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Cation Exchange Separation of Metal Ions Using HF-H_3BO_3 Media

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Using hydrofluoric-boric acid media, a new cation exchange method for the mutual separation of metals which form stable fluoride complexes has been developed. The addition of boric acid to a hydrofluoric acid solution reduces the free fluoride ion concentration to about one hundredth because of the formation of fluoroboric acid. This reduction of the free fluoride ion concentration makes it easy to control the formation of metal fluoride complexes, favoring their separation. As the fluoroboric acid has a buffer action relating to the fluoride ion concentration, the distribution coefficients of metal ions are not affected by the increase in the concentrations of metal ions, even at a low concentration of fluoride ions in the solution. By the use of hydrofluoric-boric acid media, such metals as zirconium, titanium, aluminium, and uranium can be separated from each other. The distribution coefficients of eighteen metals were investigated both in hydrofluoric acid and hydrofluoric-boric acid solutions.

Although the ion exchange method in hydrofluoric acid solutions has been widely used for the separation of metals, most of the works have used anion exchange resin in mixed media of hydrofluoric and hydrochloric[1–4] or nitric[5,6] acids. In the absence of hydrochloric or nitric acid, separation can be done to only two groups,[7–9] that is, metals which form stable fluoride complexes and others. The presence of Cl^- or NO_3^- is believed to be effective in differentiating the adsorbabilities of metal fluoride complexes to the anion exchange resin.[6,10] In more than 0.1 M (1 M=1 mol dm^{-3}) of hydrofluoric acid, metals which form stable fluoride complexes, namely hard acid-metals,[11] form highly fluorinated complexes, such as ZrF_6^{2-}, TiF_6^{2-}, and AlF_6^{3-}, and the difference in the adsorbabilities of these complexes either on cation or anion exchange resin is not large enough to separate them from one another.

If the concentration of hydrofluoric acid can be controlled to a certain value far less than 0.1 M, at which such lower fluorinated complexes as ZrF_5^-, TiF_3^+, and AlF^{2+} are formed, the mutual separation of metals based on the difference in the charges of the fluoride complexes may be expected. However, it is not easy to control hydrofluoric acid to a constant concentration of less than 0.1 M in practical operations including the dissolution of the sample in hydrofluoric acid.

By adding boric acid, which is widely used as a masking agent for fluoride ions, the present author has now succeeded in controlling the fluoride ion concentration without reducing the total hydrofluoric acid concentration (C_{HF}). Boric and fluoroboric acids themselves do not form stable complexes with metal ions in acidic solutions, and fluoroboric acid can easily be removed from the solution by evaporation. Hydrofluoric–boric acid media have the practical advantage that the concentration of the free fluoride ion is almost unchanged with the amount of metal ions which consume fluoride ions.

In the present work, cation exchange adsorption data for metal ions in hydrofluoric–boric acid media are investigated in comparison with the data in hydrofluoric acid, and a new mutual-separation method for hard acid-metals is developed using hydrofluoric–boric acid media.

Experimental

Chemicals and Apparatus. Standard solutions of metal ions (0.01 M) were prepared by dissolving the materials described below in 13 M HF with and without the addition of a small amount of nitric acid or hydrochloric acid: V(IV) from $VOSO_4 \cdot 3H_2O$, V(V) from NH_4VO_3, W(VI) from $Na_2WO_4 \cdot 2H_2O$, Mo(VI) from $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, Nb(V) from Nb_2O_5, and others from metals. After dissolution, the concentration of the residual hydrofluoric acid in each solution was adjusted to about 0.2 M.

A Shimadzu UV-210 spectrophotometer and a Nippon Jarrell-Ash AA-855 atomic absorption spectrophotometer were used for the determination of the metals.

Ion Exchange Resin. A sulfonated, polystyrene-type, strongly acidic cation exchange resin, Diaion SK #1, a product of Mitsubishi Chemical Ind., Ltd. (8% DVB, 75 to 150 μm, H+-form), was used. After the resin had been washed in a column with sufficient volume of 4 M hydrochloric acid and with distilled water until the effluent was free from chloride, it was dried to a constant weight at 105 °C and stored in a vacuum desiccator.

Determination of Distribution Coefficient. A sample solution containing 2×10^{-4} M of a metal ion and a definite concentration of hydrofluoric acid or hydrofluoric-boric acid was prepared. Fifty ml of the solution was added onto 0.500 g of the dried resin in a 150-ml polyethylene bottle, and the bottle was shaken gently for 24 h at room temperature (the equilibrium was attained within 4 h). After the filtration of the resin, the metal ion concentration in the solution was determined by means of a suitable method (*cf.* Table 1).

