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A Novel Quantitative Separation of Cr(III) from Numerous Metal Ions on β-Stannic Arsenate Thin Layers in DMSO–HCl Systems

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Abstract

This paper deals with the thin-layer chromatography of metal ions on β-stannic arsenate using dimethylsulfoxide solvent system. A novel quantitative separation of Cr(III) has been developed on these thin layers. The method is precise and accurate and can be applied for the quantitative separation of Cr(III) from mixtures containing Cu, Nb, Ta, Ce, Ni, Co, Al, Zn, Mn, Th, La, Cd, and Pt. A mechanism dealing with this separation is also been presented based on the kinetic inertness of Cr(III), the properties of DMSO, and the selectivity of β-stannic arsenate.

INTRODUCTION

The separation of Cr(III) from numerous metal ions is important in industry and in medicinal chemistry. It has been associated in carcinogenic hazards (*1*, *2*) and hence elaborate procedures have been developed for the determination of the element in biological samples (*3–6*). Of the various separation procedures, ion exchange is probably the most versatile as it can be used for the selective separation of metal ions on a micro as well as on a macroscale. Chromium is usually separated (*7–10*) by ion exchange as Cr(VI). Procedures for ion-exchange separations of Cr(III) are rare. Fritz and Latwesen (*11*) separated Cr(III) quantitatively as an anionic complex with H_2SO_4 on Dowex-50W × 8 resin in the H^+ form. Mulokozi and Mosha (*12*) have also separated the element in the trivalent state from Fe(III) and Al(III) only. Fe(III) and Al(III) were eluted with 2% oxalic acid. The desorption of Cr(III) from the column was difficult and hence it was desorbed after converting it to Cr(VI) with alkaline sodium peroxide.

We have developed a method which can be used to separate Cr(III) from numerous metal ions on stannic arsenate layers. The following pages summarize the results of our study.

EXPERIMENTAL

Reagents

Stannic chloride pentahydrate (Poland), sodium dihydrogen arsenate (Reidel, Germany), and dimethylsulfoxide (B.D.H., England) were used. All other chemicals were of Analar grade.

Test Solutions

The ions for test solutions, unless otherwise stated, were taken in the following valence states:

Monovalent	Ag, Tl
Divalent	Co, Ni, Cu, Zn, Pd, Cd, Pb, Mn, Hg
Trivalent	Cr, Fe, Sb, La, Ce, Au, Bi, In, Ga, Al
Tetravalent	Se, Zr, Th, Pt, Ti
Pentavalent	V, Ta, Nb
Hexavalent	Mo, W, U

The test solutions were taken as nitrates as far as possible for use with solvent systems containing nitric acid. Sb, Au, Bi, and Ti were taken as chlorides. When HCl-containing solvent systems were used, most cations were taken as chlorides. Tantalum and niobium were dissolved by fusing their pentoxides with sodium carbonate and potassium nitrate, and dissolving the solid mass in concentrated sulfuric acid. Vanadium pentaoxide was dissolved in dilute NaOH solution. Sodium selenite, sodium molybdate, and sodium tungstate were dissolved in distilled water.

Detectors

Hydrogen sulfide, alizarine Red S, dimethylglyoxime, stannous chloride, pyrogallol, potassium ferrocyanide, chromotropic acid, and diphenylcarbazide were used to detect the various ions by their usual color reactions. Al, Zn, and Mn were detected by treating with oxime and observing the characteristic fluoroscence under UV radiations.

Apparatus

The thin-layer chromatography (TLC) applicator of Toshniwal (India) was used to prepare thin layers on 20 × 3.5 cm glass plates. Glass jars (24 × 6 cm) were used for development.

