent but were held more strongly than the elements under A, the values of D rising to ca. 200 for Sb(V) in solutions containing 1 N HF.

Arsenic(V) was not expected to be adsorbed since only weak adsorption was reported from HCl (0.1-1 M)-1 M HF. The solutions were prepared from the corresponding sodium salt without heating. More than one elution band was observed in 0.1 N HNO_3 -1 N HF, the first peak corresponding to $D = 7.4$. In HF solutions As(V) is adsorbed strongly, whilst weak adsorption was found at low concentrations of H_2SO_4 .

Antimony(III) showed low values of D (< 10) in all solutions. No results have been reported at low concentrations of HNO_3 or H_2SO_4 . In dilute HF D rises to nearly 100. Formation of chloride complexes affects the adsorption of Sb(III) at higher concentrations of HCl even in solutions containing HF.

Antimony(V) was adsorbed rather strongly, the values of D being about twice as high in H_2SO_4 -HF as in HNO_3 -HF. An equilibration period of several days was applied in some cases, since slow equilibration has been reported,¹ but this had no obvious effect. In HCl-1 M HF $D = 3 \times 10^2$ was reported as the lowest value. ($D = 2 \times 10^3$ in 0.1 M HCl-1 M HF and $D = 6 \times 10^4$ in 9 M HCl-1 M HF).

Vanadium(V) gave D values of ca. 50 in 0.1 N H_2SO_4 containing HF. In 0.1 N HNO_3 -HF lower results were obtained. Rather low results, $D < 20$, have also been reported in dilute HF and HCl-HF solutions.

C. Mo(VI), Ti(IV), and Zr (IV). The distribution coefficients are extremely large for these elements in 0.1 N H_2SO_4 solutions containing HF. They are known to form negatively charged fluoride complexes and Mo and Zr are strongly adsorbed by Dowex 1 in dilute H_2SO_4 , whilst Ti is adsorbed to a lesser degree. In low concentrations of HNO_3 and HCl weak adsorption has been reported for these elements, whilst they seem to be held strongly in dilute HF.

Molybdenum(VI) is adsorbed more weakly in the presence of HF in H_2SO_4 solutions, while addition of HF otherwise increases the adsorption markedly especially in dilute HCl-solutions.²⁹ (Values of $D > 10^3$ were reported at very low HCl concentrations.)

Titanium(IV) is remarkably strongly held by Dowex 1 in 0.1 N H_2SO_4 -0.1 N HF ($D = 2400$) and in 0.1N H_2SO_4 -1 N HF ($D = 1000$), considering the

low values of D in H_2SO_4 solutions ($D < 10$) and the moderate values in HNO_3 -HF. Lower values were also found in HCl-HF. Titanium was weakly adsorbed in 1 N HNO_3 -HF solutions.

Zirconium(IV) showed adsorption characteristics similar to Ti(IV) in H_2SO_4 -HF and HNO_3 -HF solutions. The values for HCl-HF solutions seem to be comparable with the values in HNO_3 -HF. Zirconium was rapidly eluted with 1 N HNO_3 -HF solutions.

D. Nb(V), Sn(IV), Ta(V), and W(VI). At low acidities these elements are strongly adsorbed from HF solutions containing HNO_3 , H_2SO_4 or HCl and also from pure dilute HF. A marked decrease in adsorption takes place when the concentration of HNO_3 , H_2SO_4 or HCl increases again to 1 N, the values of D for Ta, however, remaining at a high level. At higher acidities the adsorption increases in HCl-0.5 or 1 M HF for Nb, Sn(IV) and to a minor extent for Ta, while D_w decreases regularly to a minimum near 8 M HCl-1 M HF ($D = ca. 7$). A similar increase is not likely to occur in H_2SO_4 -HF solutions and, according to Huff,¹⁰ does not take place in HNO_3 -HF.

Niobium(V) was found to give $D = 160$ in 0.1 N HNO_3 -1 N HF and $D = 90$ in 0.1 N HNO_3 -0.1 N HF. Similar values were obtained in 0.1 N HCl-0.5 N HF. In 0.1 N H_2SO_4 -HF Nb was held more strongly. A higher value was found in 0.1 N H_2SO_4 -0.1 N HF ($D = 765$) than in 0.1 N H_2SO_4 -1 N HF ($D = 580$). This might be due to the presence also of negatively charged sulphate complexes since strong adsorption by Dowex 2 from H_2SO_4 solutions has been reported.³²

Tin(IV) was also adsorbed more strongly from HF solutions containing 0.1 N H_2SO_4 than from comparable HNO_3 solutions, HCl taking an intermediate position. Tin(IV) is rapidly eluted with 1 N HNO_3 containing HF, while rather strong adsorption still remains in comparable H_2SO_4 and HCl solutions.