The distribution coefficient, K_d, was determined by means of the following equation:

$$K_d = (\text{Amount of metal ion in resin/Amount of metal ion in solution}) \times (\text{ml of solution/g of resin}) \quad (\text{ml/g}).$$

Column Operation. About 4 g of dry-form resin which had been swelled well with distilled water was packed in a polyethylene column (10 mm $\phi \times$ 120 mm), and the column was conditioned with about 50 ml of an eluent (with a definite concentration of hydrofluoric acid or hydrofluoric-boric acid the same as in the test solution). After the addition of 10 ml of a test solution containing from 1 to 5 mg of a metal ion, the same eluent was passed through the column. The effluent was collected with a fraction collector, and the concentration of the metal ion in each fraction was determined by the method shown in Table 1.

Results

Distribution Coefficients. The distribution coefficients of 18 elements for cation exchange resin (Diaion SK #1) in hydrofluoric acid and hydrofluoric–0.65 M boric acid media are shown in Tables 2 and 3, along with the stability constants of metal fluoride complexes (log K_1). The metals are arranged in the order of the K_d values in 0.1 M hydrofluoric acid. The K_d values of zirconium, titanium, aluminium, and uranium were investigated more precisely, as is shown in Fig. 1. In both media, the K_d values of metals increased with a decrease in the hydrofluoric acid concentration. The effect of the boric acid concentration on the K_d values is not so great as that of the hydrofluoric acid concentration. For example, when the boric acid concentration was changed from 0.65 M to 0.4 M in 0.2 M HF media, the K_d values of Ti(IV) and Al(III) were decreased to 42 and 420 from 77 and 580 respectively.

Ringbom[12)] described how the ion exchange separation of two metals by the column filtration method

TABLE 1. METHODS USED FOR THE DETERMINATION OF METAL IONS

Metal ion	Method
Co(II), Cd(II), Mn(II), Fe(III), Al(III), V(IV), V(V), Cr(III), Ni(II), and Cu(II)	Atomic absorption spectrometry
Sn(IV) and Mo(VI)	Oxine extraction-photometry[a),b)]
U(VI)	Arsenazo III photometry[c)]
W(VI)	Thiocyanate photometry[d)]
Zr(IV) and Hf(IV)	Xylenol Orange photometry[e)]
Ti(IV)	Diantipyrylmethane photometry[f)]
Nb(V)	Sulfochlorophenol S photometry[g)]
Ta(V)	4-(2-Pyridylazo)resorcinol photometry[h)]

a) H. Hashitani *et al.*, *Bunseki Kagaku*, **16**, 478 (1967). b) K. Motojima *et al.*, *Bunseki Kagaku*, **11**, 47 (1962). c) K. Motojima *et al.*, *Bunseki Kagaku*, **18**, 208 (1969). d) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd ed, Interscience, New York (1959), p. 886. e) K. L. Cheng, *Talanta*, **2**, 61 (1959). f) H. Ishii, *Bunseki Kagaku*, **16**, 110 (1967). g) H. Hashitani *et al.*, *Bunseki Kagaku*, **24**, 303 (1975). h) R. Kajiyama *et al.*, *Bunseki Kagaku*, **15**, 153 (1966).

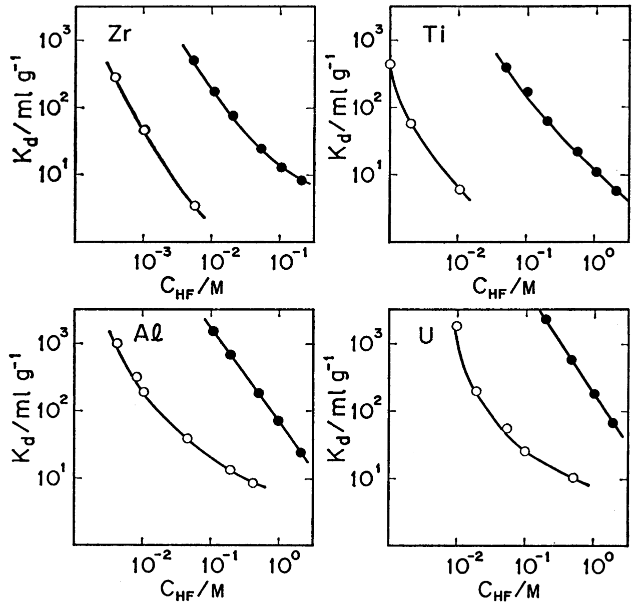

Fig. 1. Distribution coefficients of Zr(IV), Ti(IV), Al(III), and U(VI) in HF (○) and HF–H_3BO_3 (●) media. [H_3BO_3]: 0.65 M.