Solvent Systems

The following solvent systems were used in these studies.

$$\text{DMSO} + 4\ M\ \text{HNO}_3\ (1:1)$$

$$\text{DMSO} + 1\ M\ \text{HCl}\ (1:1)$$

$$\text{DMSO} + 1\ M\ \text{HCl}\ (1:4)$$

$$\text{DMSO} + 1\ M\ \text{HCl}\ (4:1)$$

$$\text{DMSO} + 4\ M\ \text{HCl}\ (1:1)$$

$$\text{DMSO} + 6\ M\ \text{HCl}\ (1:1)$$

Preparation of Thin-Layer Plates

β-Stannic arsenate was prepared by mixing 0.05 *M* solutions (*13*) of stannic chloride and sodium arsenate in a volume ratio of 3 : 2 and digesting the resulting precipitate at room temperature for 24 hr. After filtering and drying the precipitate was cracked in demineralized water and then placed in 2 *M* HNO_3 to convert it to the H^+ form. The material was finally washed with demineralized water and dried at 40°C. One hundred grams of stannic arsenate granules thus obtained were mixed in about 50 ml of distilled water and the slurry was made by grinding the mixture vigorously in a glass mortar for a long time. This step proved to be very important for complete adhesion. The grinding of the granules must be complete and the slurry should be in the form of a fine paste without any solid particles.

The slurry was then spread over the clean glass plates with the help of the applicator to give 0.1 mm thick layers. The plates were ready for use after drying at room temperature.

Procedure

For Qualitative Works

Cation solutions were spotted on the plates which were developed in the chosen solvent system by the ascending technique. The ascent of the solvent was fixed at 10 cm in all cases. After development the plates were dried and the cation spots were detected using the appropriate spraying reagent.

For Quantitative Work

The stock solution of chromium chloride containing 4×10^4 μg/ml was prepared. It was diluted 200 times. Twenty microliters of the solution containing 4 μg of Cr was then applied to β-stannic arsenate plates. The other cations to be separated were also applied in the amounts shown in Table 3. After the spot was dried the plate was developed in DMSO + 6 *M* HCl (1:1) until the developer ascended 10 cm on the plate. A pilot plate was run simultaneously in order to locate the exact position of the Cr(III) spot with the help of the coloring reagent. The area on the working plate corresponding to the detected spot on the pilot plate was scratched and chromium was washed out several times with 0.5 *N* H_2SO_4 at room temperature ($\approx$25°C) to ensure complete elution. This step needed about 25 ml of the acid solution. The volume of the solution was then reduced to about 10 ml by heating on a hot plate. It was cooled and 0.5 ml of 0.1 *N* $KMnO_4$ was added to oxidize (*14*) Cr(III) into Cr(VI). Three to five drops of 50% sodium azide were then added to decolorize the brownish tint. The solution was transferred into a 25-ml volumetric flask and 1 ml of diphenylcarbazide solution was added followed by 2 ml of NaH_2PO_4 solution. The absorbance of this color was measured at 540 mμ and the amount of Cr(III) was obtained from the calibration curve (*15*).

RESULTS

The R_F values in the various solvent systems are summarized in Table 1. When $R_L - R_T > 0.3$ it was considered as tailing and referred to in the table as *T*. The separations achieved are listed in Table 2. Table 3 summarizes the quantitative separation of Cr(III) in binary mixtures as well

