

CHROM. 5423

## THIN-LAYER CHROMATOGRAPHIC BEHAVIOR OF A NUMBER OF METALS ON DEAE-CELLULOSE IN ORGANIC SOLVENT-SULFURIC ACID MIXTURES

K. OGUMA AND R. KURODA

*Laboratory for Analytical Chemistry, Faculty of Engineering, University of Chiba, Yayoi-cho, Chiba (Japan)*

(Received May 4th, 1971)

## SUMMARY

The thin-layer chromatographic behavior of a number of metals on DEAE-cellulose and on microcrystalline cellulose, Avicel SF, has been surveyed in binary solvent mixtures containing  $H_2SO_4$  and an organic solvent.  $R_F$  values were measured as a function of the concentrations of  $H_2SO_4$  and the organic solvent. Although ion-exchange adsorption of sulfatocomplexes on DEAE-cellulose can be observed in aqueous  $H_2SO_4$  solutions, enhanced ion exchange is found to occur in binary media containing a protic solvent such as methanol and acetic acid. Even though increased retention of many metals, including sulfatocomplex-forming metals, on DEAE-cellulose can also be observed in  $H_2SO_4$ -aprotic solvent mixtures, such as acetone and dioxane, the mechanism involved is not ion exchange proper, but partition appears to play an appreciable role.

The chromatographic systems developed permit many useful separations of analytical interest to be conducted effectively.

## INTRODUCTION

The paper and thin-layer chromatographic (TLC) behavior of a number of metals on DEAE-cellulose (abbreviated to DEAE) has already been investigated in different binary solvent mixtures consisting of HCl (ref. 1,2),  $HNO_3$  (ref. 3) or HSCN (ref. 4) and an organic solvent.  $R_F$  values of Fe(III),  $ReO_4^-$ , La, In and  $UO_2^{2-}$  on DEAE as well as aminoethyl papers in aqueous  $H_2SO_4$  of varying concentration have been reported by LEDERER AND OSSICINI<sup>5</sup>.

This work has been extended to investigate the TLC behavior of 46 metals on DEAE in binary solvent mixtures containing  $H_2SO_4$ , which should provide a better understanding of the system involving weakly basic ion exchangers. Generally metals forming sulfatocomplexes exhibit a stronger adsorption on DEAE in mixed solvents containing a protic solvent like methanol and acetic acid than that in aqueous  $H_2SO_4$  media.

Although considerable retention of metals on DEAE can be observed in acetone- and dioxane- $\text{H}_2\text{SO}_4$  mixtures, competitive partition may play an important role in the case of metals forming sulfatocomplexes, in addition to the contribution of the ion-exchange process.

The solvent systems investigated permit many useful chromatographic separations of analytical interest to be conducted very effectively on DEAE.

## EXPERIMENTAL

### *Test solutions*

Unless otherwise mentioned 0.1 *M* stock solutions (0.1 *N* in  $\text{H}_2\text{SO}_4$ ) were prepared from the sulfate, oxide or metal. For Ti(IV), Zr, Hf, Hg(II) and In the stock solutions were 3 *N* in  $\text{H}_2\text{SO}_4$ . For Bi(III) and Th, 3 *N*  $\text{HNO}_3$  solutions were prepared using the metal and nitrate, respectively. Stock solutions were adjusted to 0.1 *N* in HCl for platinum metals\* and Au(III), 3 *N* for Sb(III) and 6 *N* for As(III) and Sn(IV). Ammonium or sodium salts of Mo(VI), W(VI), Re(VII), Se(IV) and Te(IV) were simply dissolved in deionized water. For Nb see the previous paper<sup>4</sup>.

### *Preparation of the thin-layer plates*

A cellulose anion exchanger, DEAE (diethylaminoethylcellulose, Serva, for TLC) and a microcrystalline cellulose, Avicel SF (Avicel Sales Division, FMC Corp.) were used as adsorbents. A portion of DEAE, about 6.5 g, slurried with 30 ml of deionized water and 20 ml of 0.5 *M*  $(\text{NH}_4)_2\text{SO}_4$ -0.02 *M*  $\text{H}_2\text{SO}_4$  solution, was placed in a large column, washed with a sufficient volume of the acid sulfate solution above and finally with deionized water. Two 6.5 g portions of DEAE, prepared thus, were combined, slurried with 29 ml of deionized water, and spread to a thickness of 250  $\mu\text{m}$  on five 20  $\times$  20 cm glass plates. The plates were dried 2.5 h at 40° after air-drying for 1 h and stored in a desiccator containing a saturated KBr solution.

For the preparation of the microcrystalline cellulose plates, 18 g of Avicel SF was soaked in 100 ml of deionized water and centrifuged. After slurrying with 30 ml of deionized water, the Avicel SF was spread on five 20  $\times$  20 cm plates to a thickness of 250  $\mu\text{m}$ . The plates were dried and stored as above.

### *Application and detection*

The application procedure was the same as described in the previous paper<sup>4</sup>. The solvent systems investigated were aqueous  $\text{H}_2\text{SO}_4$  solutions of varying concentration, and binary mixtures consisting of an organic solvent and an aqueous  $\text{H}_2\text{SO}_4$  solution of varying concentration. Methanol, acetic acid, acetone and dioxane were used as the organic solvent.