TABLE 2. CATION-EXCHANGE DISTRIBUTION COEFFICIENTS OF METAL IONS IN HF

Metal ion	HF (M) 0.1	0.2	0.5	1.0	2.0	log K_1[14)]
Cd(II)	$>5\times10^3$	$>5\times10^3$	$>5\times10^3$	$>5\times10^3$	2.5×10^3	0.5
Co(II)	$>5\times10^3$	$>5\times10^3$	$>5\times10^3$	$>5\times10^3$	2.0×10^3	—
Mn(II)	$>5\times10^3$	$>5\times10^3$	$>5\times10^3$	$>5\times10^3$	1.9×10^3	0.7
Ni(II)	$>5\times10^3$	$>5\times10^3$	$>5\times10^3$	$>5\times10^3$	1.6×10^3	0.7
Cu(II)	$>5\times10^3$	$>5\times10^3$	$>5\times10^3$	$>5\times10^3$	1.5×10^3	1.0
V(IV)	420	180	80	31	13	3.0
Fe(III)	192	50	10	5	3	5.0
Cr(III)	45	32	25	11	10	4.5
V(V)	30	16	10	3	3	—
U(VI)	20	12	10	8	5	4.5
Al(III)	9	8	7	6	5	6.0
Ti(IV)	3	3	3	3	<3	6.5
Zr(IV)	3	3	3	3	<3	9.1
Hf(IV)	3	3	3	3	<3	—
W(VI)	<3	<3	<3	<3	<3	—
Mo(VI)	<3	<3	<3	<3	<3	—
Sn(IV)	<3	<3	<3	<3	<3	—
Nb(V)	<3	<3	<3	<3	<3	—
Ta(V)	<3	<3	<3	<3	<3	—

TABLE 3. CATION-EXCHANGE DISTRIBUTION COEFFICIENTS OF METAL IONS IN HF–0.65 M H_3BO_3 MEDIA

Metal ion	HF (M)				
	0.1	0.2	0.5	1.0	2.0
Fe(III)	$>5\times10^3$	$>5\times10^3$	4.5×10^3	800	177
Cd(II)	$>5\times10^3$	$>5\times10^3$	2.8×10^3	730	185
Mn(II)	$>5\times10^3$	$>5\times10^3$	2.5×10^3	581	164
Co(II)	$>5\times10^3$	$>5\times10^3$	2.4×10^3	562	154
Ni(II)	$>5\times10^3$	$>5\times10^3$	2.6×10^3	657	118
Cu(II)	$>5\times10^3$	$>5\times10^3$	1.9×10^3	427	97
Cr(III)	$>5\times10^3$	$>5\times10^3$	1.8×10^3	284	145
U(VI)	4.3×10^3	2.1×10^3	580	180	63
V(IV)	2.0×10^3	1.3×10^3	480	190	66
Al(III)	1.6×10^3	580	180	63	20
Ti(IV)	181	77	21	11	7
V(V)	125	90	68	60	58
Mo(VI)	16	10	7	5	3
Sn(IV)	15	7	6	5	3
Zr(IV)	13	10	8	4	<3
Hf(IV)	11	8	6	4	<3
W(VI)	10	6	5	3	<3
Nb(V)	10	8	6	5	<3
Ta(V)	10	6	5	<3	<3

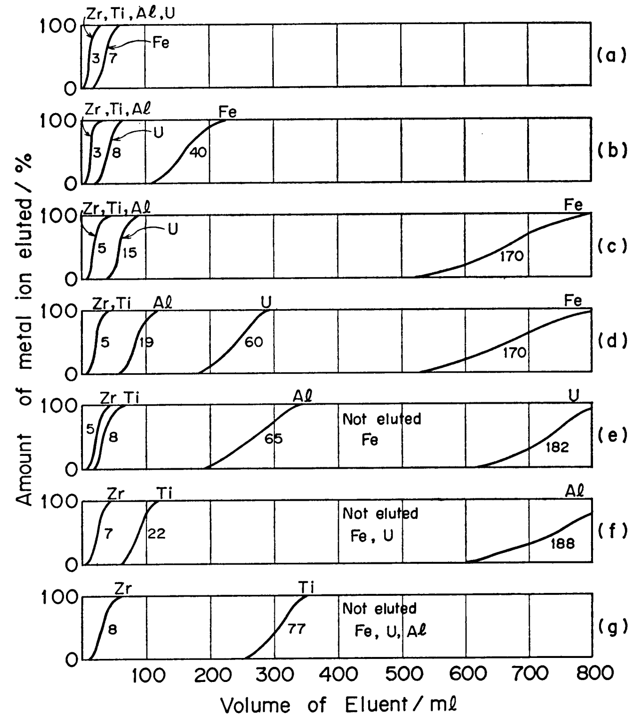

Fig. 2. Column elution behavior of metal ions in HF and HF–H_3BO_3 media.
Diaion SK #1: 4 g, flow rate: 1.2 ml/min. Figures in each column are K_d values obtained. (a): 0.5 M HF, (b): 0.2 M HF, (c): 0.1 M HF, (d): 2 M HF–0.65 M H_3BO_3, (e): 1 M HF–0.65 M H_3BO_3, (f): 0.5 M HF–0.65 M H_3BO_3, (g): 0.2 M HF–0.65 M H_3BO_3.

can be achieved when the K_d value of one ion is larger than from 10^2 to $10^{2.5}$ and that of the other is less than from $10^{0.5}$ to 10^1.