TABLE 1

The R_F Values of Some Ions in DMSO Systems

		Solvent composition					
Sample no.	Ion	DMSO + 1 M HCl (4:1)	DMSO + 1 M HCl (1:1)	DMSO + 1 M HCl (1:4)	DMSO + 6 M HCl (1:1)	DMSO + 4 M HCl (1:1)	DMSO + 4 M HNO_3 (1:1)
1	Ag	0.00	0.00	0.00	—	—	0.05
2	Tl	0.05	0.08	0.00	—	—	0.00
3	Co	0.00	*T*	0.80	0.95	0.00, 0.97	0.95
4	Ni	0.05, 1.00	*T*	0.83	0.95	0.00, 0.96	0.98
5	Cu	0.00	*T*	0.56	0.89	0.00, 0.96	0.92
6	Zn	0.00	0.77	0.00	0.82	0.80	0.90
7	Pd	*T*	*T*	0.00, 0.90	—	—	0.00, 0.97
8	Cd	0.00	0.80	0.80	0.90	0.91	0.81
9	Pb	*T*	*T*	0.05	—	—	0.17
10	Mn	0.00	0.75	0.00	0.82	0.80	0.90
11	Hg	*T*	*T*	0.00, 0.80	*T*	0.89	*T*
12	Cr	0.00	0.00	0.00	0.00	0.00	0.00
13	Fe	0.00	*T*	*T*	*T*	0.00, 0.95	0.00
14	Sb	0.00	0.15	0.05	*T*	*T*	0.00
15	La	0.07	0.96	0.77	0.83	—	0.92
16	Ce	0.00, 0.9	*T*	0.53	0.80	0.88	0.97
17	Au	*T*	0.00, 0.95	0.00, 0.85	0.00, 0.85	0.93	*T*
18	Bi	*T*	0.00	*T*	—	—	*T*
19	In	0.00	—	0.91	—	—	0.95
20	Ga	0.00	0.00	0.90	—	—	0.97
21	Al	0.00	0.60	0.00	0.87	0.82	0.95
22	Se	0.00	0.96	0.00	—	—	0.95
23	Zr	0.00	0.00	0.00	0.15	0.15	0.07
24	Th	0.07	0.86	0.10	0.87	0.87	0.97
25	Pt	0.00, 0.9	0.95	0.90	0.96	0.00, 0.95	*T*
26	V	0.00	0.00	0.00	0.00	0.07	0.00
27	Ta	0.00	0.73	0.70	0.80	0.75	0.92
28	Nb	0.00, 0.96	0.87	0.77	0.90	0.90	0.92
29	Mo	0.05	*T*	0.11	—	—	0.10
30	W	0.00	0.10	0.00	—	—	0.12
31	U	*T*	*T*	*T*	*T*	*T*	0.95
32	Ti	0.07	0.15	0.00	*T*	*T*	0.00
33	Hg(I)	*T*	0.8	*T*	—	—	0.05
34	Fe(II)	0.00	*T*	0.06	—	—	0.00

TABLE 2

Separations Achieved in DMSO–HCl Systems

Solvent system	Separations achieved
DMSO + 6 *M* HCl (1:1)	V(0.00)–Nb(0.90) V(0.00)–Ta(0.80) Cr(0.00)–Cu(0.90) Cr(0.00)–Nb(0.90) Cr(0.00)–Ta(0.90) Cr(0.00)–Ce(0.80) Zr(0.15)–Nb(0.90) Zr(0.15)–Ta(0.80) Cr(0.00)–Co(0.95) Cr(0.00)–Ni(0.95) Cr(0.00)–Zn(0.82) Cr(0.00)–Mn(0.82) Cr(0.00)–Pt(0.96) Cr(0.00)–La(0.83) Cr(0.00)–Th(0.87) Cr(0.00)–Cd(0.90)
DMSO + 4 *M* HCl (1:1)	Cr(0.00)–Al(0.82) Cr(0.00)–Hg(0.89)
DMSO + 4 *M* HNO_3 (1:1)	Zr(0.07)–Th(0.97) U(0.95)–V(0.00)
DMSO + 1 *M* HCl (1:1)	Al(0.6)–In(0.00) Al(0.6)–Ga(0.00)

TABLE 3

Quantitative Separation of Cr(III)

Sample no.	Amount of Cr(III) loaded (μg)	Amount of other metal ion loaded (μg)	Amount of Cr(III) found (μg)	% Error	Standard deviation σ (parts per thousand)
1	4.00	158.625 Cu	4.00	0.00	96.2
2	4.00	233.75 Nb	3.40	+15.00	
3	4.00	453.70 Ta	4.35	−8.70	
4	4.00	350.325 Ce	4.65	−16.20	
5	4.00	146.725 Ni	4.00	0.00	
6	4.00	147.35 Co	3.70	+7.50	
7	4.00	163.40 Zn	4.35	−8.70	
8	4.00	137.325 Mn	3.70	+7.50	
9	4.00	580.32 Th	3.70	+7.50	
10	4.00	347.25 La	3.40	+15.00	
11	4.00	256.025 Cd	4.00	0.00	
12	4.00	67.425 Al	4.35	−8.70	
13	4.00	501.525 Hg	4.65	−16.20	
14	4.00	488.075 Pt	4.35	−8.70	
15	4.00	Mix	4.35	−8.70	
16	3.00	—	2.70	+10.00	
17	2.00	—	2.35	−17.50	

as in a synthetic mixture containing Cu, Nb, Ta, Ce, Ni, Co, In, Mn, Th, La, Cd, and Pt.

