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The effect of hydrofluoric acid on the cation exchange behavior of metal ions

Robert Bart Brown
Iowa State University

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THE EFFECT OF HYDROFLUORIC ACID ON THE
CATION EXCHANGE BEHAVIOR OF METAL IONS

by

Robert Bart Brown

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Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

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INTRODUCTION AND LITERATURE SURVEY

Historical Background

The phenomenon of ion exchange has been known for thousands of years (1, pp. 1-2), but it was not studied fully until the nineteenth century when agricultural chemists began to study the mechanism of fertilizer action. In 1819 the Italian chemist, Gazzari, observed that clay decolorizes liquid manure and retains soluble substances which can later be released to plants (2). In 1850 H. S. Thompson published his study of the ability of soils to sorb the ammonium ion from solutions and liberate calcium in its place (3). In the same year J. T. Way published a comprehensive study on the ability of various types of soil to retain fertilizers (4). Studies of inorganic systems continued, but inorganic ion-exchange material suffers from low capacity and instability in systems containing strong acid. These difficulties were overcome in 1935 when Adams and Holmes (5) published their monumental study on the preparation and use of synthetic organic ion-exchange resins. They prepared eleven resins and studied the behavior of thirty cations on them. The synthesis of organic resins has now developed so that resins can be synthesized with almost any desired property. This has put a

very powerful tool in the hands of analytical chemists.

As one is confronted with the task of analyzing complex materials, two methods of operation are available. A method may be chosen which allows analysis of the materials without separation, or a method may be chosen which requires separation prior to the actual determination. Unfortunately methods, such as x-ray fluorescence, which do not require prior separation quite often lack the accuracy needed. When this is the case, separation is necessary, and ion exchange is an extremely useful separation tool. In addition to the actual chromatographic separations, ion exchange is useful in concentrating trace components of systems to levels at which they are conveniently determined, in removing interfering ions prior to analysis, and in the dissolution of difficultly soluble ionic materials.

The usefulness of ion exchange in analytical chemistry may be shown by a number of examples where traditional methods were extremely laborious and time-consuming. One case is the separation of zirconium and hafnium. These elements can be separated on a cation-exchange column using sulfuric acid (6). The separation of the alkali metals is also conveniently carried out by ion exchange (7). Another

separation which has proved to be of great importance is the separation of the rare earths worked out by Spedding et al. (8-11). The separation of a mixture of zirconium, titanium, niobium, tantalum, tungsten, and molybdenum is also easily accomplished by ion exchange; by classical means this separation would be more difficult (12).

Useful as these separations are, they were developed for the specific system at hand. A more general approach is desirable in order to be able to design separation schemes for a wide variety of samples. Strelow (13), and Kraus and Nelson (14) have thoroughly investigated the hydrochloric acid system. Strelow determined the distribution coefficients for forty-three metals on cation-exchange resin at various concentrations of hydrochloric acid. Kraus and Nelson have studied almost all the elements on anion-exchange resin from solutions containing up to 12 M hydrochloric acid. Numerous separations can be devised using these data. Nelson et al. (15) have begun a systematic study of the cation-exchange behavior of metals in concentrated hydrochloric and perchloric acid solutions. This series of papers promises to be another step toward developing a general approach to ion-exchange separations.

Anion Exchange Using Hydrofluoric Acid

Hydrofluoric acid is an effective agent in the prevention of hydrolysis of metals in the fourth and fifth groups of the periodic chart. As a result its effect on the sorbabilities of metals is of interest in order to develop a general scheme of separations which is to include these elements. In their anion-exchange studies, Kraus and Nelson (14) investigated the distribution coefficients of twenty-three elements in mixtures of hydrochloric and hydrofluoric acid. The hydrofluoric acid concentration was kept constant at either 0.5 or 1 M and the hydrochloric acid concentration was varied up to 12 M. The hydrochloric acid represses the ionization of the hydrofluoric acid so that in many cases the extremely high complexation of the metals which might have been expected is avoided, and several interesting separations are given. For example they were able to separate a mixture of nickel, manganese, cobalt, copper, iron, and zinc. In a later paper involving similar techniques Nelson et al. (16) added aluminum, yttrium, rare earths, thorium, vanadium, and beryllium to the list of elements studied. Of these six elements, only beryllium shows significant sorption in this mixed-acid system.

In systems of hydrochloric and hydrofluoric acids the

number of parameters which may be varied to change the sorbability of an ion on anion-exchange resin is large. For example consider an ion which forms both chloro- and fluoro-complexes. The amount of complexation by fluoride is determined by the fluoride ion concentration of the solution and this, in turn, is determined by the acidity of the solution. At a constant hydrofluoric acid concentration the addition of hydrochloric acid decreases the fluoride ion concentration and thus tends to lower the distribution coefficient. Opposing the decrease in distribution coefficient is a tendency to form the chloro-complex which would be sorbed. Opposing both of these is the mass action of additional chloride ion which tends to displace the metal complexes. If the hydrochloric acid is partially neutralized, the tendency to form chloro-complexes is decreased, the mass action effect remains, and the ability of the fluoride to inhibit hydrolysis is retained. When the concentration of hydrofluoric acid is varied while the hydrochloric acid concentration remains constant, apparently the major effect is one of mass action. Ion-exchange resin in the chloride form has been used for much of the work done using hydrofluoric acid. It might be expected that there would be a decrease in the fluoride ion concentration due to

its sorption by the resin, but in general the resins have a much greater affinity for the chloride ion so that this effect is small (17).

The hydrochloric-hydrofluoric acid system on anion-exchange resin has been used by Hague and Macklan (18) for the determination of titanium, zirconium and hafnium, niobium, and tantalum in steel. In this method these elements are precipitated by cupferron and ignited to the oxides. The oxides are dissolved in the mixture of hydrochloric and hydrofluoric acid and added to an anion-exchange column. Titanium, zirconium, and hafnium are eluted with 50% HCl - 10% HF; molybdenum, tin, and iron are eluted with 12.5% HCl - 20% HF - 7.2% NH_4Cl ; niobium is eluted with NH_4Cl - HF; and tantalum is eluted with NH_4Cl - NH_4F .

Muenchow (19) has found it possible to determine niobium and tantalum in steel by extracting them into methyl isobutyl ketone. These are re-extracted into water with hydrogen peroxide and then added to anion-exchange column with hydrochloric acid and hydrofluoric acid. Iron, nickel, and tungsten (which accompany niobium and tantalum in the extraction) are eluted with 2 N HCl - 6 N HF; niobium is eluted with 3 N HCl - 0.05 N HF; and tantalum is eluted with 4 N NH_4Cl - 2 N

NH₄F.

Korkish (20) was able to analyze for titanium in steel by sorbing it on anion-exchange resin from a solution of 10% NaF - 0.1 N H₂SO₄ to remove it from interfering elements. The titanium is then removed by elution with H₂O₂ in H₂SO₄.

Athavale et al. (21) found it possible to sorb the components of steel on anion-exchange resin and elute all the interferences from the titanium with 1% HCl - 2% HF. The titanium is determined after elution with 3 M HCl.

Wish (22) determined the distribution coefficients of molybdenum, niobium, neptunium, and zirconium on Dowex 2 anion-exchange resin at constant concentration of hydrochloric acid while the concentration of hydrofluoric acid was varied. He also studied these elements plus uranium at 0.3 M HF with varying hydrochloric acid content. He then applied these results to radiochemical analysis.

Schindewolf and Irvine (23) determined the distribution coefficients of titanium, scandium, germanium, and gallium on Dowex 1 anion-exchange resin at hydrofluoric acid concentration from 0.5 M to 15 M. In all cases there is a remarkable decrease in the distribution coefficient as the hydrofluoric acid concentration is increased indicating possible separa-

tions.

Aluminum has been separated from zirconium by Freund and Miner (24) by anion exchange. From a solution of 0.06 M HCl - 0.8 M HF zirconium is retained on an anion-exchange column while aluminum is eluted.

Anion exchange with hydrofluoric acid was used by Bergstresser (25) to separate niobium and tantalum. Tantalum is retained on an anion-exchange column from 3 M HCl - 0.1 M HF while niobium is eluted.

Toy and Van Santen (26) have used anion exchange to determine small amounts of silicon in silver-infiltrated tungsten. The samples are dissolved in hydrogen peroxide - hydrofluoric acid. This solution is passed through a column of Dowex 1. The SiF_4 is retained by the column while the tungsten is not. The SiF_4 is then eluted with 8 M HCl.

Kallman et al. (27) studied the separation of niobium and tantalum on anion-exchange resin. In this method iron, titanium, tungsten, molybdenum, uranium, and manganese are eluted with 25% HCl - 20% HF. Niobium is eluted with 14% NH_4Cl - 4% HF; and tantalum is eluted to 14% NH_4Cl - 4% HF neutralized to pH 6.

Plutonium has been separated from other elements by

Kressin and Waterbury (28). It is sorbed on anion-exchange resin from 7.2 M HNO₃ and then eluted with 0.36 M HCl - 0.01 M HF.

Boni (29) devised a separation of radionuclides using a complex scheme with anion exchange with hydrofluoric acid. A mixture of chromium, cesium, zirconium, niobium, neptunium, cobalt, iron, and zinc is passed through an anion-exchange column in 0.1 N H₂SO₄ - 0.3 N HF. Chromium, cesium, neptunium, cobalt, iron, and zinc pass through while niobium and zirconium are retained. Both niobium and zirconium are removed with 6 N HCl - 0.5 N HF. They are then passed through an anion-exchange column in 11 N HCl - 0.5 N HF. Zirconium is eluted while niobium is retained. Niobium is then eluted with 6 N HCl - 0.5 N HF. Neptunium, cobalt, iron, and zinc are then sorbed on an anion-exchange column from 12 N HCl while chromium and cesium pass through. Neptunium is eluted from the column with 3.5 N HCl - 0.5 N HF, the cobalt with 5 N HCl, the iron with 0.5 N HCl, and the zinc with 0.005 N HCl. A similar separation scheme is given for radionuclides in biological materials.

Forsling (30) has studied the elution of zirconium and hafnium. The eluting solution used is 0.22 M HCl with hydro-

fluoric acid concentrations varying from 0.00002 to 0.02 M.

The anion-exchange separation of niobium and tantalum has been studied by Cabell and Milner (31). Tantalum is eluted with 3 M HCl - 0.1 M HF; and niobium is eluted with 4 M NH₄Cl - 1 M NH₄F.

Schindewolf and Irvine (32) found that from dilute hydrofluoric acid scandium and titanium are strongly sorbed on an anion-exchange column while vanadium is eluted. Also arsenic (III) is not sorbed on anion-exchange resin from dilute hydrofluoric acid while germanium and gallium are sorbed.

Hague et al. (33) studied the elution of titanium, tungsten, molybdenum, and niobium from Dowex 1 by HCl-HF. Titanium is eluted with 25% HCl - 5% HF, tungsten with 40% HCl - 5% HF, molybdenum with 40% HCl - 10% HF, and niobium with 14% NH₄Cl - 4% HF.

In an extension of the work by Hague et al. Wetlesen (34) adapted the method to Amberlite IRA-400 resin for the separation of titanium, niobium, and tantalum.

Sugawara (35) used anion exchange to separate titanium, zirconium, tungsten, and molybdenum. He found that zirconium and titanium are eluted with 8 M HCl. Tungsten is eluted with 10% HF - 60% HCl. Molybdenum is eluted with 5% HF - 25% HCl.

Hibbs and Wilkins (36) have used tandem cation- and anion-exchange columns in a novel separation of aluminum, titanium, and nickel. All three elements are sorbed on a strong-acid resin. On elution with 0.8 M HF - 0.06 M HCl, aluminum is removed from both columns, titanium is transferred from the cation-exchange column to the anion-exchange column, and nickel is retained by the cation-exchange column.

Wilkins (37) has also developed an anion-exchange method using hydrofluoric acid for the separation of nickel, chromium, cobalt, iron, titanium, tungsten, molybdenum, niobium, and tantalum. From a mixture of aluminum, manganese, nickel, chromium, cobalt, iron, titanium, tungsten, molybdenum, niobium, and tantalum, those retained by an anion-exchange resin from 2.5% HF are titanium, tungsten, molybdenum, niobium, and tantalum. Titanium is eluted by 8 M HCl; tungsten is eluted with 10% HF - 60% HCl, molybdenum by 20% HF - 25% HCl, niobium by 14% NH₄Cl - 4% HF, and tantalum by 14% NH₄Cl - 4% NH₄F.

Tada and Horiguchi (38) used anion exchange to separate cobalt, tungsten, titanium, and tantalum. Cobalt is eluted with 1:4 HF, tungsten and titanium are eluted with 5:1:4:: HCl:HF:H₂O, and tantalum with 14% NH₄Cl - 4% HF at pH 2.

The use of hydrofluoric acid in anion-exchange analysis

of alloys has been investigated by Dixon and Headridge (39). They found that the chloride form of an anion-exchange resin sorbs titanium, zirconium, niobium, tantalum, molybdenum, and tungsten from 1 M HF while aluminum, vanadium, chromium, manganese, iron, cobalt, nickel, and copper are eluted. They then worked out a method for the separation of the sorbed group. Titanium is eluted with 0.01 M HF - 9 M HCl, tungsten with 3 M HF - 10 M HCl, niobium with 0.2 M HF - 7 M HCl, molybdenum with 3 M HF - 3 M HCl, and tantalum with 1 M NH_4F - 4 M NH_4Cl .

Nikitin and Katykhin (40) devised an anion exchange separation of lead, bismuth, and polonium. On AV-17x14 in the chloride form they were able to elute lead with 0.1 M HCl - 0.1 M HF, bismuth with 20-8 M HF, and polonium with 3 M HNO_3 .

Faris and Nikitin are among the workers who have investigated sorption on anion-exchange resin from hydrofluoric acid alone. Using Dowex 1 in the fluoride form Faris (41) studied the distribution coefficients of most metals and found that nineteen metals, mostly of the transition series and phosphorous form sorbed species. For all elements, except niobium, as the amount of hydrofluoric acid is increased the distribution coefficient decreases, presumably by mass action.

Niobium exhibits a minimum and then a maximum as the hydrofluoric acid concentration is increased from about 12 M to 24 M. This behavior is useful in the separation of niobium and tantalum. Nikitin (42) has studied the distribution coefficients on the fluoride form of the anion-exchange resin AB-17x14. Using these data he was able to obtain the following group separations: chromium, iron, zinc, and lead are eluted with 1 M HF; aluminum, silicon, phosphorus, cobalt and arsenic are eluted with 5 M HF; beryllium, scandium, vanadium, and selenium are eluted with 10 M HF; bromide, molybdenum, tellurium, bismuth, and uranium are eluted with 15 M HF; titanium, zirconium, technetium, lead, tin, hafnium, tungsten, iridium, and rhenium are eluted with 20 M HF; niobium and tantalum are eluted with 1 M HF - 4 M NH_4Cl .

Cation Exchange Using Hydrofluoric Acid

In contrast with the relatively large number of workers who have investigated the use of hydrofluoric acid in anion-exchange systems, little work has been done in applying hydrofluoric acid to cation-exchange systems.

Hettel and Fassel (43) sorbed a mixture of the rare earths, zirconium, titanium, and hafnium on Dowex 50 cation-exchange resin. Zirconium, titanium, and hafnium are eluted

with 3.4 M HF while the rare earths are not eluted. They also found that under the same conditions iron, cobalt, calcium, magnesium, beryllium, and manganese are not eluted.