According to Ringbom's criterion, the following can be expected for the column-elution behavior of metal ions from the K_d values in Tables 2 and 3: (1) In 2 M hydrofluoric acid, Cd(II), Co(II), Mn(II), Ni(II), and Cu(II) are retained in the column. In addition to these metals, V(IV) and Fe(III) are retained in 0.5 M and 0.1 M HF respectively. The adsorptions of Cr(III), V(V), and U(VI) are not quantitative, not even in 0.1 M. Other metals are not retained in the range from 0.1 to 2 M. (2) In hydrofluoric acid media, the number of elements retained in the column increases. In 2, 0.5, or 0.1 M HF containing 0.65 M H_3BO_3, Cr(III) and Fe(III), U(VI) and Al(III), or Ti(IV) and V(V) are retained respectively, in addition to the metals which are retained in the respective concentration of the hydrofluoric acid medium. Hard acid-metals, such as Zr(IV), Hf(IV), Mo(VI), W(VI), Sn(VI), Nb(V), and Ta(V), are not retained at all in either medium. From the K_d values shown in Tables 2 and 3, the possibility of the mutual separation of Zr(IV), Ti(IV), and Al(III) can be presumed in hydrofluoric–boric acid media

Elution Behavior. In order to ascertain the practical conditions for the separation of metals, the elution behavior of Zr(IV), Ti(IV), Al(III), U(VI), and Fe(III) was investigated in hydrofluoric acid and hydrofluoric–boric acid media using a column filled with 4 g of dry-form resin (10 mm$\phi\times$120 mm). The elution curves are shown in an integrated form in Fig. 2. The inflection points of the elution curves give the volume of the elution maxima (V_{max}, in ml). The K_d values were calculated from the elution maxima using the following relation:[13)]

$$V_{max} = K_d \times w,$$

where w is the weight of dry resin (g). The calculated K_d values shown in Fig. 2 are in good agreement with the K_d values obtained by the batch method shown in Tables 2 and 3. This fact indicates that the elution was carried out while keeping the ion exchange equilibrium at the flow rate used (1.0 to 1.5 ml/min).

In both hydrofluoric acid and hydrofluoric–boric acid media, metal ions are retained more strongly in the column with a decrease in the concentration of hydrofluoric acid. In hydrofluoric–boric acid media, the metals investigated were retained more tightly than in hydrofluoric acid. For example, as may be seen in Fig. 2 (a), Zr(IV), Ti(IV), Al(III), U(VI), and Fe(III) were eluted when 60 ml of 0.5 M HF was passed through the column, while in 0.5 M HF–0.65 M H_3BO_3 (Fig. 2 (f)) Fe(III) and U(VI) were not eluted even when more than 800 ml of the eluent was passed, and Al(III) was retained in the column until 600 ml.

On the basis of the results shown in Fig. 2, a separation scheme for Zr(IV), Ti(IV), Al(III), U(VI), and Fe(III) was designed. These metals were eluted successively by the following solutions: Zr(IV) by 0.2 M HF–0.65 M H_3BO_3, Ti(IV) by 0.5 M HF–0.65 M H_3BO_3, Al(III) by 2.0 M HF–0.65 M H_3BO_3, U(VI)

Table 4. Effect of amount of metal ion on the distribution coefficient by the batch method

Metal ion	Examined		K_d/ml g^{-1}	
	mg	mmol	HF-H_3BO_3	HF
			(0.02—0.65 M)	(10^{-3} M)
Zr(IV)	0.2	2.1×10^{-3}	25	67
	0.5	5.3×10^{-3}	28	97
	2.0	2.1×10^{-2}	30	250
	20.0	2.1×10^{-1}	27	—
			(0.2—0.65 M)	(4×10^{-3} M)
Ti(IV)	1.0	2.1×10^{-2}	77	44
	10.0	2.1×10^{-1}	79	172
	50.0	1.04	75	230
			(1.0—0.65 M)	(0.01 M)
Al(III)	2.0	7.4×10^{-2}	65	106
	20.0	7.4×10^{-1}	63	203
	100	3.7	60	400
			(2.0—0.65 M)	(0.05 M)
U(VI)	1.0	4.2×10^{-3}	63	45
	10.0	4.2×10^{-2}	60	40
	50.0	2.1×10^{-1}	52	40

Dry resin : 4 g, volume of solution : 50 ml.

by 0.1 M HF, and Fe(III) by 0.5 M HF.

Effect of Amounts of Metal Ions on K_d. In the hydrofluoric–boric acid media, the concentration of free fluoride ions is extremely low, as will be discussed in the Discussion section, because the fluoride ions are consumed by the complex formation with boric acid. Therefore, it is considered that the K_d values might be affected by the amount of metal ions as a result of the deficiency of fluoride ions in addition to the loading.