Tantalum(V) showed extremely high values of $D (> 10^3)$ in 0.1 N HNO_3 and 0.1 N H_2SO_4 solutions containing HF. The values reported in this case are, however, meant to give only the order of magnitude since certain problems occurred in the determination of the low amounts of Ta present. (X-Ray spectrography was used exclusively.) Similar results have been reported for HCl-HF. In 1 N HNO_3 -1 N HF Ta(V) is the only element strongly adsorbed. This has been used by Huff¹⁰ to separate Ta from a large amount of other elements.

Tungsten(VI) is adsorbed to about the same extent as Nb(V) in HNO_3 -HF and H_2SO_4 -HF. Slightly higher values than for Nb were obtained for mixtures with 0.1 N H_2SO_4 . In HCl-1 M HF remarkably high values (D increasing to 6×10^3) were found at the lowest concentrations of HCl.²⁹

Concluding remarks

The results given in this paper for cation exchange show such large differences in adsorption that in many cases separation of traces of metals from a large amount of an element not adsorbed should be possible. Differences due to the presence of HCl, HNO_3 , or H_2SO_4 seem to be of minor importance. A study of the separation of the elements in group A from large quantities

of Fe(III) will be given in a later paper. Some of these acid mixtures will be of special interest in the separation of traces from Fe(III), Al(III), and possibly also Cr(III), which are eluted from both cation and anion exchange resins in 0.1 N HNO₃-1 N HF and 0.1 N H₂SO₄-1 N HF and probably also in 0.1 N HCl-1 N HF, while most other elements are strongly adsorbed. However, solubility problems may arise and thus reduce the advantages of these systems.

In most cases the distribution coefficients of strongly adsorbed elements were lower by anion exchange than by cation exchange. However, trace amounts of many adsorbable elements should be easily separated also by anion exchange from large amounts of an element not adsorbed. Dixon and Headridge³ used this method to separate small amounts of W, Nb, Mo, and Ti from 4 g of iron. Evidently it will also be possible to separate other elements from iron in the same way. Weakly acidic solutions of HF seem to be most suited for this purpose. In certain cases more than one other acid component might be useful.

The differences in adsorbability of metals by anion exchange between the various acid systems containing HF that have been compared were less pronounced than expected. It was thought that the adsorption of fluoride complexes in resins loaded with sulphate or nitrate would be less strong than in chloride resins. Certain differences occurred but it seems to be necessary to use pure fluoride systems to obtain a significant increase in adsorption. The concentration of fluoride is limited in acid solutions, but it is doubtful if separations in more concentrated fluoride solutions would be of practical interest, apart from solubility problems. Solutions containing 1 M NH₄F and NH₄Cl are very effective to elute several fluoride complexes.³

Hydrochloric acid forms complexes with many metals that compete favourably with chloride ions for resin sites even in concentrated solutions. This fact constitutes the main difference between adsorption by anion exchange from HCl-HF solutions on one hand and from HNO₃-HF and H₂SO₄-HF solutions on the other. This difference is marked for some elements in the solutions investigated here but can be expected to be still more pronounced at higher acidities. In concentrated HCl many elements are adsorbed remarkably strongly including Fe(III), Mo(VI), Sb(V), Sn(IV), V(V), and Zr(IV), several other elements being adsorbed to a more limited extent. In most cases the effect of 1 N HF is insignificant. Only Ti(IV) and Zr(IV) are appreciably influenced.¹

At high concentrations of HF, HNO₃, and H₂SO₄ strong adsorption has not been reported for any element treated in this paper. In most cases the values of *D* decrease with increasing acidity. It seems reasonable to assume that a necessary condition for adsorption of an element from a mixed acid system is that adsorption occurs under similar conditions from one of the acid components. Some difficulties may arise in prediction of the behaviour of Nb, Sb, Sn, Ta, and W in HNO₃-HF and H₂SO₄-HF solutions of higher acidities, since the values of *D* are not known in detail for the acid components. Huff¹⁰ found regularly decreasing curves for adsorption of elements of interest here in HNO₃-HF solutions with increasing concentrations of HNO₃, apart from minor deviations for Bi and Nb. It is likely that this will also be true for H₂SO₄-HF solutions. All elements studied in this investigation are less

adsorbed from 1 N H₂SO₄-HF than from comparable 0.1 N H₂SO₄-HF solutions. However, in the case of Nb, Ta, and W further studies are necessary. To sum up, it cannot be expected that the HNO₃-HF and H₂SO₄-HF systems, at least at higher acid concentrations, are as well suited for mutual separations of adsorbed anionic species as are HCl-HF solutions.

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