Nelson et al. (15) used small amounts of hydrofluoric acid to prevent hydrolysis of niobium, tantalum, and protactinium in their study of cation exchange in concentrated hydrochloric and perchloric acid solutions. However, the major effect is not due to fluoride. They also used hydrofluoric acid mixed with other acids in their elutions. In their procedure scandium eluted with 0.1 M HF - 4 M HCl, and 9 M HCl - 0.2 M HF is used to elute hafnium.

Fritz et al. (44) have reported the elution characteristics of thirty-five elements from hydrogen and ethylenediammonium forms of cation-exchange resin. These data were used to predict a large number of possible separations.

Eberle (45) has found that under different conditions, behavior different from that reported by Fritz et al. may be expected. He found that if chromium(III) is evaporated to dryness with HF and passed through a 3 x 10 cm. column which has been equilibrated with 0.084 M HF in a solution of 0.084 M HF it is not retained by the column and under the same conditions vanadium(IV) is eluted to some extent. The

ion-exchange column completely removes gallium from solution under these conditions.

Wilkins (46) has been able to separate aluminum and yttrium by eluting aluminum from a cation exchange column with hydrofluoric acid.

Using the resin, KV-2x6 in the hydrogen form, Nikitin (42) studied the distribution coefficients of metals in hydrofluoric acid. From the data obtained he devised group separations. Anions are eluted with 1 M HF; chromium, iron, calcium, arsenic, cadmium, and indium are eluted with 5 M HF; sodium, rubidium, cesium, manganese, lead, and bismuth are eluted with 10 M HF; nickel, zinc, technetium, and mercury are eluted with 15 M HF; and cobalt, copper and tellurium are eluted with 20 M HF.

No attempt has been made to give an exhaustive review, but rather the major developments in ion exchange using hydrofluoric acid were listed.

EXPERIMENTAL METHODS

Apparatus

Laboratory ware

Kimble "Nomax" burettes and Kimble "Exax" pipettes were used throughout this work. Distribution coefficients were determined in 100 ml. polyethylene bottles with screw caps. Standard polyethylene beakers and 150 ml. platinum evaporation dishes were used. All volumetric glassware used was Class A. Ion-exchange columns were polyethylene columns 15 cm. long with an inside diameter of 1.6 cm. The cross-sectional area was 2.0 cm^2 . The resin column was supported on a plug of Dynel wool, and the flow rate was controlled by means of a screw clamp. Solutions were added to the column through a polyethylene funnel supported in the column by a rubber stopper. The column is illustrated in Figure 1.

pH meter

All pH measurements were made with a Precision Scientific Company A. C. Titrometer equipped with Beckman 40498 glass and 39170 calomel reference electrodes.

Spectrophotometer

A Beckman Model B spectrophotometer was used for all spectrophotometric measurements. One and five cm. borosili-

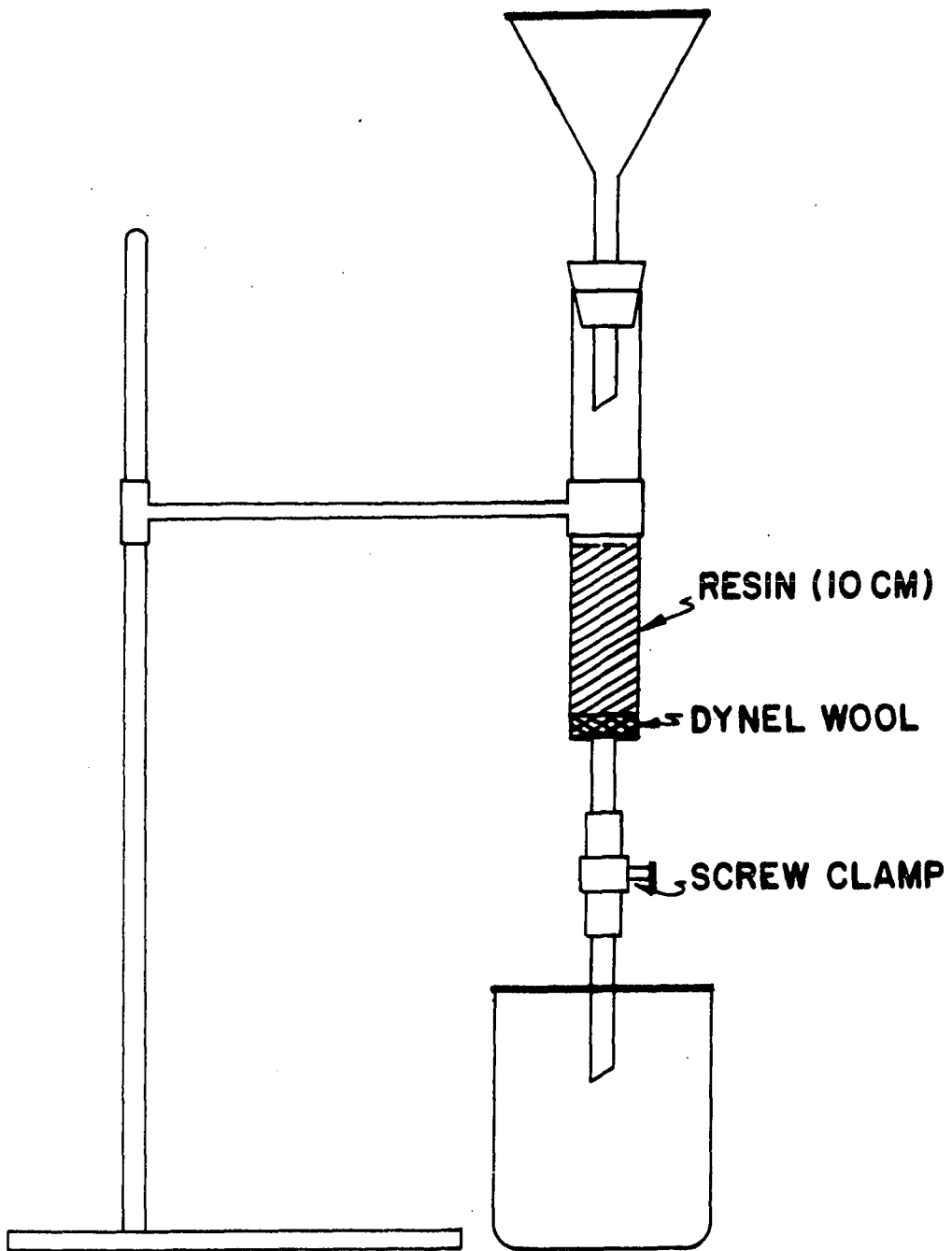


Figure 1. Ion-exchange column

cate glass cells were used.

Stirrer

A Burrell shaker was used in the equilibration of samples for distribution studies.

Conductivity bridge

A Model RC 16B2 conductivity bridge from Industrial Instruments, Inc. was used for conductance measurements.

Reagents

Ion-exchange resin

J. T. Baker Chemical Company "Analyzed Reagent" grade Dowex 50W cation-exchange and Dowex 1 anion-exchange resin were used. Except where stated otherwise, the resin contained 8% divinylbenzene. The resin used for column experiments was 100 to 200 mesh, but in some batch experiments 20 to 50 mesh resin was used. The cation-exchange resin was regenerated for continual use as follows. About two pounds of the resin were first backwashed with distilled water to remove the fine particles. It was then washed with 4 liters of 10% ammonium citrate (pH 3.0 to 3.5) to remove metal ions. It was then converted to the hydrogen form by washing with 4 liters of 3 M hydrochloric acid. The resin was then washed with distilled water until a negative test for chloride was obtained

using acidified silver nitrate. The resin was then sucked dry, washed with acetone, and allowed to dry in the air. This resin contained approximately 25% water. The anion-exchange resin was prepared by first backwashing approximately 500 grams to remove the fine particles and purified by washing with 2 liters of 3 M hydrochloric acid and 2 liters of 0.1 M hydrochloric acid. The resin was then converted to the fluoride form by washing with 1 M sodium fluoride until a negative test was obtained for chloride. The resin was then washed with distilled water and acetone and allowed to dry in the air. This resin contained approximately 25% water.

Disodium dihydrogen (ethylenedinitrilo)-tetraacetate dihydrate

The EDTA was Baker Chemical Company "Analyzed Reagent".

Metal ions investigated

Most metal ions investigated were used as perchlorates or reagent grade nitrates. The perchlorates were obtained from G. F. Smith Chemical Company. Zirconium perchlorate was prepared by extracting hafnium-free zirconyl chloride with thiocyanate in methyl isobutyl ketone to remove any iron present. Zirconium hydroxide was then precipitated with ammonia and the precipitate washed free of chloride. The

precipitate was then dissolved in 5 M perchloric acid. Tin (IV) was used as the chloride.

Organic solvents

J. T. Baker purified methyl alcohol and isopropyl alcohol were used.

Metal perchlorate or nitrate solutions

The required amount of the metal salt was dissolved in water with enough perchloric acid to prevent hydrolysis. Niobium and tantalum metals were dissolved in hydrofluoric acid and nitric acid mixtures. Beryllium carbonate was dissolved in perchloric acid. These solutions were standardized at the time of their use by an appropriate analytical procedure.

Other chemicals

All other chemicals used except for indicators were common reagent grade laboratory chemicals. Also, unless otherwise stated the word water refers to distilled, deionized water.

Analytical Procedures

EDTA

Solutions of EDTA were standardized by titration with standard zinc(II) and copper(II) solutions using Naphthyl Azoxine S as described by Fritz et al. (47). The standard

zinc and copper solutions were prepared by dissolving an accurately weighed amount of the pure metal in acid and diluting to volume.

Uranium(VI)

Uranium was analyzed by the oxidation-reduction method of Sill and Peterson (48).

Bismuth(III), tin(IV), and zirconium(IV)

The analyses were carried out by back titration after addition of excess EDTA using Xylenol Orange indicator. The method for tin and zirconium was given by Kinnunen and Wennerstrand (49) and that for bismuth by Körbl and Pribil (50).

Iron(III), mercury(II), titanium(IV), aluminum(III), and vanadium(IV)

These elements were analyzed by back titration after addition of excess EDTA using Naphthyl Azoxine S indicator as described by Fritz *et al.* (47).

Zinc(II), copper(II), and cadmium(II)

These analyses were performed by a direct titration with EDTA using Naphthyl Azoxine S as indicator (47).

Beryllium(II)

This element was determined gravimetrically using 2-methyl-8-hydroxyquinoline as described by Motojima (51).

Manganese(II)

This analysis was a direct titration with EDTA using Eriochrome Black T indicator in the presence of ascorbic acid and cyanide (52, p. 217).

Chromium(III)

Chromium was analyzed by oxidation to chromium(VI) with ammonium persulfate followed by reduction to chromium(III) by an iron(II) solution (53, p. 529).

Barium(II), calcium(II), and strontium(II)

These analyses were performed by titration with EDTA using the silver electrode as described by Fritz and Garralda (54).

Niobium(V)

Niobium was analyzed spectrophotometrically using the color of the peroxide complex in concentrated sulfuric acid (53, p. 609).

Tantalum(V)

Tantalum was analyzed spectrophotometrically using the color of its arsenazo complex (55, p. 582).

Fluoride

This analysis was performed by a spectrophotometric method using the cerium complex of alizirin complexone as

described by Yamamura et al. (56).

Determination of Distribution Coefficients

Anders Ringbom (57, pp. 205-208) has stated that from a knowledge of the selectivity coefficient of an ion exchanger and formation constants for metal complexes, distribution coefficients can be calculated thus making their determination unnecessary. With complex systems, however, these calculations are laborious and, at best, give approximate answers. The behavior of actual systems may vary considerably from the theoretical. In addition, the effect of adding water-miscible organic solvents is only qualitatively predictable, so that in order to be able to achieve practical analytical separations a systematic study of the behavior of the actual system is desirable if not necessary.

Systematic studies of ion-exchange behavior may be carried out by determining distribution coefficients by either a column or batch method. The column method requires that an elution curve be determined for each eluent studied and is thus suited to automation. In the batch method two determinations are needed to establish the distribution coefficient in a given concentration of complexing agent. Because of this greater simplicity, the batch method was chosen for this

work. A weight distribution coefficient, D , defined by Equation 1, is obtained.

$$D = \frac{\text{Millimoles of ion on resin/gram of resin}}{\text{Millimoles of ion in solution/ml of solution}} \quad (1)$$

The volume distribution coefficient is related to the weight distribution coefficient by the equation

$$D_v = D\rho \quad (2)$$

where ρ is the density of the bed (kg. of dry resin per liter of bed).

The detailed procedure for the determination of the distribution coefficient is as follows. An exactly-known amount of the metal in question (about 0.25 millimole) was added to an accurately weighed, approximately one gram sample of the air-dried resin to be used in a 100 ml. polyethylene bottle. The weight of dry resin was determined from the air-dried weight and the moisture content determined by drying samples of resin to constant weight at 110°C. Then 50.00 ml. of hydrofluoric acid of the desired concentration and in the desired organic solvent, if used, were added; and the mixture was equilibrated at room temperature. The time allowed for equilibration was not less than 2 hours for aqueous samples and not less than 4 hours for samples containing organic solvents. An aliquot, usually 50.00 ml., was then withdrawn

through a plug of Dynel wool to filter any resin particles. The solution was then evaporated in a platinum dish to remove excess acid and then fumed with sulfuric or perchloric acid to remove the last traces of fluoride. The acid most often used to remove fluoride was perchloric (58), but when this was not possible, sulfuric acid was used. The solution was then analyzed by an appropriate means, and the distribution coefficient was calculated. It should be pointed out that in general the determination of extremely high and extremely low distribution coefficients is not as accurate as those for intermediate values. With very high distribution coefficients the amount of material remaining to be analyzed in solution is low while with low distribution coefficients it is approximately equal to the amount added so that analytical errors influence the value obtained. It will be seen, however, that in devising an analytical scheme, except in most unusual cases, knowledge that a distribution coefficient is extremely high or extremely low is sufficient.

Column Separations

When the distribution coefficients are known, the behavior of the system on an ion-exchange column can be predicted from Equation 3.

$$\bar{v} = (D_v + i)Ad \quad (3)$$

where D_v is the volume distribution coefficient and \bar{v} is the volume of eluent which moves the band maximum d cm. on a column of A cm.² cross-sectional area and has a fractional interstitial volume i . In order to achieve a separation, conditions are chosen so that D_v and thus \bar{v} of one species is as low as possible, preferably less than 1, while the distribution coefficients of all other components of the system are as high as possible. After elution, conditions are changed to lower the distribution coefficient of another metal and it is eluted. In theory the number of elements which can be thus eluted is unlimited as long as their separation factor, α , or the ratio of their D_v values remains large enough so that one element is eluted before the other one begins to appear in the effluent.

Cornish (59) has fully developed a procedure for designing the most efficient column for a particular separation when the distribution coefficients for the materials to be separated is known. The diameter of the column is determined from the requirement that the loading be 50 mg. per cm.² or less. Large loads lead to tailing of the elution band.

If D_1 and D_2 are the distribution coefficients of the

two ions of interest the ratio, a_2/a_1 , is defined by Equation 4,

$$\frac{a_2}{a_1} = \frac{D_2 + 1}{D_1 + 1} . \quad (4)$$

The cross-contamination, η , is given by the ratio of Δm_2 to m_1 , where Δm_2 is the amount of the second ion in the first peak with the assumption that the cross contamination of both peaks are equal. That is

$$\eta = \frac{\Delta m_2}{m_1} = \frac{\Delta m_1}{m_2} . \quad (5)$$

The percent purity of each solute is then $100(1 - \eta)$. Once the desired purity of the products has been determined, the amounts of ions to be separated, m_1 and m_2 , and the ratio, a_2/a_1 , is determined, the number of theoretical plates required for the separation can be determined from a chart after the function,

$$\eta \frac{(m_1^2 + m_2^2)}{2m_1m_2} \quad (6)$$

is calculated.