The effect of the amount of metal ions on K_d in the batch method is presented in Table 4. In this experiment, 4 g of the dry resin was used in order to keep the loading less than 0.1, the metal ion solutions were made free from fluoride ions, and the concentration of hydrofluoric acid was chosen so that the K_d values of the metals were between 10 and 100 in solutions containing 1 mg of metal ions.

It is evident that, in hydrofluoric–boric acid solutions, the K_d values are almost unchanged upon variations in the amount of metal ions. On the contrary, in dilute hydrofluoric acid, the K_d values of Zr(IV), Ti(IV), and Al(III) became larger with the increase in the amount of metal ions because of the consumption of free fluoride ions by the metals.

The effect of the amount of zirconium on the column-elution behavior is shown in Fig. 3 as an example. With an increase in the amount of Zr(IV), the elution of Zr(IV) was retarded extensively in 10^{-3} M HF and moderately in 10^{-2} M HF (Figs. 3 (a) and (b)). In 0.1 M HF–0.65 M H_3BO_3, however, the elution of Zr(IV) was hardly affected by an increase in the amount of Zr(IV) up to 250 mg (Fig. 3 (c)). Less than 100 mg of Zr(IV) did not affect the elution of Ti(IV) (Fig. 3 (d)). Although the elution of Ti(IV) is expected to be retarded when the concentration of the fluoride ion is reduced because of the complex formation with a large amount of Zr(IV), the elution of Ti(IV) was slightly accelerated with more than 250 mg of Zr(IV).

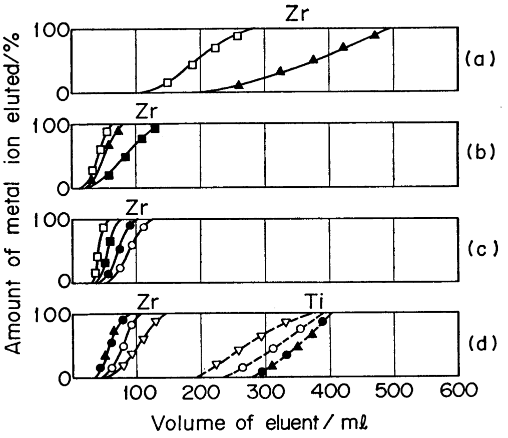

Fig. 3. Effect of amount of Zr(IV) on elution behaviors of Zr(IV) and Ti(IV).
Diaion SK #1: 4 g, flow rate: 1.2 ml/min. (a): 10^{-3} M HF, (b): 10^{-2} M HF, (c): 0.1 M HF–0.65 M H_3BO_3, (d): 0.2 M HF–0.65 M H_3BO_3. Ti: 2 mg, Zr; □: 0.5 mg, ▲: 5 mg, ■: 25 mg, ●: 100 mg, ○: 250 mg, ▽: 500 mg.

Discussion

The experimental results may be summarized as follows:

(1) The K_d values of metals which form stable fluoride complexes are larger in hydrofluoric–boric acid media than in hydrofluoric acid.

(2) The K_d values are scarcely affected by the amount of metal ions in hydrofluoric–boric acid media, whereas they are considerably affected in dilute hydrofluoric acid solutions.

(3) Mutual separations of hard acid-metals using cation exchange resin are possible when hydrofluoric–boric acid solutions are employed as the eluent.

Factors Which Control Cation Exchange Equilibria of Metal Ions in Media Containing Fluoride Ions. The K_d values of metals for the cation exchange resin in a solution involving complexing agent can be expressed by the equation presented by Helfferich.[14] The equation can be rewritten as Eq. 1, considering the adsorption of a metal, M^{n+}, to H^+-form cation exchange resin in a solution containing the fluoride ion as a complexing agent:

$$K_d = \sum_{j=0}^{N} [x_j K^{MF_j}_{(n-j)H}([H^+]_r/[H^+])^{n-j}], \quad (1)$$

$$x_j = [MF_j^{(n-j)+}]/[M^{n+}](1+[F^-]\beta_1+\cdots+[F^-]^N\beta_N)$$
$$= [F^-]^j\beta_j / \sum_{k=0}^{N}([F^-]^k\beta_k), \quad (2)$$

where j is the number of fluoride ions complexed, N is the maximum coordination number of F^- for M^{n+}, β_j is the cumulative stability constant, and r shows the concentration in the resin phase. The $K^{MF_j}_{(n-j)H}$ term is an exchange constant or a selectivity coefficient which indicates the adsorbability of $MF_j^{(n-j)+}$ to H^+-form resin. As is evident from Eq. 1, the K_d value depends on the fraction, x_j, of a species, $MF_j^{(n-j)+}$, in relating to the total metal species, the selectivity coefficient, $K^{MF_j}_{(n-j)H}$, and the concentration ratio of hydrogen ions in the resin and the solution phase.