DISCUSSION

The selective separation of Cr(III) is a happy consequence of three important effects: (1) the kinetic inertness of Cr(III), (2) the unique properties of DMSO, and (3) the selectivity of the β-stannic arsenate layers. We will discuss them one by one.

The ion-exchange behavior of Cr(III) is characterized by the tendency of the element to be held tenaciously on cation exchange resins so that it is not easily desorbed. This is a consequence of the kinetic inertness of Cr(III) (*16*). In ion exchange the kinetic inertness of chromium has found application in cation exchange separation of the element from others in solutions containing citrate (*11*). The same property was utilized by Mulokozi (*12*) and co-workers to separate Cr(III) from Fe(III) and Al(III). Ligand substitution in aquochromium ion is so slow that Cr(III) is very difficult to elute with oxalic acid which easily elutes Fe and Al by forming anionic complexes with them.

DMSO has certain unique properties, i.e., its high dielectric constant, its ability to solvate metal ions in preference to anions, and a specific solvent effect. This is in contrast to the earlier solvents of low dielectric constant, i.e., butyl alcohol, where the selectivity was due to the favored formation of nondissociated compounds. DMSO, on the other hand, favors the formation of chloro complexes in an HCl medium (*17*).

In order to bring out clearly the effect of solvent composition on the selectivity of a material for the Cr(III) ion, it is useful to define a new quantity "relative selectivity" = R_F of the metal ion/R_F of the Cr(III) ion. This quantity shows the preference of the exchanger for the Cr(III) ion with respect to the metal ion. The greater the preference, the greater is the relative selectivity. A plot of relative selectivity versus the mole fraction of DMSO for different metal ions is given in Fig. 1. These curves show that the relative selectivity is low in two cases: (1) when the mole fraction of DMSO > 0.4, and (2) when the mole fraction of DMSO $<$ 0.1. In the former case the movement of both ions is very small and hence the relative selectivity is approximately equal to 1. In the latter case both the ions move to a large extent and again the relative selectivity is approximately 1. When, however, the mole fraction of DMSO is less than 0.4 and greater than 0.1, the relative selectivity is high and some interesting results are obtained. It is in this range that the solvent system is most