A second chart gives the height equivalent to a theoretical plate for various resin sizes and flow rates. Knowing the height equivalent to a theoretical plate and the number of theoretical plates required, the length of the column required can be calculated. In practice the column is

usually oversized to insure proper separation, but even with the over design there can be a considerable saving of time since "over-separation" does not occur to as large an extent as when the column is designed by trial-and-error.

In this work and in some other work (44) using hydrofluoric acid on cation exchange, the resin is washed with water before addition of the sample. In other work (45) the resin is equilibrated with hydrofluoric acid before addition of the sample. This prior equilibration should result in earlier elution, especially of those elements which form strong fluoride complexes.

In all elutions the metal was sorbed on the resin from a non-complexing acid and then eluted from the resin with the specified amount of hydrofluoric acid. The effluent was collected either in platinum or polyethylene dishes and evaporated to a small volume, perchloric or sulfuric acid was added, and the solution was fumed in platinum ware to remove fluoride. The solution was then analyzed by a suitable analytical procedure.

DISTRIBUTION COEFFICIENTS IN AQUEOUS HYDROFLUORIC ACID

Complexation of Metals by Fluoride

The major factor which determines the selectivity of an ion-exchange resin for a particular ion is the charge on that ion. The higher the charge, the more strongly the ion is held by the resin. The hydrated radius of the ion has an effect, but this is minor in comparison with the effect of charge. If the metal reacts with a neutral molecule such as ammonia, its exchange characteristics may be altered; but the exchange constant, $K_B^A = \frac{[\bar{A}](B)}{(A)[\bar{B}]}$, where $[\bar{A}]$ and $[\bar{B}]$ represent the concentration of species in the resin phase and (A) and (B) represent the concentration of species in the solution phase, is seldom changed an order of magnitude (57, p. 206). If, on the other hand, a metal ion reacts with a negative ion, the charge is decreased and there will be less tendency for the metal to be held by the resin. The most dramatic change in behavior is observed when the charge is neutralized or when a negative ion is formed.

The fluoride ion is known for its ability to react with certain metals. Schwarzenbach (60) has attempted to give rules which would allow the prediction of complexation. The ions which have inert gas configurations, such as the alkali

metal, alkaline earth, and aluminum ions bond mainly by electrostatic attraction and have no tendency to react with either the cyanide or sulfide ions which are large and easily polarized. Small, highly charged ions will tend to react more strongly with these ions and form stable complexes. These requirements are met by fluoride and hydroxide ions. The large alkali metal ions probably exist in aqueous solution mainly as the stable hydrated ions and have little tendency to form other complexes. Boron(III) and aluminum(III) in the third periodic group have inert gas configurations and tend to form strong complexes with the fluoride and hydroxide ions.

Reference to Table 1 shows that these generalities are usually valid. Those ions with the highest charge tend to form by far the strongest complexes with fluoride, and those ions have inert gas configurations. Table 1 should be used with caution since the ionic strengths at which the constants were determined are not uniform.

The unusual behavior of chromium should be recalled here. Chromium(III) complexes are inert. Chromium tends to form inner orbital complexes and all of its substitution reactions are slow (61). For example, if chromium(III) and hydrofluoric acid each about 10^{-2} M and 0.01 M in acid are mixed, equilib-

rium is not reached for about two weeks even though the equilibrium constant for the formation of CrF_3 is $10^{10.2}$. This behavior of chromium is reflected in its ion-exchange behavior. If chromium is evaporated to dryness with hydrofluoric acid and then passed through a column in 0.0038 M hydrofluoric acid, it is not retained (45); but if it is not heated first, it is not eluted in 200 ml. of 1 M hydrofluoric acid (44). Unusual behavior has been noted in the sulfate system. When the sample of chromium(III) containing sulfate is passed through cation-exchange resin part of the chromium is retained and part passes through. It has been reported that when the column is maintained at 90°C ., elution with sulfuric acid is complete (62, p. 240-241). Thus the behavior of chromium(III) on cation-exchange resin is strongly dependent on its pretreatment.

Hydrofluoric acid is a weak acid; the ionization constant is 1.15×10^{-3} (63). In aqueous solution the possible species present are HF , H^+ , F^- , and HF_2^- , but there is no evidence of H_2F_2 (64, pp. 251-252). Hydrofluoric acid forms a constant boiling mixture which contains 36% hydrofluoric acid and boils at 120°C . (65, p. 104). These facts indicate that there can be significant competition for the fluoride

Table 1. Formation constants for metal-fluoride complexes

Ion	$\log \beta_1$	β_2	β_3	β_4	β_5	β_6	Source
Al^{+3}	6.1	11.15	15	17.7	19.4	19.7	-a
Ba^{+2}	<0.45						-b
Be^{+2}	5.1	8.8	11.8				-a
Cd^{+2}	0.46	0.53					-a
Cr^{+3}	4.4	7.7	10.2				-a
Cu^{+2}	0.7						-a
Fe^{+3}	5.2	9.2	11.9				-a
Hg^{+2}	1.0						-a
Mg^{+2}	1.3						-a
Ni^{+2}	0.7						-a
Pb^{+2}	<0.3						-a
Sn^{+4}						25	-a
Th^{+4}	7.7	13.5	18.0				-a
TiO^{+2}	5.4	9.8	13.7	17.4			-a
UO_2^{+2}	4.5	7.9	10.5	11.8			-a
Zn^{+2}	0.77						-b
Zr^{+4}	8.8	16.1	21.9				-a

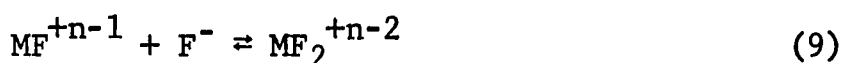
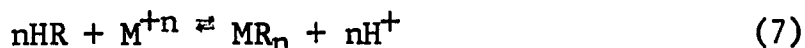
^aRingbom (57, p. 314).

^bBjerrum, Schwarzenbach, and Sillén (66, pp. 88-93).

ion by the hydrogen ion in cases where metal-fluoride complexes are not strong; but when metal-fluoride complexes are strong, the metal is better able to compete with the hydrogen ions for the fluoride ions.

Distribution Coefficients on the Hydrogen Form Resin

Using the general procedure described, distribution coefficients were determined in aqueous hydrofluoric acid solutions using the hydrogen form of Dowex 50W for seventeen metal ions. These are shown in Tables 2, 3, and 4 and in Figures 2, 3, and 4. In general these values are in agreement with the behavior which would be expected from the values in Table 1. The stronger a metal-fluoride complex, the lower the concentration of hydrofluoric acid required to complex it in the solution phase.



R = resin.

Titanium(IV), zirconium(IV) (and hafnium), and tin(IV) are among the elements which form the strongest fluoride complexes, and at 0.045 M their distribution coefficients are less than 0.5, indicating that they would be rapidly eluted

Table 2. Distribution coefficients of metal ions as a function of hydrofluoric acid concentration

HF M	Metal ion						
	Ti(IV)	Zr(IV)	Be(II)	Al(III)	U(VI)	Ca(II)	Sn(IV)
0.0091	7.73	99.7	136	474	530	3470	
0.018	3.37	10.1	56.1	131	531	3470	
0.027	1.51	0.422	20.4	31.0	243	3470	
0.045	0.20		17.7	14.8	102	1700	0.33 ^a
0.073			9.43	2.00	41.7	1700	
0.091			2.51	2.00	26.7	1130 ^b	

^aBelow this hydrofluoric acid concentration hydrolysis of Sn(IV) is evident.

^bAbove this hydrofluoric acid concentration CaF₂ precipitates.

Table 3. Distribution coefficients of metal ions as a function of hydrofluoric acid concentration

HF M	Metal ion		
	Fe(III)	V(IV)	Cr(III)
0.091	215	928	644 ^a
0.18			337
0.45	6.45	65.4	94.9
0.91	1.85	24.1	30.6
1.8	0.071	5.66	23.7
2.7		2.14	
4.5			29.6

^aThese samples were heated to incipient boiling with hydrofluoric acid before adding to the resin.

Table 4. Distribution coefficients of metal ions as a function of hydrofluoric acid concentration

HF M	Metal ion						
	Mn(II)	Zn(II)	Cd(II)	Cu(II)	Hg(II)	Sr(II)	Ba(II)
0.091		37,800		32,300		3,710	
0.18						3,710	7,150
0.45	16,500	19,900	11,500	16,100		1,860	7,170
0.91	6,350	7,890	17,200	6,400	38,100	1,850	9,580
1.8	2,290	1,400			4,390	1,850	7,150
2.7	964	902	1,260	946	3,020		
4.5	334	336	531	360	1,480	706	2,820
9.1		107		121			
13.6		51.3		57.7			

Figure 2. Distribution coefficients of titanium(IV), zirconium(IV), beryllium(II), aluminum(III), and uranium(VI) as a function of hydrofluoric acid concentration

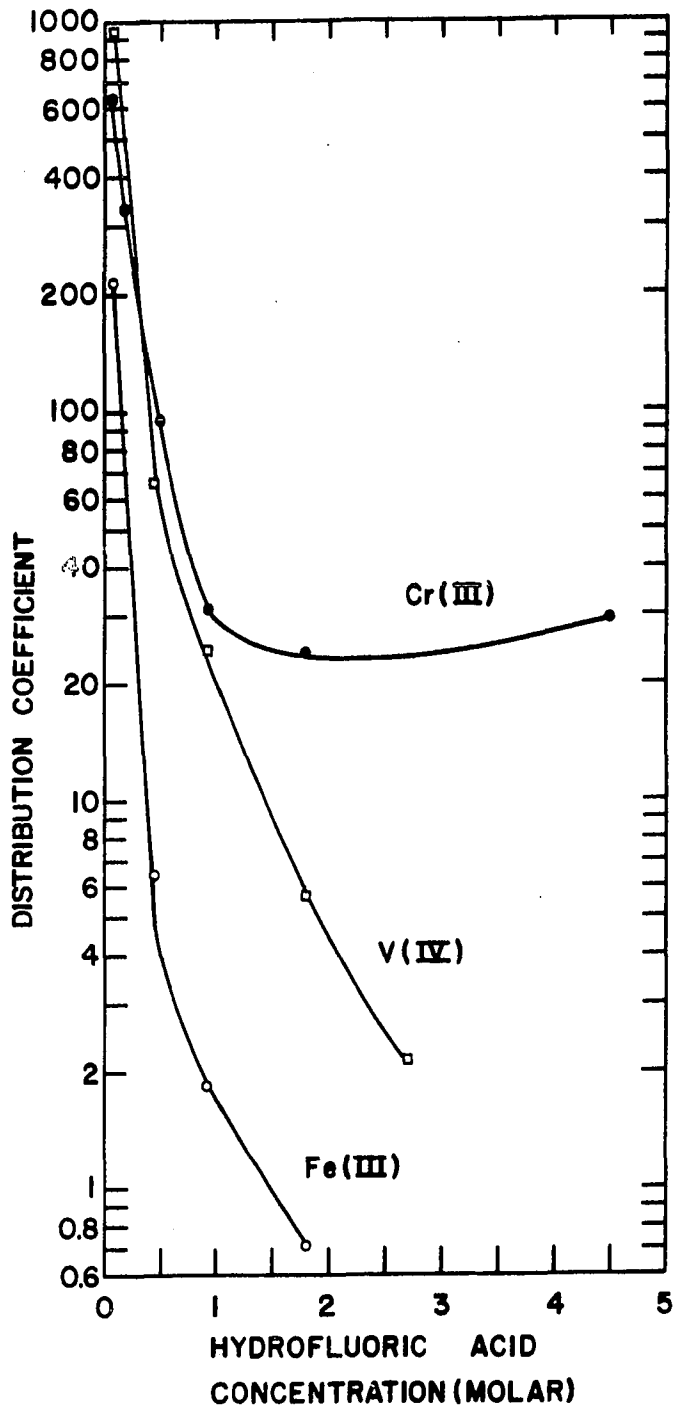
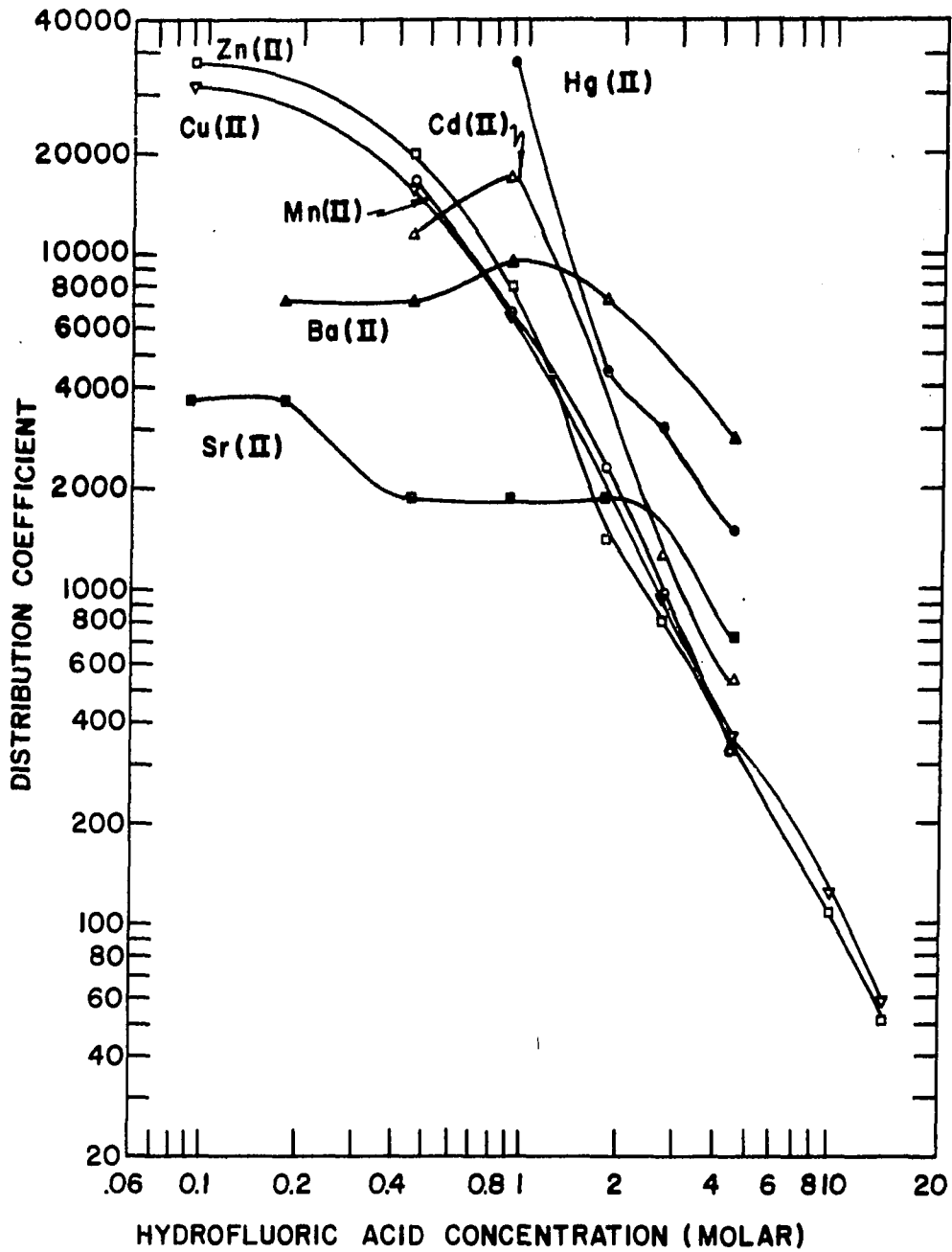


Figure 4. Distribution coefficients of manganese(II), zinc(II), cadmium(II), copper(II), mercury(II), strontium(II), and barium(II) as a function of hydrofluoric acid concentration



from a column with this concentration. At lower hydrofluoric acid concentrations they should be retained by the resin. However, below 0.045 M hydrofluoric acid solutions of tin(IV) are cloudy indicating that hydrolysis takes place. If hydrolysis takes place on a column, there would be a tendency to tail and interfere with other separations.