Assuming that the ion exchange equilibrium is mainly controlled by one kind of cation species, $MF_j^{(n-j)+}$ $(n-j \geq 1)$, Eq. 1 can be simplified to Eq. 1′:

$$K_d = x_j K^{MF_j}_{(n-j)H}([H^+]_r/[H^+])^{n-j}. \qquad (1)'$$

When the amount of metal ion exchanged is negligibly small compared with the capacity of the resin, $[H^+]_r$ is considered to be constant, and, of course, $K^{MF_j}_{(n-j)H}$ is constant. The relation among K_d, x_j, and $[H^+]$ can then be expressed as Eq. 3:

$$\log K_d = \log x_j - (n-j)\log[H^+] + \text{constant}. \qquad (3)$$

The charge of the adsorbed species can be obtained from Eq. 3 by changing the hydrogen ion concentration at a constant fluoride ion concentration and, therefore, at a constant x_j.

Ion Exchange Equilibria of Metals in HF. In Fig. 4, the K_d values of various metals in hydrofluoric acid solutions containing 10^{-4} M of free fluoride ions are illustrated as a function of $[H^+]$. From the log K_d—log $[H^+]$ plots of zirconium, titanium, aluminium, uranium, and iron, the linear relations are obtained with slopes of −1.1, −1.7, −1.9, −1.6, and −2.3 respectively. It is considered from these slopes that species of ZrF_3^+, TiF_2^{2+}, AlF^{2+}, UO_2^{2+}, and FeF^{2+} are mainly adsorbed to the resin in the media mentioned above.

In Fig. 5, the K_d values of zirconium and titanium in hydrofluoric acid solutions of pH 1 are illustrated as a function of the concentration of free-fluoride ions, which is calculated using Eq. 4:

$$[F^-] = [HF]/K_{HF}[H^+] = [HF]/10^3 \times 10^{-1} = 10^{-2}\, C_{HF}, \quad (4)$$

where K_{HF} is the stability constant of hydrofluoric acid. The log K_d linearly increases with the decrease in log $[F^-]$. The K_d values of zirconium and titanium increase from 1 to 100 when $[F^-]$ changes from $10^{-4.0}$ to $10^{-5.2}$ M and from $10^{-3.5}$ to $10^{-4.8}$ M respectively. Figure 5 also presents the relations between x_j and $[F^-]$ for zirconium and titanium, calculated using Eq. 2 and the stability constants given in the tables by Sillen and Martell.[15] From these relations, it follows that ZrF_3^+ and TiF_2^{2+} are the main fractions when $[F^-]$ is about $10^{-5.2}$ or $10^{-4.8}$ M respectively. Therefore, it may be considered that ZrF_3^+ and TiF_2^{2+} are the main species which control the adsorption behavior. This estimation agrees with the results obtained from Fig. 4.

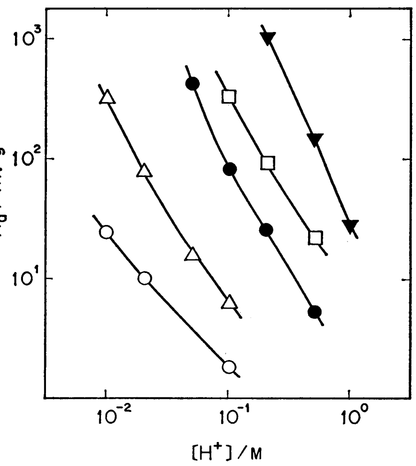

Fig. 4. Relation between K_d and $[H^+]$ in HF at 10^{-4} M $[F^-]$.
○: Zr, △: Ti, ●: Al, □: U, ▼: Fe.

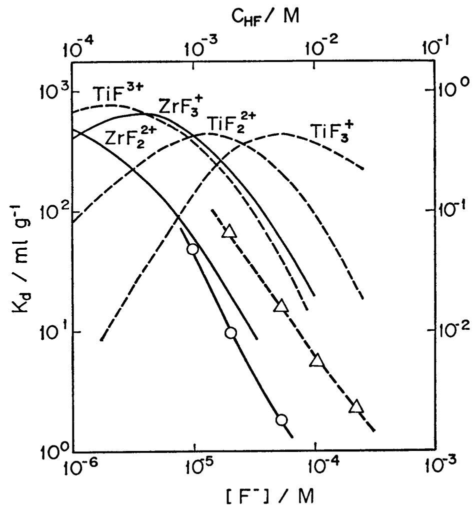

Fig. 5. Relations between changes in K_d in HF at pH 1 and fraction x_j with $[F^-]$.
○: Zr, △: Ti.