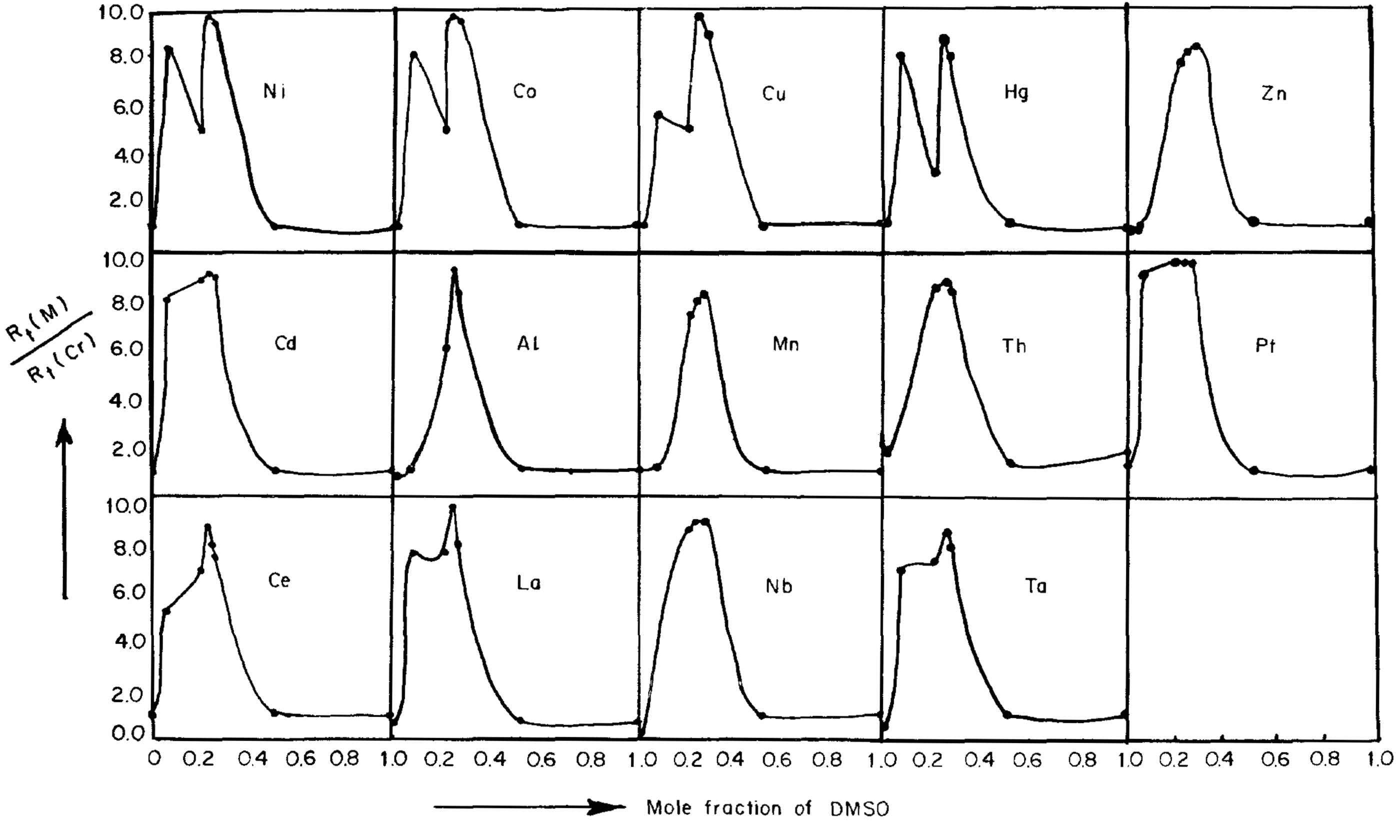

FIG. 1. Plot of relative selectivity vs the mole fraction of DMSO.

effective and Cr(III) can be separated from numerous metal ions. We will now explain the shape of these curves. When the mole fraction of DMSO is zero, we have pure 0.5 *M* HCl and most of the ions have high values owing to the high H^+ ion concentration and the complex formation due to Cl^- ions. When the DMSO concentration is very high there is no significant movement of the ions because the $[H^+]$ and $[Cl^-]$ concentrations are very small and the solvent behaves essentially as pure DMSO. In the range $0.1 < \text{DMSO} < 0.4$ the ion exchanger is selective for Cr(III) ions. This explanation holds for almost all ions depicted in Fig. 1. However, the ions are of two types: (1) those which have a minimum in the middle of the curve, i.e., Cu, Co, Ni, and Hg; and (2) those which do not have a minimum, i.e., Mn, Zn, Al, etc.

The curves of relative R_F versus mole ratio of DMSO have two maxima and one minima for some divalent cations. The distance between the first maximum and the following minimum is defined here as the dip (*D*). The order of the length of the dip is the same as the deviation (*18*) of the ionic radii (Δr_i) from their theoretical value (Fig. 2). This deviation of the ionic radii is affected by the configuration of the ion. It is zero in the case where the electrons in the *d*-orbital are spherical in distribution and the shielding is less (as in the case of Mn and Zn). When the distribution of the *d*-electrons is not spherical and hence the shielding is more (as in the case of Co, Ni, and Cu), there is more deviation from the theoretical value. The same effect may be correlated with the dip in our relative R_F value curves (Fig. 3). The point where we have the first maximum has less DMSO than the point at the minimum. Thus we can say that the DMSO affects the relative R_F values of the cations. The cations which have a spherical distribution of the *d*-electrons, i.e., Mn and Zn, are less affected by the DMSO concentration (length of the dip is low) than the cations having a nonspherical distribution of *d*-electrons and more shielding, i.e., Ni, Co, and Cu. Further, although Co, Ni, and Cu all have a nonspherical distribution, the dip for Ni is greater than the one for Co. This is because Ni has more *d*-electrons nonspherically distributed, i.e., 8, while Co has only 7, resulting in a greater shielding in the case of Ni than in the case of Co.