The group of elements with the next lowest distribution coefficients consists of beryllium(II), aluminum(III), and uranium(VI). At hydrofluoric acid concentrations of 0.1 M these elements still have distribution coefficients of about two, but at slightly a higher hydrofluoric acid concentration the distribution coefficients drop to quite low values.

Calcium(II) was studied in hydrofluoric acid concentrations from 0.0091 to 0.091 M because calcium fluoride precipitates at higher acid concentrations. In this concentration range the distribution coefficient is extremely high. Special treatment would be required for samples containing calcium since precipitation on the column would interfere seriously with proposed separations.

Iron(III), vanadium(IV), and chromium(III) have the next higher distribution coefficients. These are the elements with the next weaker fluoro-complexes. In accordance with the slow

ligand exchange of chromium(III), it is necessary to heat it to incipient boiling with the hydrofluoric acid before adding it to the resin. If this procedure is not followed, almost 100% of the metal is found on the resin.

Manganese(II), zinc(II), cadmium(II), copper(II), mercury(II), strontium(II), and barium(II) form no appreciable fluoride complexes, and therefore have extremely high distribution coefficients at hydrofluoric acid concentrations up to about 0.1 M. As the acid concentration is increased, the distribution coefficients gradually decrease. By 13.6 M hydrofluoric acid, the distribution coefficients of zinc(II) and copper(II) are still above 50. The major factor in decreasing the distribution coefficients is the mass action of the added hydrofluoric acid.

One factor that could be of major importance with regard to column pretreatment is the invasion of the resin by hydrofluoric acid. Weak electrolytes and non-electrolytes are both sorbed by ion-exchange resins in manners which can be described by the equations which describe the sorption of material by charcoal. This indicates that the effect may be one of surface sorption. For acetic acid, however, it has been shown that the concentration of acid in the water which is not

bound in the hydration spheres of the ionic sites on the resin is the same as that in the bulk solution (1). Such behavior with hydrofluoric acid is entirely possible. The inside of the resin phase has a high concentration of counter ions (about 5 M). When the resin is in the hydrogen form, this high acid concentration represses the ionization of weak acids so that the molecular acid may be sorbed. The sorption of hydrofluoric acid was determined by equilibrating the acid with a known amount of resin, rinsing the acid free, and determining the fluoride colorimetrically. The results are shown in Table 5 and Figure 5. The results give a fairly good fit for a Langmuir isotherm

$$(x/m)^{1.08} = 0.55c \quad (10)$$

where x is the amount of hydrofluoric acid sorbed, m is the mass of sorbent, and c is the concentration of hydrofluoric acid in equilibrium with the sorbent (ion-exchange resin). This sorption indicates that if the resin is treated with hydrofluoric acid before the sample is added, elements with low distribution coefficients are likely to be complexed and eluted in a significantly smaller volume of eluent than if the sample is added to a column which has not been pretreated with hydrofluoric acid. For example, if the resin has been exposed

to hydrofluoric acid, as little as 30 ml. of 0.05 M hydrofluoric acid will completely elute titanium(IV) and zirconium (IV); but if the resin has not been previously exposed to hydrofluoric acid, 60 ml. of 0.05 M hydrofluoric acid are required.

Table 5. Sorption of hydrofluoric acid by Dowex 50W x 8, hydrogen form

Molarity hydrofluoric acid	Acid sorbed	<u>millimoles HF</u> <u>gram of resin</u>
0.01		1.08×10^{-2}
0.02		1.49×10^{-2}
0.03		2.25×10^{-2}
0.05		3.61×10^{-2}
0.10		1.44×10^{-1}
0.20		1.64×10^{-1}
0.50		2.87×10^{-1}
1		6.10×10^{-1}
2		1.05
3		2.07
5		2.62

Distribution Coefficients on Sodium Form Resin

The hydrogen form of the ion-exchange resin represses the ionization of hydrofluoric acid. If a form other than hydrogen form were used for the determination of distribution

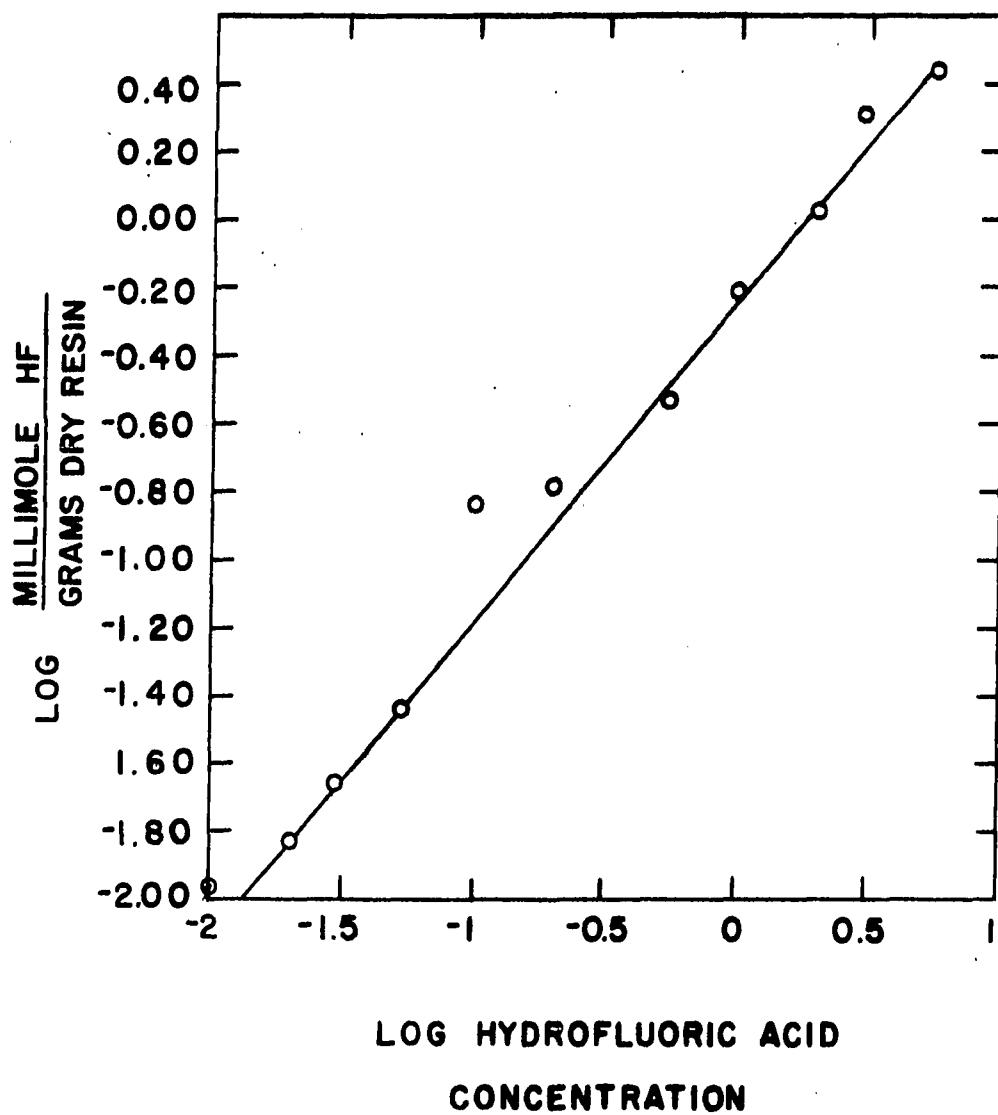


Figure 5. Sorption of hydrofluoric acid by Dowex 50W x8, hydrogen form

coefficients, the repression would not be as great and the amount of available fluoride would be greater. This should cause the distribution coefficients to be lower since the increased fluoride will increase the amount of metal-fluoride complexes. Another effect which will also tend to decrease the distribution coefficient on the sodium-form resin, is the slightly greater affinity of the sulfonic acid group of the resin for the sodium ion than for the hydrogen ion.

The distribution coefficients for seven metal ions on the sodium form of Dowex 50W x 8 ion-exchange resin are shown in Table 6 and Figures 6 and 7. The distribution coefficients on the hydrogen-form resin are included for comparison. In every case the distribution coefficients are lower on the sodium form than on the hydrogen form at low hydrofluoric acid concentrations. In the case of all the ions studied except copper(II) and uranium(VI) there is a crossover at higher hydrofluoric acid concentrations. This crossover can be explained on the basis of penetration of the resin by hydrofluoric acid. The hydrogen form of the resin has a relatively high capacity for hydrofluoric acid at higher acid concentrations. Thus it can be present in large enough quantities to complex the metals. With the sodium-form resin, the ioniza-

Table 6. Distribution coefficients of metal ions as a function of hydrofluoric acid concentration on the sodium form of Dowex 50W x 8

HF M	Metal ion						
	U(VI)	Ti(IV)	Al(III)	Zr(IV)	V(IV)	Fe(III)	Cu(II)
0.0091	90.2	4.88	127	94.6			
0.018	36.8	2.45	31.7	12.2			
0.027	16.7	3.67		0.947			
0.045			2.31	1.69			
0.091			2.75		82.7	14.0	
0.18					24.6	3.92	
0.45					14.6		
0.91					7.33		2530
1.8					2.72		1030
2.7							521
4.5					2.55		305
9.1							98.9

Figure 6. Distribution coefficients of uranium(VI), aluminum(III), titanium(IV), and zirconium(IV) on Dowex 50W x8, sodium form compared with the hydrogen form

_____ Distribution coefficients on the sodium form

----- Distribution coefficients on the hydrogen form

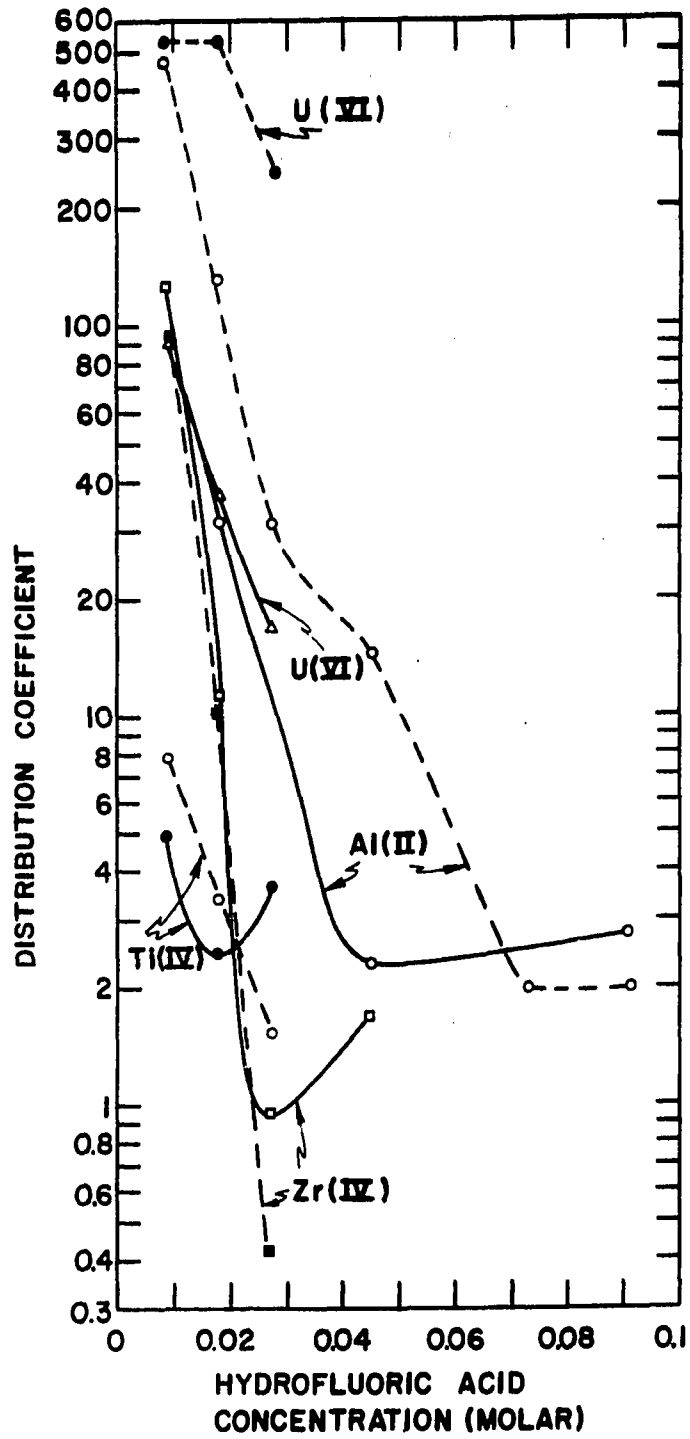


Figure 7. Distribution coefficients of copper(II) and vanadium(IV) on Dowex 50W x8, sodium form compared with the hydrogen form

_____ Distribution coefficients on the sodium form

----- Distribution coefficients on the hydrogen form

tion of the hydrofluoric acid should not be repressed to as great an extent, complexation should be less, and the distribution coefficient higher.

Distribution Coefficients on Resin with Varied Crosslinkage

It is possible that resin with eight per cent divinylbenzene might have pore sizes which would limit the exchangeability of the fluoride complexes of some of the larger ions, especially those which form oxygenated cations. To test for this sieve action, a series of distribution coefficients was determined on resins containing four and twelve per cent divinylbenzene. The results are given in Table 7. If the difference is caused by sieve action, the resin with the highest crosslinkage (highest per cent divinylbenzene) would be expected to have lower distribution coefficients than resins with lower amounts of crosslinkage.

The results do not show a general trend toward lower distribution coefficients at higher crosslinkages, so that sieve action and the closely related swelling pressure do not appear to have appreciable influence on the exchange of the metal ions. Examination of Table 1 and Figures 2-5 indicates that strength of the fluoride complex, rather than size of the fluoro complex of the metal, is the more important factor in

Table 7. Distribution coefficients of metal ions as a function of crosslinking on hydrogen form Dowex 50 resin

Metal ion	HF <u>M</u>	Distribution coefficient	
		4% divinylbenzene	12% divinylbenzene
V(IV)	0.073	834	
	0.091	602	
	0.45	5.80	
	0.91	2.37	
	1.8	0.793	
	2.7	0.560	
Al(III)	0.0091	486	219
	0.018	135	160
	0.027	51.2	158
	0.045	15.2	22.1
	0.073	6.46	10.5
	0.091	0.270	9.33
Fe(III)	0.073	229	396
	0.091	143	231
	0.45	7.15	61.2
	0.91	3.58	8.63
	1.8	1.28	3.21
Zr(IV)	0.0091	95.4	
	0.018	10.6	
	0.027	0.934	

determining the hydrofluoric acid concentration at which a metal is eluted.