Ion Exchange Equilibria of Metals in HF–H_3BO_3 Media. In HF–H_3BO_3 media, $[F^-]$ and $[H^+]$ are calculated according to the chemical equilibria given by the following equations:[15,16]

$$H_3BO_3 + F^- = BF(OH)_3^- \quad (\log\beta_1 = -0.36), \qquad (5)$$

$$H_3BO_3 + 2F^- + H^+ = BF_2(OH)_2^- + H_2O \quad (\log\beta_2 = 7.06), \qquad (6)$$

$$H_3BO_3 + 3F^- + 2H^+ = BF_3OH^- + 2H_2O \quad (\log\beta_3 = 13.69), \qquad (7)$$

$$H_3BO_3 + 4F^- + 3H^+ = BF_4^- + 3H_2O \quad (\log\beta_4 = 19.0), \qquad (8)$$

$$H^+ + F^- = HF \quad (\log K_{HF} = 3.0), \qquad (9)$$

$$HF + F^- = HF_2^- \quad (\log K_{HF_2^-} = 0.6). \qquad (10)$$

The concentrations of hydrogen and fluoride ions in solutions which contain 0, 0.2, 0.4, and 0.65 M H_3BO_3 and various concentrations of hydrofluoric acid (C_{HF}) are summarized in Fig. 6. In the presence of boric acid, $[F^-]$ is extremely low compared with the value in hydrofluoric acid in the absence of boric acid. The reason why K_d in HF–H_3BO_3 media is similar to that in dilute hydrofluoric acid, even at a high concentration of hydrofluoric acid, can be explained by the complex formation of F^- with H_3BO_3 (Eqs. 5 to 8).

For example, the K_d value of titanium in 0.33 M

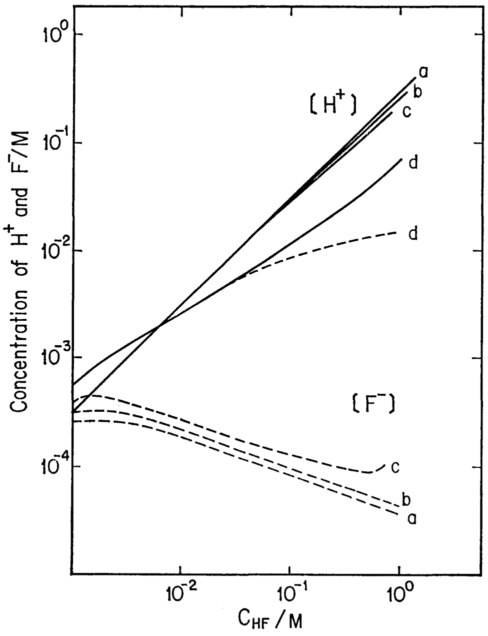

Fig. 6. Calculated concentration of H^+ and F^- in HF-H_3BO_3 media.
[H_3BO_3]; a: 0.65 M, b: 0.4 M, c: 0.2 M, d: 0 M.

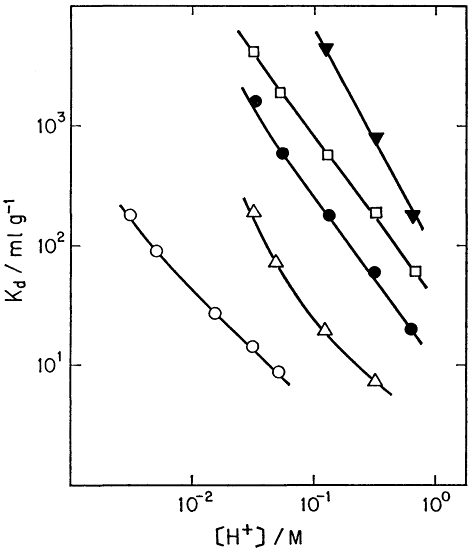

Fig. 7. Relation between K_d and concentration of H^+ in HF-H_3BO_3 media.
[H_3BO_3]: 0.65 M, ○: Zr, △: Ti, ●: Al, □: U, ▼: Fe.

HF-0.65 M H_3BO_3 (pH=1) is nearly equal to that in 3.2×10^{-3} M HF, the pH of which is adjusted to 1 (see Figs. 1 and 5). The concentration of the free-fluoride ion in 0.33 M HF-0.65 M H_3BO_3 is considered to be 5.2×10^{-5} M from Fig. 6, while the [F^-] in 3.2×10^{-3} M HF is 3.2×10^{-5} M from Eq. 4.

As is shown in Fig. 6, [F^-] decreases slightly and [H^+] increases proportionally with the increase in C_{HF} in HF-H_3BO_3 media. From Fig. 5 and Eq. 3, the K_d value should increase with the decrease in [F^-] and should decrease with the increase in [H^+]. It can be seen from Fig. 1 that the K_d values of metals in HF-H_3BO_3 media decrease with the increase in C_{HF}. This indicates that K_d in HF-H_3BO_3 media is not governed by the change in [F^-], but by the change in [H^+].