We find that the maxima in the relative selectivity versus mole ratio plots occur at a mole ratio of 0.3. This is a general property of DMSO. Maxima in the log *D* versus mole percent of DMSO plots occur generally in the vicinity of 30 to 40 mole-%. This is the composition range known to exhibit extreme values for a number of physical properties such as viscosity (maximum), negative enthalpy of mixing (maximum), surface

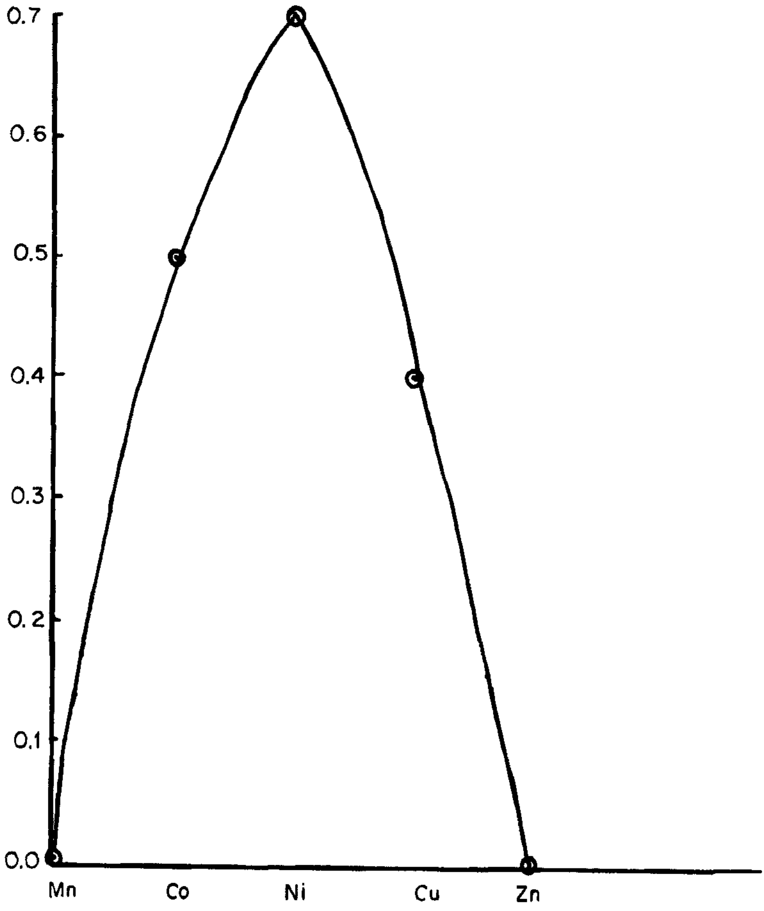

FIG. 2. Deviation of ionic radii from the theoretical value for Mn(II), Co(II), Ni(II), Cu(II), and Zn(II).

tension (minimum), density (maximum), and proton activity (minimum) (*17*).

Two stannic arsenate phases may be distinguished: (1) the α-phase (*19*) with an Sn/As ratio of 1, and (2) the β-phase (*13*) with an Sn/As ratio of 1.84. When the adsorption of the various ions on the α-phase was studied, it was found that Pb, Cr, and Fe showed total adsorption and hence these ions could be easily separated from numerous ions. Therefore, separations of various metal ions from Pb and Fe were developed. How-