Mann and Swanson (67) have provided a theory which explains the trend toward higher distribution coefficients at higher crosslinkages. The hydrated radius of a univalent ion such as hydrogen is large, while that of an ion with a higher charge is smaller. In a resin with high crosslinkage the disruption of the hydration shell of the univalent ion is greater than with a more highly charged, but smaller ion. It is thus the hydrogen ion which is actually experiencing the results of the sieve action.

Determination of the Limiting Mean Ligand Number of the Eluted Species

Fritz and Waki (68) have developed a method for determining the limiting mean ligand number of the species eluted from a cation exchange resin. This method was applied to aluminum (III) and zirconium(IV) in hydrofluoric acid.

The distribution of aluminum(III) between a cation-exchange resin and a solution containing hydrofluoric acid is given by Equation 11.

$$D = \frac{[Al^{+3}] + [AlR^{+2}] + [AlR_2^+] + [AlR_3]}{(Al^{+3}) + (AlF^{+2}) + (AlF_2^+) + (AlF_3) + \dots} \quad (11)$$

In this equation \underline{R} represents a resin site, $[\]$ represents concentration in the resin phase, and $(\)$ represents concentration in the aqueous phase. It should be noted that AlFR^+ , AlFR_2 , and AlF_2R are possible species, but these, if they exist, are present in extremely small amounts and will be ignored in this derivation.

If the terms in Equation 11 are replaced by their equivalent formation constants and Al^{+3} terms are factored out, the following equation is obtained.

$$D = \frac{[\text{Al}^{+3}]}{(\text{Al}^{+3})} \cdot \frac{1 + \beta_{\text{AlR}} [\text{R}] + \beta_{\text{AlR}_2} [\text{R}]^2 + \beta_{\text{AlR}_3} [\text{R}]^3}{1 + \beta_{\text{AlF}} (\text{F}^-) + \beta_{\text{AlF}_2} (\text{F}^-)^2 + \beta_{\text{AlF}_3} (\text{F}^-)^3 + \dots} \quad (12)$$

By Donnan equilibrium $[\text{Al}^{+3}] / (\text{Al}^{+3})$ is proportional to $[\text{H}^+]^3 / (\text{H}^+)^3$ (1, pp. 134-135) so that

$$D = k \frac{[\text{H}^+]^3}{(\text{H}^+)^3} \cdot \frac{1 + \beta_{\text{AlR}} [\text{R}] + \beta_{\text{AlR}_2} [\text{R}]^2 + \beta_{\text{AlR}_3} [\text{R}]^3}{1 + \beta_{\text{AlF}} (\text{F}^-) + \beta_{\text{AlF}_2} (\text{F}^-)^2 + \beta_{\text{AlF}_3} (\text{F}^-)^3 + \dots} \quad (13)$$

where k is an activity term. If the activity coefficients, $[\text{H}^+] / (\text{H}^+)$, and $[\text{R}]$ remain constant, Equation 13 can be reduced to

$$\log D/D_0 = K - \log \{ 1 + \beta_{\text{AlF}} (\text{F}^-) + \beta_{\text{AlF}_2} (\text{F}^-)^2 + \beta_{\text{AlF}_3} (\text{F}^-)^3 + \dots \} \quad (14)$$

Here D_0 represents the distribution coefficient of aluminum at the highest hydrofluoric acid concentration used. Since it is easier to work with analytical concentration of fluoride, C_F , than with equilibrium constants, (F^-) , the latter can be replaced with their equivalents

$$C_F = (F^-) + (HF) = (F^-) \{ 1 + \beta_{HF}(H^+) \}. \quad (15)$$

Combining Equations 14 and 15

$$\log D/D_0 = K - \log \left\{ 1 + \frac{\beta_{AlF} C_F}{1 + \beta_{HF}(H^+)} + \frac{\beta_{AlF_2} C_F}{(1 + \beta_{HF}(H^+))^2} + \frac{\beta_{AlF_3} C_F^3}{(1 + \beta_{HF}(H^+))^3} + \dots \right\}. \quad (16)$$

If β'_{AlF} is used in place of $\frac{(AlF^{+2})}{(Al^{+3})(C_F)}$, β'_{AlF_2} in place of $\frac{(AlF_2^+)}{(Al^{+3})(C_F)^2}$, etc.

$$\log D/D_0 = K - \log \left\{ 1 + \beta'_{AlF} C_F + \beta'_{AlF_2} C_F^2 + \beta'_{AlF_3} C_F^3 + \dots \right\}. \quad (17)$$

On differentiating Equation 17 the following results are obtained:

$$d \log D/D_0 = dK - d \log \left\{ 1 + \beta'_{AlF} C_F + \beta'_{AlF_2} C_F^2 + \beta'_{AlF_3} C_F^3 + \dots \right\}. \quad (18)$$

Multiplying both sides of the equation by $1/(d \log C_F)$;

$$\frac{d \log D/D_0}{d \log C_F} = \frac{d \log \left\{ 1 + \beta'_{A1F} C_F + \beta'_{A1F_2} C_F^2 + \beta'_{A1F_3} C_F^3 + \dots \right\}}{d \log C_F} \quad (19)$$

Since $d \log x = dx/x$,

$$\frac{d \log D/D_0}{d \log C_F} = \frac{(-\beta'_{A1F} - 2\beta'_{A1F_2} C_F - 3\beta'_{A1F_3} C_F^2 + \dots) dC_F}{(1 + \beta'_{A1F} C_F + \beta'_{A1F_2} C_F^2 + \beta'_{A1F_3} C_F^3) (d \log C_F)} \quad (20)$$

If both the numerator and the denominator of Equation 20 are multiplied by C_F

$$\frac{d \log D/D_0}{d \log C_F} = \frac{(\beta'_{A1F} C_F - 2\beta'_{A1F_2} C_F^2 - 3\beta'_{A1F_3} C_F^3 + \dots) dC_F}{(1 + \beta'_{A1F} C_F + \beta'_{A1F_2} C_F^2 + \beta'_{A1F_3} C_F^3 + \dots) (d \log C_F) (C_F)} \quad (21)$$

If $\beta'_{A1F} C_F$, etc. in Equation 21 are replaced by their equivalents, Equation 22 results.

$$\frac{d \log D/D_0}{d \log C_F} = \frac{\left(-\frac{A1F^{+2}}{A1^{+3}} - 2 \frac{A1F_2^{+}}{A1^{+3}} - 3 \frac{A1F_3}{A1^{+3}} + \dots \right) d \log C_F}{\left(1 + \frac{A1F^{+2}}{A1^{+3}} + \frac{A1F_2^{+}}{A1^{+3}} + \frac{A1F_3}{A1^{+3}} + \dots \right) d \log C_F} \quad (22)$$

If the numerator and denominator of Equation 22 are multiplied by $(A1^{+3})$, Equation 23 results.

$$\frac{d \log D/D_0}{d \log C_F} = \frac{-(A1F^{+2}) - 2 (A1F_2^{+}) - 3 (A1F_3) + \dots}{(A1^{+3}) + (A1F^{+2}) + (A1F_2^{+}) + (A1F_3) + \dots} = \bar{n} \quad (23)$$

where \bar{n} is defined as the average number of ligands per central atom in a complex. A convenient definition is

$$\bar{n} = \frac{C_L - [L]}{C_M} \quad (24)$$

where C_L and C_M represent the analytical concentrations of ligand and metal respectively and $[L]$ represents the equilibrium concentration of ligand.

From Equation 23 it may be seen that when $\log D/D_0$ is plotted against $\log C_F$, the limiting slope of the resulting curve gives the limiting mean ligand number of the eluted species. Table 8 gives the distribution coefficients at constant ionic strength for aluminum and zirconium. Both sodium perchlorate and perchloric acid were used to maintain constant ionic strength. The function, $\log D/D_0$, is plotted against $\log C_F$ for aluminum in Figures 8 and 9, and for zirconium in Figures 10 and 11. From the tangents drawn as shown in these figures the values of the mean ligand number as shown in Table 9 are obtained. Also shown are values of \bar{n} calculated using the values of the formation constants given in Table 1.

Two points of caution should be added about comparisons of these results. First, there is some difficulty in choosing the correct tangent for the graphical determination of the mean ligand number. Second, the ionic strengths used in this

Figure 8. Determination of \bar{n} for aluminum in 0.023 M hydrofluoric acid by cation exchange

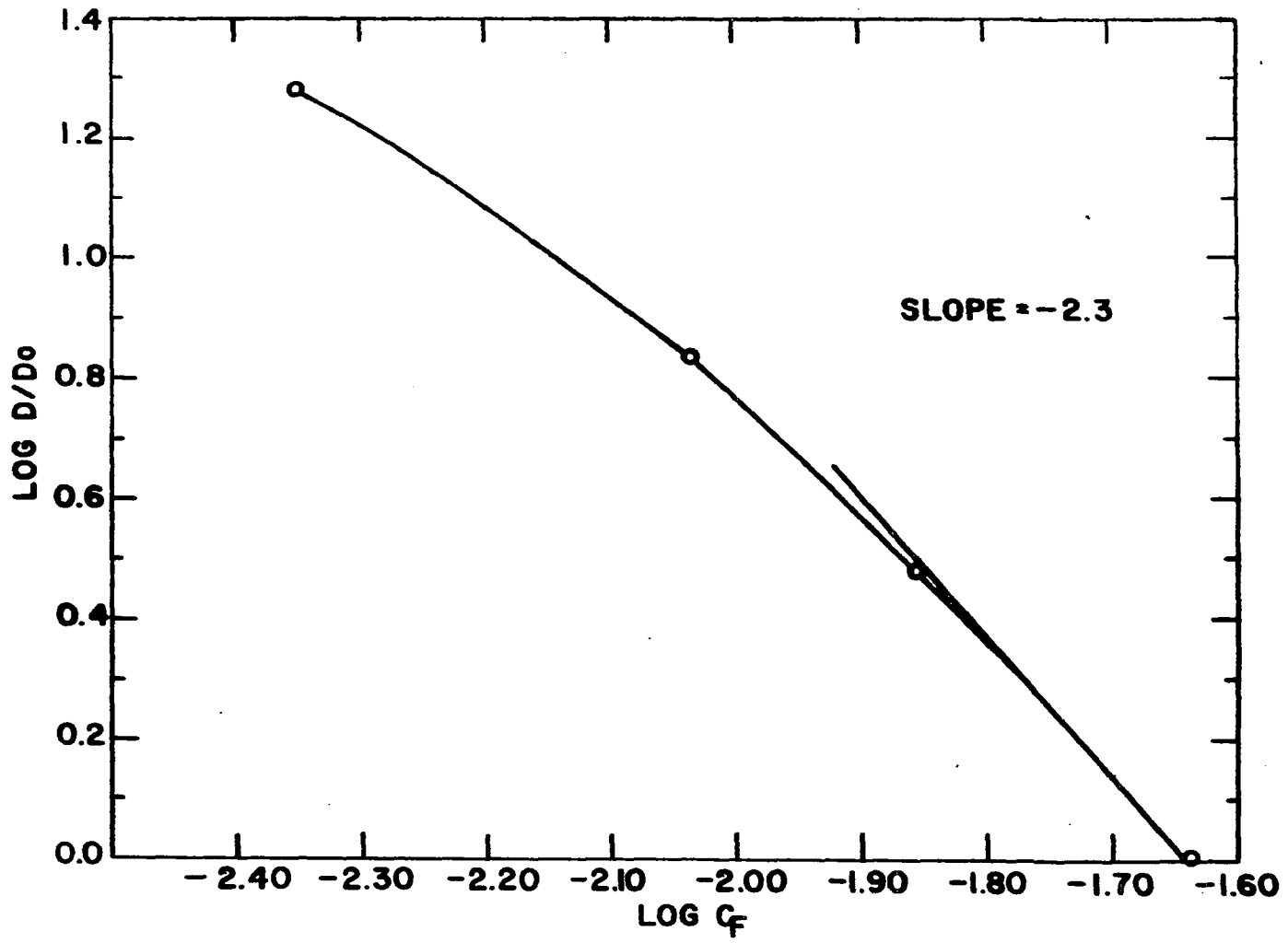


Figure 9. Determination of \bar{n} for aluminum in 0.045 M hydrofluoric acid by cation exchange

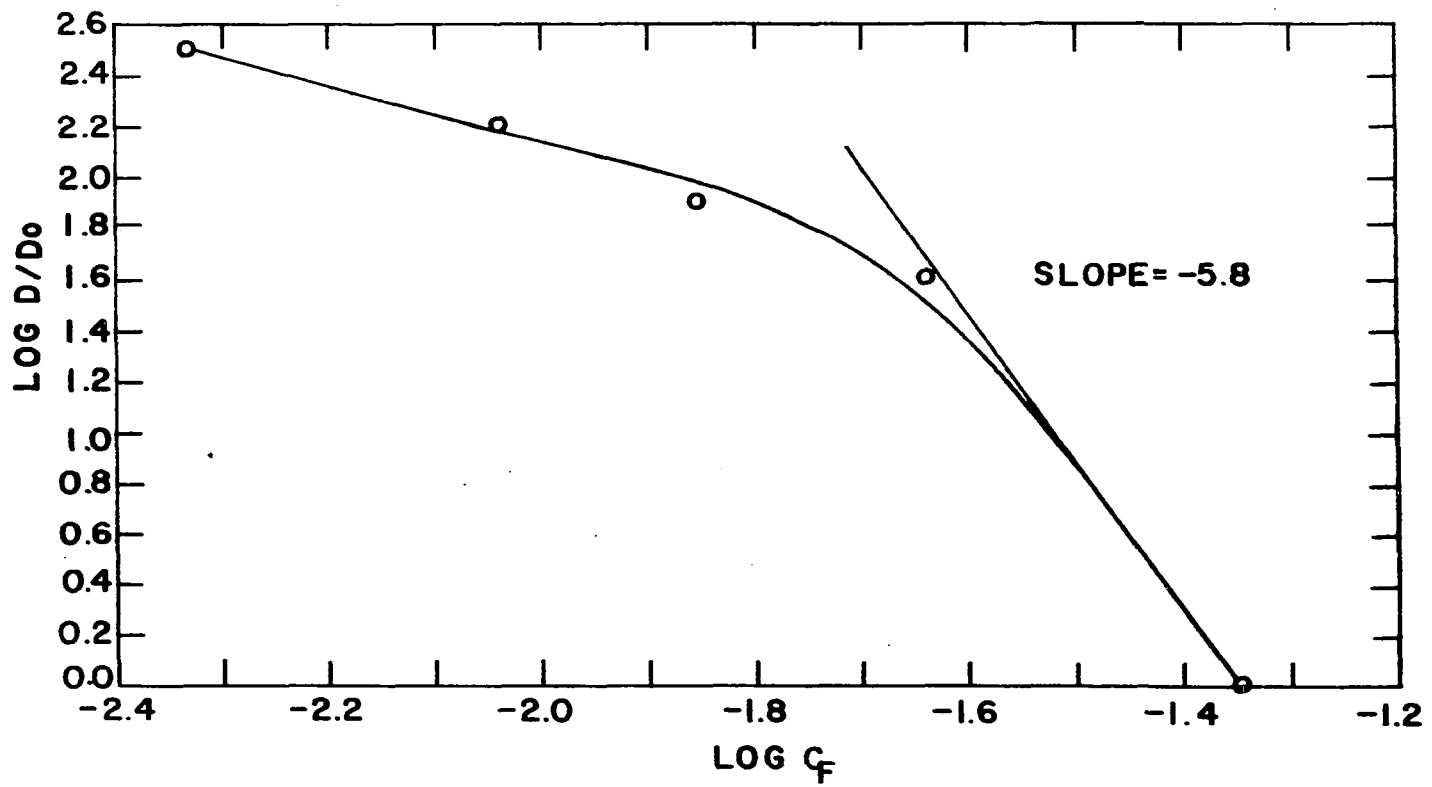


Figure 10. Determination of \bar{n} for zirconium in 0.023 M hydrofluoric acid by cation exchange