Using the [H^+] value presented in Fig. 6, the K_d values in HF-H_3BO_3 media given in Fig. 1 were replotted against [H^+] instead of C_{HF}: the relations are shown in Fig. 7. The plots of log K_d—log [H^+] are almost straight lines, the slopes of which are similar to those of the lines in Fig. 4. This fact indicates that the adsorbed species in HF-H_3BO_3 media, in which [F^-] is reduced to about 10^{-4} M, are the same as those in a hydrofluoric acid solution, in which [F^-] is about 10^{-4} M.

Fluoride-ion Buffer Action of HF-H_3BO_3. In HF-H_3BO_3 media, BF_4^- and BF_3OH^- are the main species, as is to be expected from the values shown in Eqs. 7 and 8. If a fluoride ion is consumed by a metal ion, fluoride may be supplied from BF_4^- and BF_3OH^- and the concentration of free fluoride ions in the media may thus be kept constant.

This buffer action is effective when the concentration of metal ions is less than one-fifth of the concentration of hydrofluoric acid. For example, the K_d of zirconium in 0.02 M HF-0.65 M H_3BO_3 is not changed up to 4×10^{-3} M of zirconium (20 mg/50 ml), as is shown in Table 4. The F^- buffer action in HF-H_3BO_3 media is remarkable in the column-elution behavior, not only when the amount of an element is changed, but also when the amounts of other coexisting elements are changed, as is shown in Fig. 3.

The F^- buffer action can be expected even in a hydrofluoric acid solution if the concentration is higher than 0.1 M, but the action is not appreciable in the solution with a concentration of less than 0.1 M used in the present work.

Merits of the Use of HF-H_3BO_3 Media in the Cation Exchange Separation of Metals. Using HF-H_3BO_3 media, a successive cation exchange separation of zirconium, titanium, aluminium, and uranium, which has been found difficult in other media, is possible, as is shown in Fig. 2.

From the point of view of practical analysis, the proposed method has the following advantages:

(1) In the analysis of hard acid-metals, anion exchange methods in HF-HCl or -HNO_3 media have been used for separating them from each other. In these methods, metals that form more stable fluoride complexes, M_{ms}, are retained in the column, while metals that form less stable fluoride complexes, M_{ls}, are eluted from the column. Therefore, in the separation of such M_{ls} as aluminium or titanium in a matrix of such M_{ms} as zirconium, an extremely large amount of the resin and an eluent containing hydrofluoric acid are required.[17] In the proposed method using the cation exchange resin, the separation mentioned above can be attained using relatively small amounts of resin and eluent, because M_{ls} are retained in the column and M_{ms} are eluted from the column. The successive elution of impurities retained in the column after eluting matrix elements is also possible. The F^- buffer action of HF-H_3BO_3 media and the reduction of the fluoride-ion concentration with H_3BO_3 are effectively used in the proposed method.

(2) Generally, metals and alloys containing hard acid-metals as the main components are dissolved with the aid of hydrofluoric acid. It is not easy to control the concentration of hydrofluoric acid in the resulting solution to a constant concentration of less than 0.1 M. In HF–H_3BO_3 media, however, it is not so hard to adjust the hydrofluoric acid concentration to the desired value, because separation is carried out at more than 0.1 M HF.

In this connection, the fluoroboric acids in the effluent can easily be evaporated prior to the subsequent determination.

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References

1) K. A. Kraus and G. E. Moore, *J. Am. Chem. Soc.*, **73**, 9, 13, 2900 (1951).

2) J. L. Hague, E. D. Brown, and H. A. Bright, *J. Natl. Bur. Stand.*, **53**, 261 (1954).

3) J. B. Headridge and E. J. Dixon, *Analyst (London)*, **87**, 32 (1962).

4) J. I. Kim, H. Lagally, and H. -J. Born, *Anal. Chim. Acta*, **64**, 29 (1973).

5) E. A. Huff, *Anal. Chem.*, **36**, 1921 (1964).

6) L. Danielsson, *Acta Chem. Scand.*, **19**, 1859 (1965).

7) J. P. Faris, *Anal. Chem.*, **32**, 520 (1960).

8) J. S. Fritz, B. B. Garralda, and S. K. Karraker, *Anal. Chem.*, **33**, 882 (1961).

9) J. Korkish and A. Huber, *Talanta*, **15**, 119 (1968).

10) K. A. Kraus and F. Nelson, "Special Technical Publication," American Society for Testing Materials, Philadelphia (1958), No. 195, p. 27.

11) R. G. Pearson, *J. Chem. Educ.*, **45**, 581, 643 (1968).

12) A. Ringbom, "Complexation in Analytical Chemistry," Wiley-Interscience, New York (1963), p. 229.

13) Ref. 12, p. 220.

14) F. Helfferich, "Ion Exchange," McGraw-Hill, New York (1962), p. 202.

15) L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London (1964 and 1971), Special Publication Nos. 17 and 25.

16) R. E. Mesmer, K. M. Palen, and C. F. Baes, Jr., *Inorg. Chem.*, **12**, 89 (1973).

17) H. Freund and F. J. Miner, *Anal. Chem.*, **25**, 564 (1953).