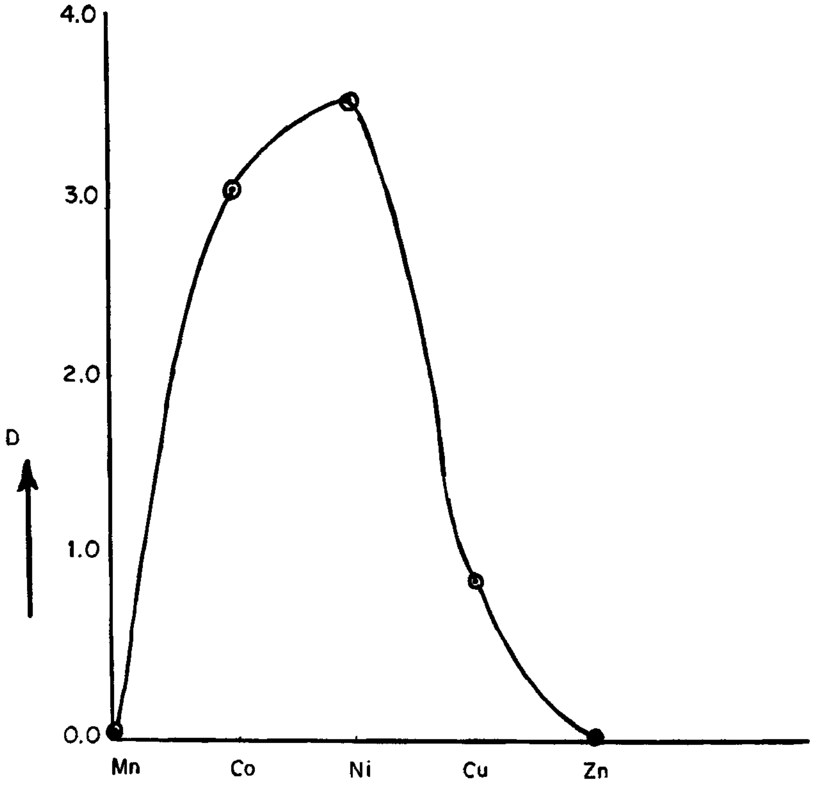

FIG. 3. Plot of the length of the dip (*D*) vs cations.

ever, Cr was irreversibly adsorbed and could not be eluted. It was suggested at the time that the irreversible adsorption of Cr is due to the formation of chromium arsenate. We therefore synthesized chromium arsenate in the hope of obtaining a highly insoluble product, but our hopes were belied when we found that chromium arsenate is comparatively more soluble than other arsenates and dissolves completely in 4 *M* HCl and 4 *M* HNO_3. It was therefore apparent that the irreversible adsorption of Cr was not due to the formation of chromium arsenate but due to some other reason.

When we studied the ion-exchange behavior of β-stannic arsenate we found to our surprise that even though it selectively adsorbs Cr in DMSO–HCl systems, the Cr ions can be easily desorbed in 0.5 *M* HCl. The fact that in the DMSO–HCl system most cations have high R_F values while Cr has a low R_F value is due to the kinetic inertness of Cr(III). This kinetic inertness is lifted in the case of aqueous 0.5 *M* HCl. The question as to why it is lifted in the case of the β-phase but not in the case of the α-phase is difficult to answer at the moment, but it appears that the Sn/As ratio has something to do with it. In the α-phase the Sn/As ratio is low and hence metal ions are strongly attracted to the ligand arsenate. However, in the β-phase the Sn/As ratio is 1.84. Since the metal ions associated with the same number of arsenate ions in this case is higher, additional metal ions are not so strongly bound to the exchange sites and can be desorbed. This conclusion, however, needs further study. It will be interesting to prepare phases of inorganic ion exchangers with varying compositions and to follow the kinetics of adsorption of various ions on these phases as was done by Mulokozi (*12*).

The most important advantage of this work lies in the fact that we have been able to separate Cr(III) quantitatively from the binary mixtures containing larger amounts of other metals such as Cu, Nb, Ta, Se, Co, Ni, Zn, Mn, Pt, La, Th, Cd, Al, and Mg (Table 3). Thus the technique presents a solution to the problem of separating Cr(III) with high precision and accuracy from similar metals. The method works satisfactorily even when we wish to separate Cr from an alloy containing these metals. Some determinations to this effect have actually been performed by preparing a synthetic mixture of these metal chlorides along with Cr and separating the chromium in such a mixture on thin layers of stannic arsenate.

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