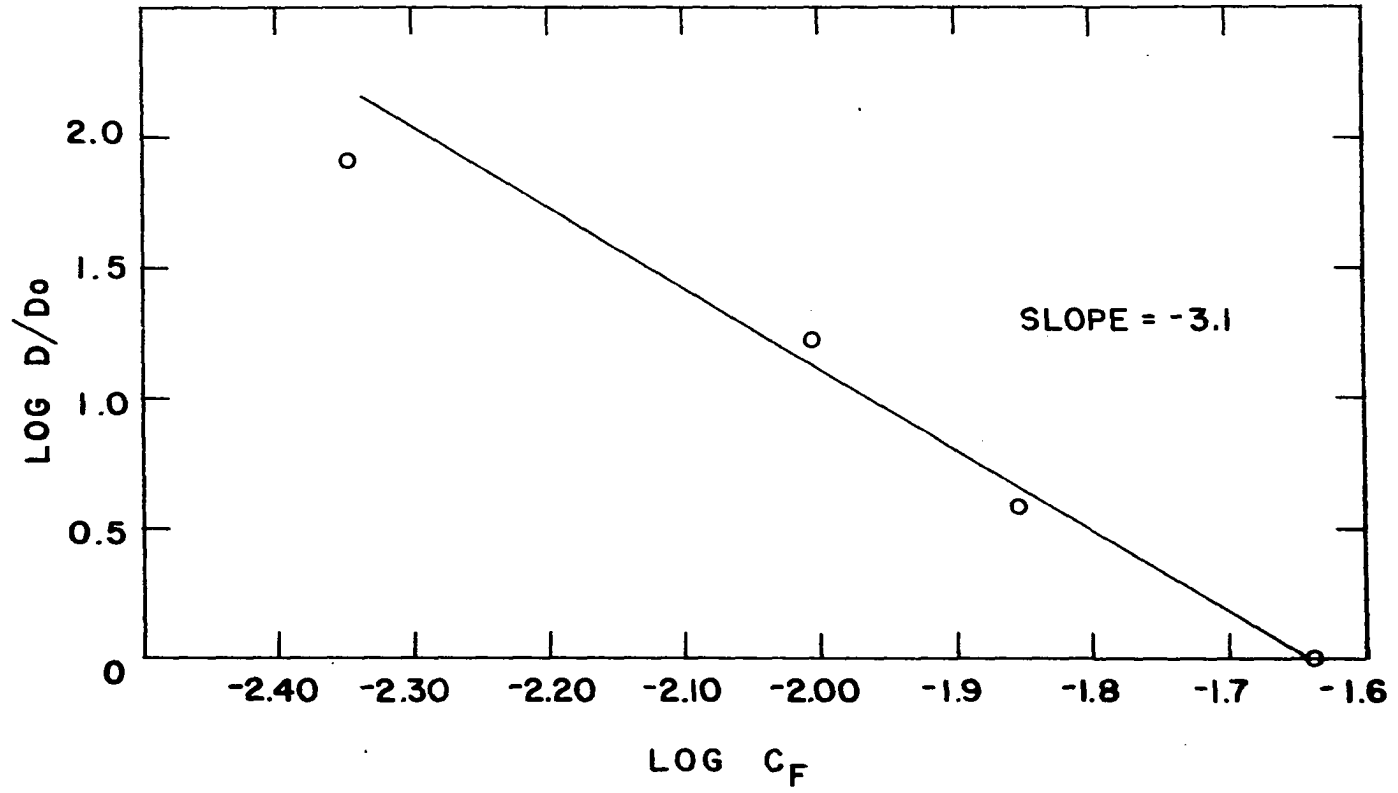
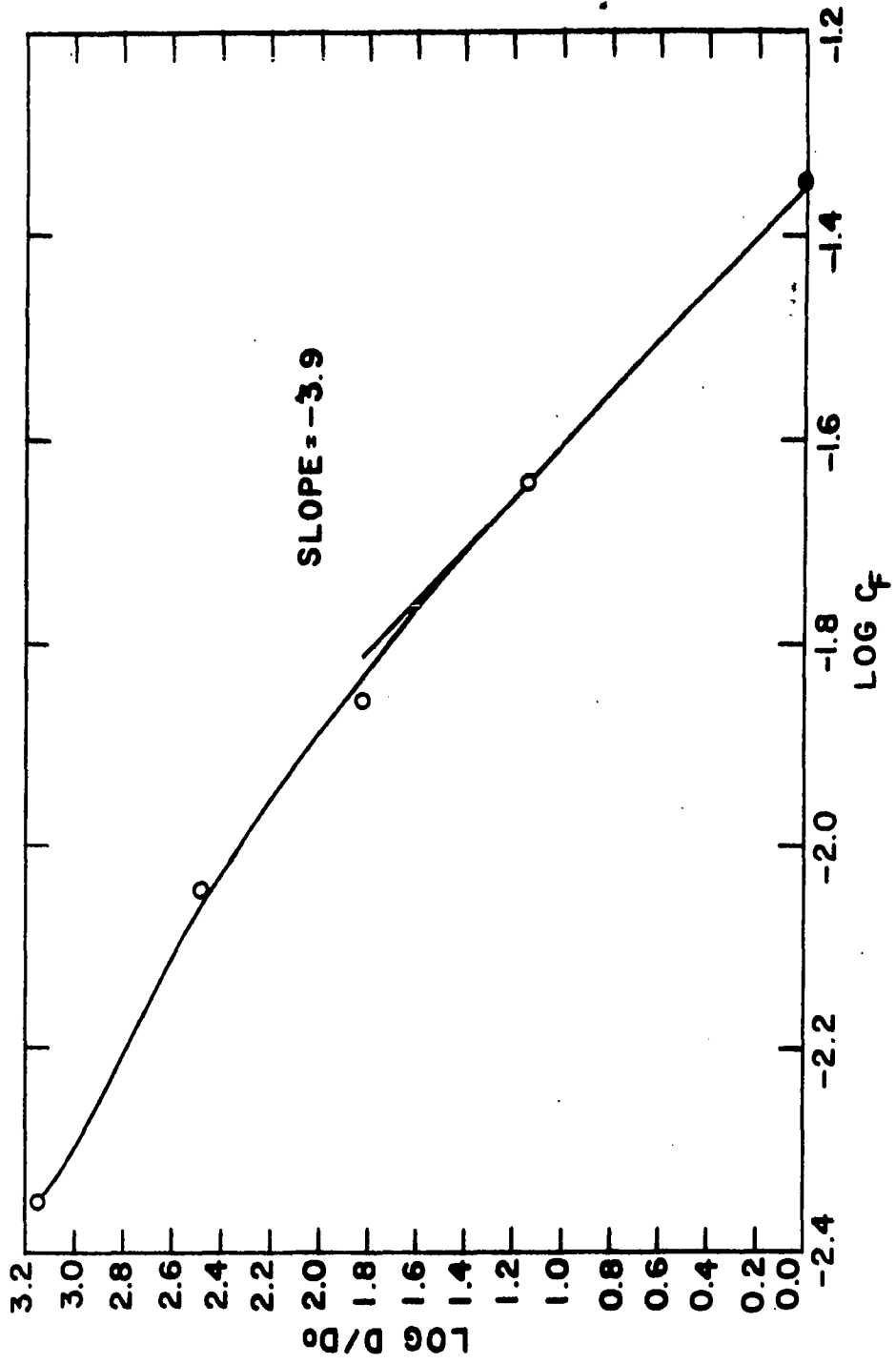


Figure 11. Determination of \bar{n} for zirconium in 0.045 M hydrofluoric acid by cation exchange



work are different from those used in obtaining the values in Table 1. In Table 1 the values of the ionic strength used are 0.53 for aluminum and 2 for zirconium. The values used in this work are 0.75 for aluminum and 1.20 for zirconium.

From Table 9 it is evident that when perchloric acid is used to maintain constant ionic strength there is reasonable agreement between the values for the mean ligand numbers obtained by cation exchange and the calculated values. On the other hand when sodium perchlorate is used, there is considerable deviation. This is not surprising because in the derivation of Equation 23 it was assumed that the resin was in the hydrogen form and that the ratio, $[H^+]/(H^+)$, was constant. This ratio would not necessarily be constant when the sodium ion is present. The difference in the affinity of the resin for the hydrogen and sodium ions could be taken into account, but the derivation would be correspondingly more complex. From these experiments with the mean ligand number it appears that the species eluted are those that would be expected from the formation constants of the fluoro-complexes.

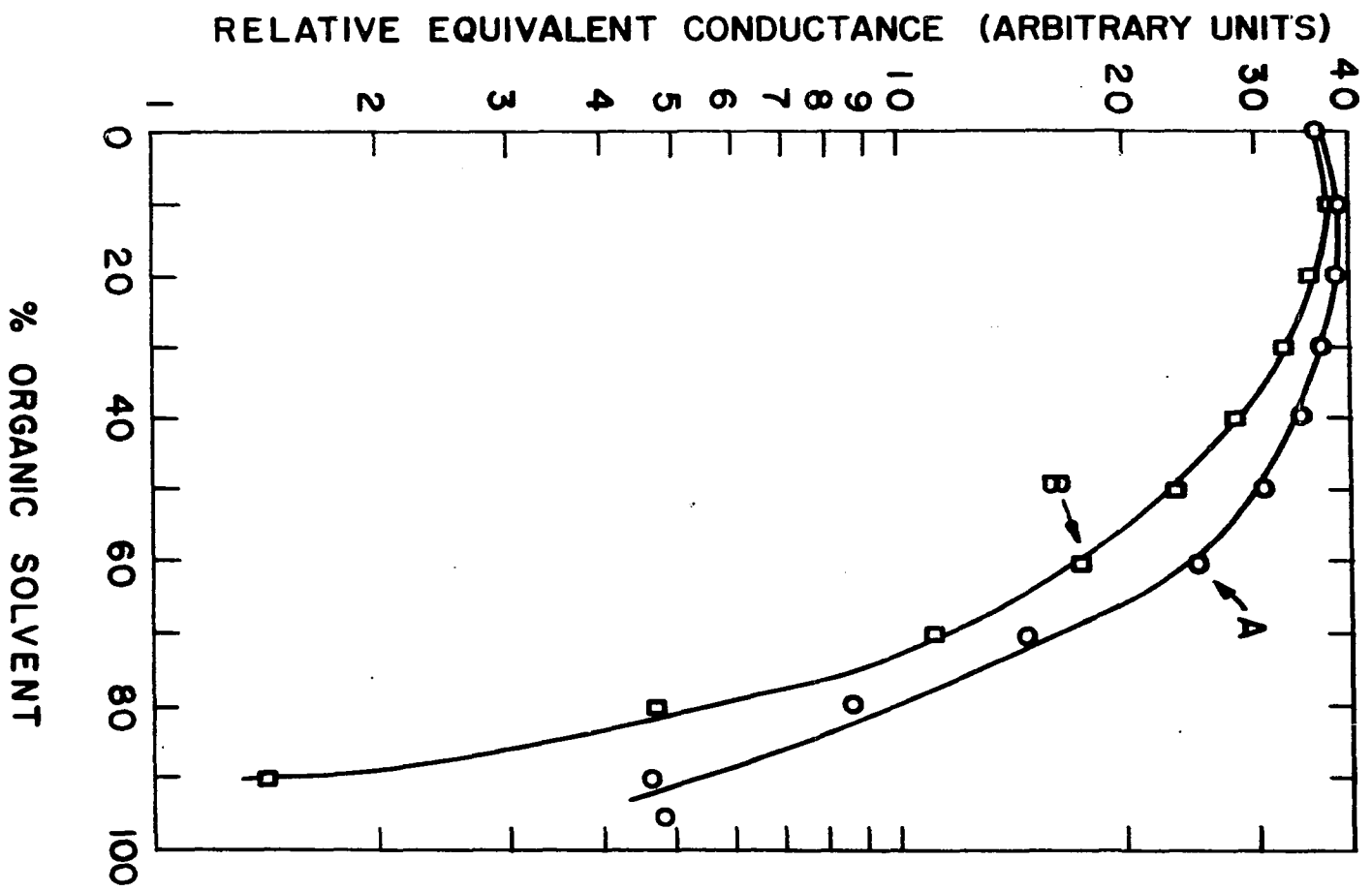
DISTRIBUTION COEFFICIENTS IN HYDROFLUORIC ACID
WITH MIXED SOLVENTS

The addition of a miscible organic solvent to an ion-exchange system has been shown to have a marked effect on both the cation- (69) and anion- (70) exchange behavior of metals. When a resin is in equilibrium with a mixed solvent, one component of the solvent will be preferentially sorbed. The resin usually sorbs the most polar component of a mixture. Water is usually greatly favored because of the tendency of the polar resin sites to form hydration shells. The general requirements in a mixed-solvent system are that the exchanging species must be soluble, there must be ions in both solutions, and the ions must be free to move (1, p. 507).

Ion exchange using pure acetone resembles ion exchange of weak aqueous electrolytes because electrolytes tend to be less completely ionized in this medium than in aqueous systems. In mixed solvents this repression of ionization varies with the concentration. The solution inside the resin phase contains relatively more water than the external phase. Ionic species prefer the water-rich phase and tend to be extracted into it. Figure 12 shows the relative equivalent conductance of hydrofluoric acid in mixed systems of water-

Figure 12. Conductance of hydrofluoric acid as a function of the percent organic solvent in partially aqueous systems

- A. Acetone-water system
- B. Isopropyl alcohol-water system



isopropyl alcohol and water-acetone. As ionization is decreased, the amount of fluoride available for complexation is decreased. In the resin phase, the concentration of hydrofluoric acid is relatively high. This, combined with the decreased water activity in the resin, and the low dielectric constant of the resin matrix itself, is favorable to the formation of complexes or ion-pairs. This will lead to an increase in the distribution coefficient of the metal as higher amounts of organic solvent are added (71).

Table 10 and Figures 13-17 show the effect of organic solvents on the distribution coefficients of aluminum(III), zirconium(IV), titanium(IV), vanadium(IV), and zinc(II).

These all show an increase in distribution coefficient; while some rise over the entire range of organic solvent, others show decreases in distribution coefficient at high organic solvent content. This reversal in the distribution coefficient can be explained by assuming that the lower water activity at the high organic solvent content leads to poorer solvation of the ions and causes ion-pair formation to become significant in the exterior phase.

The distribution coefficients of niobium(V) and tantalum(V) were determined from 0 to 90% acetone at 0.028 M hydro-

Table 10. Distribution coefficients of metal ions as a function of organic solvent in hydrofluoric acid solutions

Metal ion	HF M	Per cent organic	Distribution coefficient	
			Acetone	Isopropyl alcohol
Al(III)	0.028	8.83	64.2	68.1
		17.6	81.2	
		44.1	263	649
		70.6	1500	3480
		79.5	2730	3190
		88.3	3190	1990
Al(III)	0.068	8.47	7.27	
		16.9	16.8	
		42.4	99.0	
		67.8	1110	
		76.3	2130	
		84.7	3420	
Zr(IV)	0.0098	8.91	95.4	91.6
		17.8	98.2	104
		44.5	169	169
		71.3	6610	438
		80.2	6660	470
Ti(IV)	0.026	8.62	5.68	
		17.2	6.34	
		43.1	24.1	
		69.0	97.9	
		77.6	112	
		86.2	65.6	
V(IV)	1	9.09		9.19
		18.2		10.8
		72.7		371
		81.8		750
		90.9		1900
Zn(II)	1	9.09		1210
		18.2		4510
		45.5		7950
		72.7		4500
		90.9		221

Figure 13. Distribution coefficient of aluminum(III) as a function of organic solvent concentration

- A. Organic solvent acetone, 0.028 M HF
- B. Organic solvent isopropyl alcohol
0.028 M HF
- C. Organic solvent acetone, 0.068 M HF

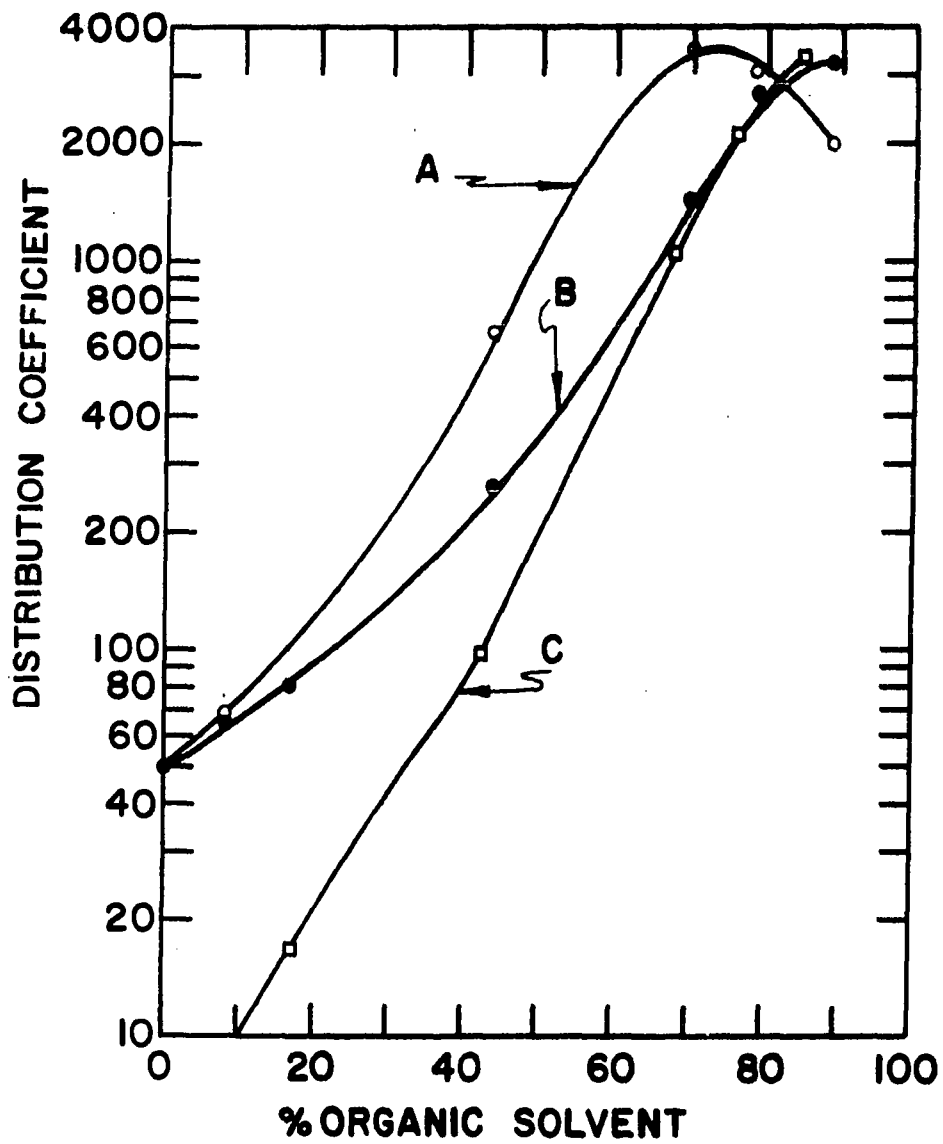
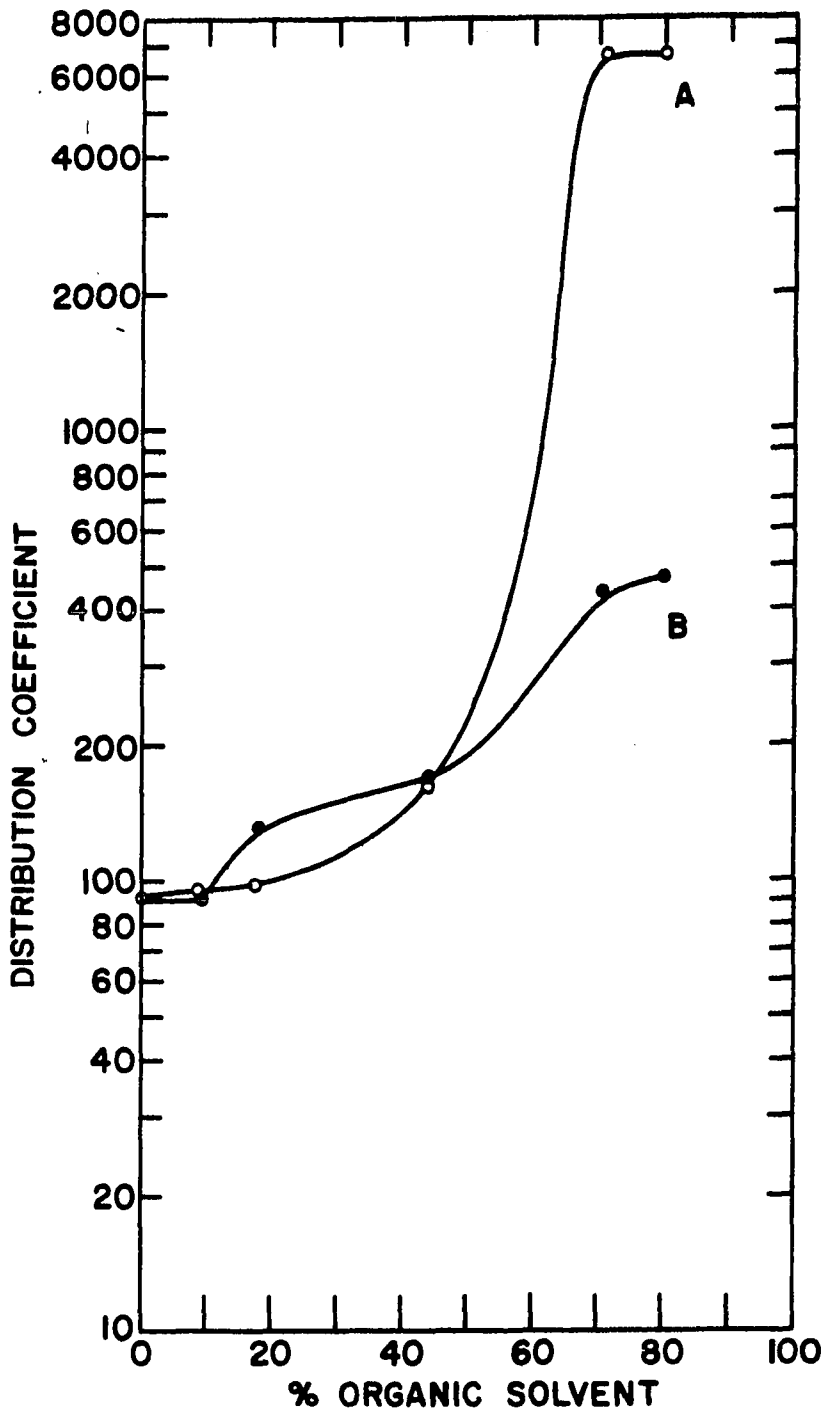


Figure 14. Distribution coefficients of zirconium(IV) as a function of organic solvent concentration

- A. Organic solvent acetone, 0.0098 M HF
- B. Organic solvent isopropyl alcohol, 0.0098 M HF



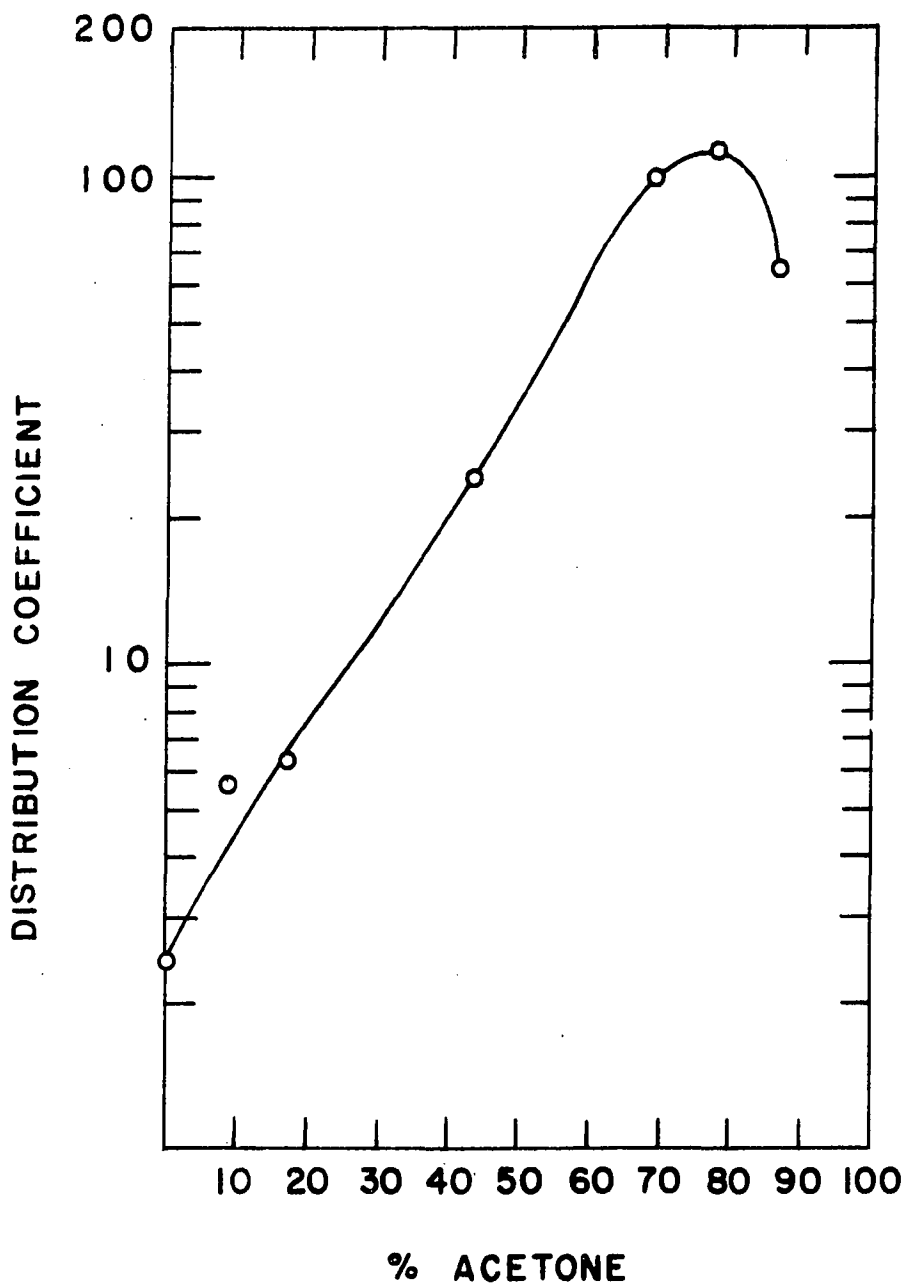


Figure 15. Distribution coefficients of titanium (IV) as a function of acetone concentration at 0.26 M HF

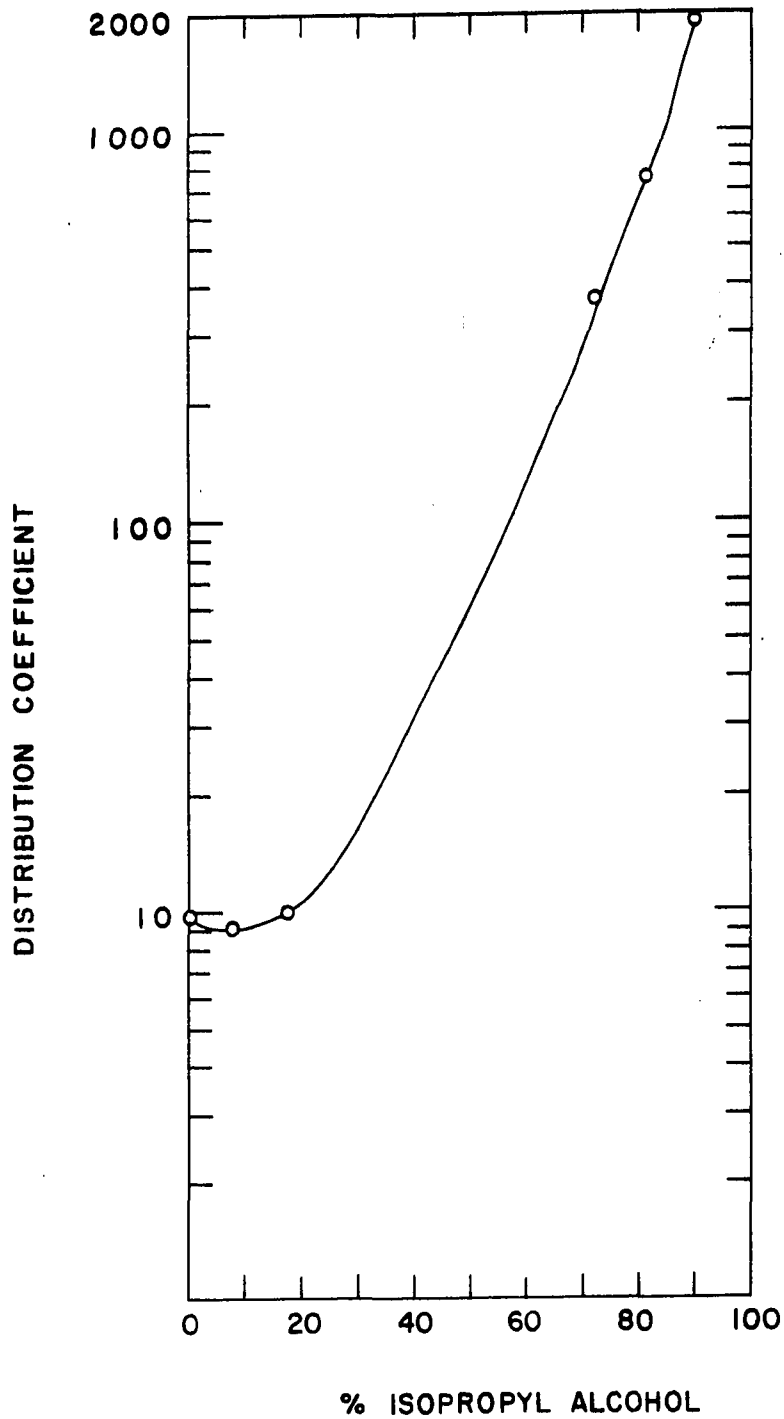


Figure 16. Distribution coefficients of vanadium(IV) as a function of isopropyl alcohol concentration at 1 M HF

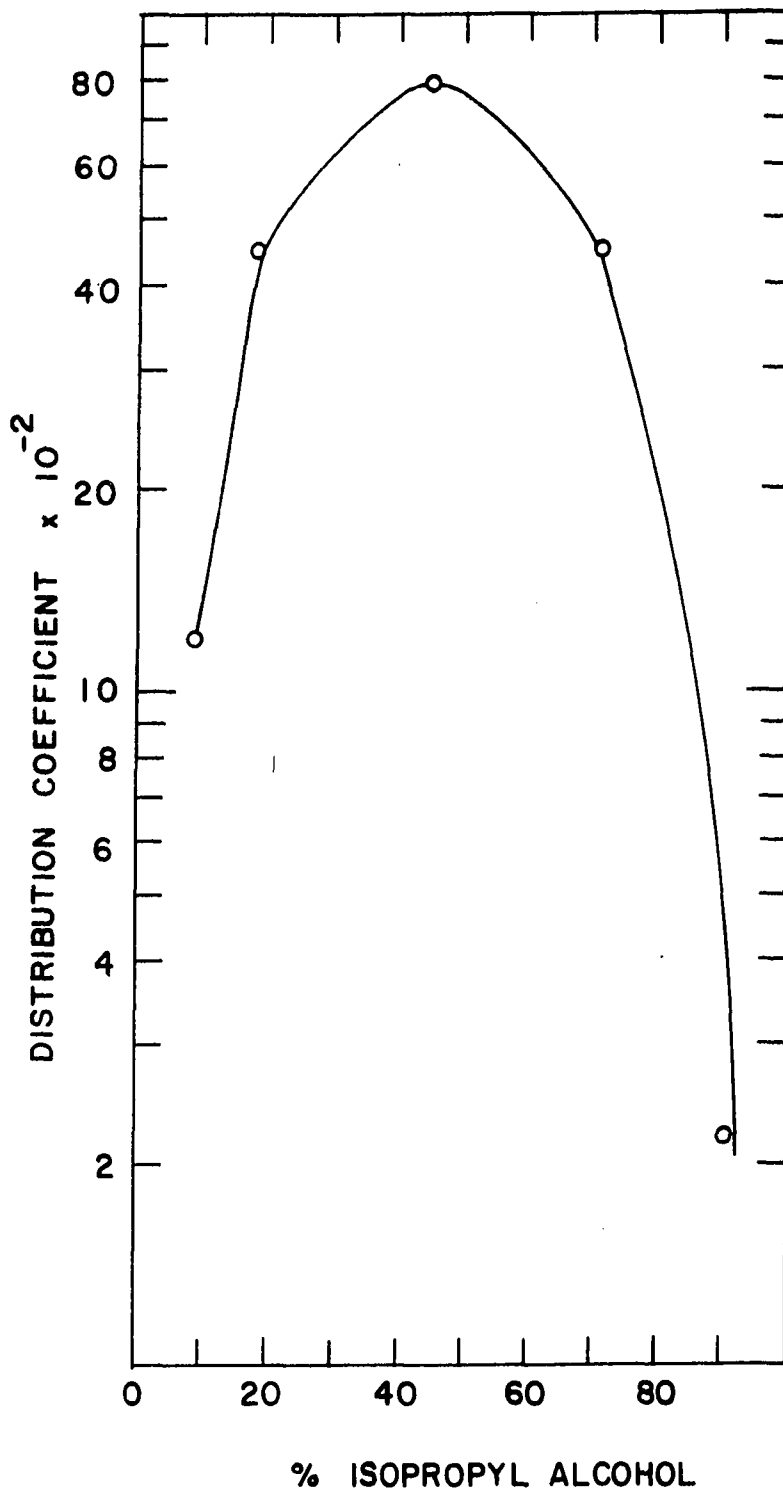


Figure 17. Distribution coefficients of zinc(II) as a function of isopropyl alcohol concentration at 1 M HF

fluoric acid. Over this entire range they were less than one which indicates that complex or ion-pair formation in the exterior phase is competitive over the entire range. Niobium (V) was also tested on an ion-exchange column using 80% acetone at 0.028 M hydrofluoric acid. With this eluent it was completely eluted from the column in less than 10 ml. confirming the low distribution coefficient.

To study the behavior of aluminum in more detail distribution coefficients on cation-exchange resin were determined as a function of organic solvent content at 0.068 M and 0.028 M hydrofluoric acid. These concentrations represent ratios of analytical concentration of fluoride to the analytical concentration of aluminum of 16 and 7.2, respectively. The similarity of the results in these cases indicates that incomplete complexation of the aluminum is not a factor in the increase in the distribution coefficient as the per cent organic solvent is increased.

As a further test of the mechanism of sorption of aluminum, distribution coefficients were determined as a function of acetone concentration on Dowex 1 anion-exchange resin in the fluoride form at 0.028 M hydrofluoric acid. These results are shown in Figure 18. This is a ratio of analytical concen-

tration of fluoride to aluminum of 7.2. If the same reasoning is applied to the anion exchange that was used in the cation exchange, it can be seen that as the amount of ionization of hydrofluoric acid in the solution decreases there will be a tendency for the aluminum to react with the hydrofluoric acid in the resin phase which should cause a rise in the distribution coefficient. If the concentration of acetone is increased to the point that ion-pair formation becomes important in the solution, the distribution coefficient on an anion exchanger should increase. This is in agreement with the observed results.

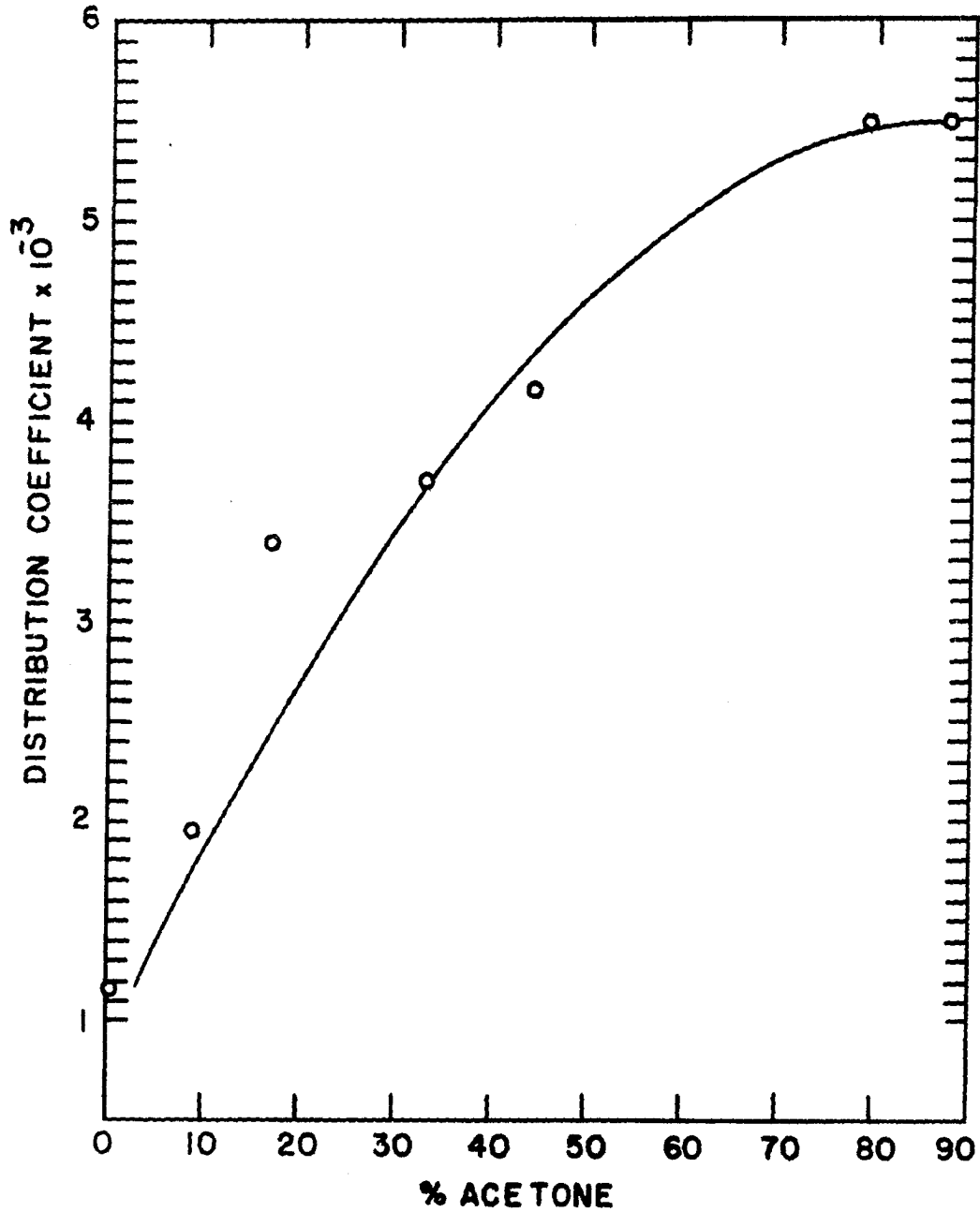


Figure 18. Distribution coefficients of aluminum(III) on Dowex 1 x8 anion-exchange resin as a function of acetone concentration at 0.028 M HF

ANALYTICAL SEPARATIONS

To illustrate the applicability of the batch distribution coefficients to analytical column separations a number of separations were performed. The conditions and results are given in Table 11. These separations were performed on a 1.6 x 10 cm. column of Dowex 50W x 8 (100-200 mesh) hydrogen-form, ion-exchange resin. Flow rates were 3 ml./min. In all cases the resin was treated with only water prior to addition of the sample.

From the distribution coefficients presented and the separations listed, it is apparent that some of a previously reported work (44) is in error. In the previous work it was reported that from a column of approximately the same dimensions as the one used in this work cadmium(II) appears in the 0-20 ml. fraction and manganese(II) in the 180-200 ml. fraction when eluted with 0.1 M hydrofluoric acid. It was also stated that barium(II), calcium(II), cobalt(II), manganese (II), strontium(II), and zinc(II) appear in the 0-20 ml. fraction and mercury(II) in the 40-60 ml. fraction when eluted with 1.0 M hydrofluoric acid. This work is not in agreement with these values and the source of error is not immediately evident. This gives rise to question about separations

Table II. Metal separations on Dowex 50W x 8 (100-200 mesh) hydrogen form using hydrofluoric acid. Column dimensions 1.6 cm. by 10 cm.

Ion mixtures	Eluent	EDTA titrations	
		Theory, ml.	Actual, ml.
Al(III)	150 ml. 0.05 <u>M</u> HF	2.15	2.17
Fe(III)	100 ml. 5 <u>M</u> HF	3.73	3.73
Ti(IV)	85 ml. 0.05 <u>M</u> HF	1.97	1.96
VO(II)	50 ml. 5 <u>M</u> HF	2.07	2.08
Zr(IV)	35 ml. 0.05 <u>M</u> HF	2.15	2.16
VO(II)	50 ml. 5 <u>M</u> HF	2.07	2.09
Fe(III)	100 ml. 2 <u>M</u> HF	3.67	3.64
Cu(II)	100 ml. 3 <u>M</u> HNO ₃	2.15	2.33
WO ₃	Excess H ₂ O ₂		
Al(III)	150 ml. 0.05 <u>M</u> HF	2.13	2.10
Al(III)	40 ml. 0.2 <u>M</u> HF	2.13	2.11
Fe(III)	100 ml. 5 <u>M</u> HF	3.70	3.68
Ti(IV)	30 ml. 0.03 <u>M</u> HF	1.96	1.98
Al(III)	Excess 5 <u>M</u> HF	2.15	2.16
Ti(IV)	30 ml. 0.03 <u>M</u> HF	1.95	1.95
UO ₂ (II)	Excess 5 <u>M</u> HF	2.32 ^a	2.33 ^a
Zr(IV)	30 ml. 0.03 <u>M</u> HF	2.15	2.13
Al(III)	50 ml. 5 <u>M</u> HF	2.14	2.16

^aml. Ce⁺⁴.

involving these elements described in the previously reported work.

Volumes of hydrofluoric acid required for elution of metal ions are given in Table 12. In general, slightly larger volumes should be collected to insure complete recovery.

These volumes were determined on columns which had not been exposed to hydrofluoric acid before elution was begun. By pretreating the column with hydrofluoric acid the volumes required would be decreased. Other concentrations of hydrofluoric acid can be used. The approximate volumes required for elution can be determined from the distribution coefficients using the method previously described.

Elution with hydrofluoric acid might be combined with other methods to give a widely applicable separation scheme. An excellent example of the combination of elution with hydrofluoric acid with other ion-exchange methods has been given by Fritz and Rettig (69). Among the separations they report is the separation of an eleven component mixture by cation exchange. From a 16.0 x 1.2 cm. column of Dowex 50W x 8 cation-exchange resin, bismuth is eluted with 35 ml. of 60% acetone - 0.5 M HCl, cadmium is eluted with 30 ml. of 40% acetone - 0.5 M HCl, zinc is eluted with 35 ml. of 60%

Table 12. Volumes of aqueous hydrofluoric acid required to elute metal ions from a 1.6 x 10 cm. column of Dowex 50W x 8 (100-200 mesh) hydrogen-form resin

Eluted with			
60 ml. 0.05 <u>M</u> HF	50 ml. 0.2 <u>M</u> HF	100 ml. 2 <u>M</u> HF	Not eluted in 200 ml. 2 <u>M</u> HF
Ti(IV)	Al(III)	Fe(III)	Ca(II)
Zr and Hf(IV)	U(VI)	VO(II)	Be(II)
Sn(IV)	Be(II)		Mn(II)
			Zn(II)
			Cd(II)
			Cu(II)
			Hg(II)
			Sr(II)

acetone - 0.5 M HCl, iron is eluted with 30 ml. of 70% acetone - 0.5 M HCl followed by 30 ml. of 80% acetone - 0.5 M HCl, copper is eluted with 55 ml. of 80% acetone - 0.5 M HCl, cobalt is eluted with 65 ml. of 90% acetone - 0.5 M HCl, the vanadyl ion is eluted with 35 ml. of 0.3% H₂O₂ - 0.01 M HCl, manganese is eluted with 70 ml. of 92% acetone - 0.1 M HCl, aluminum is eluted with 200 ml. of 1.5 M HNO₃, and yttrium is eluted with 200 ml. of 2.0 M HNO₃.

Another useful separation using hydrofluoric acid involves elements which form strong peroxide complexes as well as fluoride complexes. Niobium, tantalum, and tungsten are eluted from a cation-exchange column with hydrogen peroxide.¹ This fact can be used to separate these elements from others which form strong fluoride complexes. After elution of niobium, tantalum, or tungsten with hydrogen peroxide, elements such as zirconium and titanium can be eluted with hydrofluoric acid. Other elements can then be eluted with more concentrated hydrofluoric acid or another eluting agent to provide a separation of a complex mixture.

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