The developing and detection procedures were also the same as before<sup>4</sup>, with the exception of Be, Mg, Ti(IV), Cr(III), Zn, Cd, Al, Ga and In, which were detected by spraying with 1% 8-hydroxyquinoline in ethanol, followed by 15%  $\text{NH}_4\text{OH}$ . UV light was used when necessary.

---

\* Before use we let them stand for 1 till 2 months. See G. BAGLIANO AND L. OSSICINI, *J. Chromatogr.*, 19 (1965) 412 for the effect of ageing on  $R_F$  values of Rh(III), Ir(III) and Ru(III) in HCl solutions of varying concentration.

## RESULTS AND DISCUSSION

*Adsorption from aqueous H<sub>2</sub>SO<sub>4</sub> solutions*

$R_F$  values for 46 metals chromatographed on DEAE and Avicel SF in aqueous H<sub>2</sub>SO<sub>4</sub> solutions are illustrated in Fig. 1 as a function of H<sub>2</sub>SO<sub>4</sub> concentration. As can be seen, the metals, which form sulfatocomplexes and adsorb on a strongly basic resin<sup>6,7</sup>, can also adsorb on DEAE, showing increasing retention with decreasing concentration of H<sub>2</sub>SO<sub>4</sub>. Sc, Ti(IV), Zr, Hf, Nb, Cr(III), Mo(VI), W(VI), Fe(III), Rh(III), Ir(IV), Ga, In, As(III), Bi(III), Se(IV), Th and U(VI) are among those

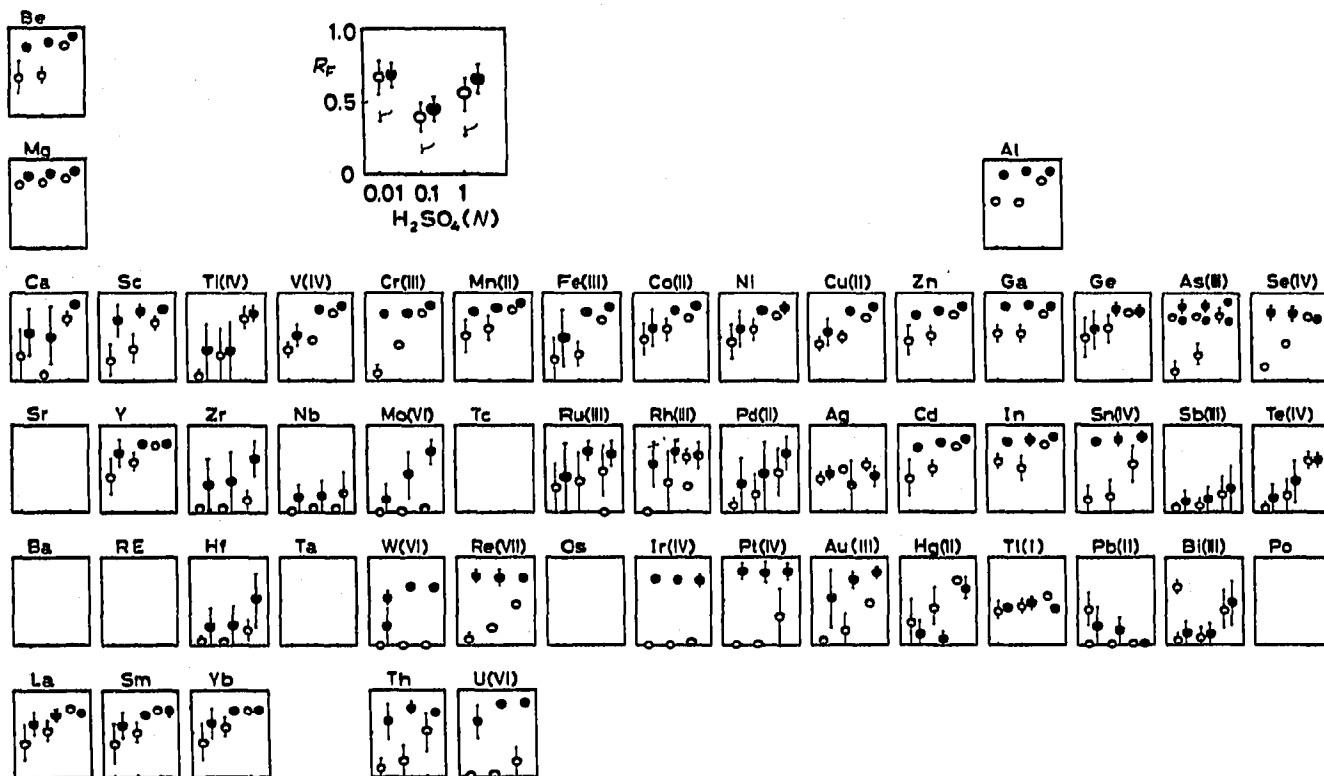


Fig. 1.  $R_F$  values of metals chromatographed on DEAE and Avicel SF in aqueous H<sub>2</sub>SO<sub>4</sub> solutions. ○ = DEAE; ● = Avicel SF. All the  $R_F$  values on the two adsorbents were obtained at the three concentrations of H<sub>2</sub>SO<sub>4</sub>, 0.01, 0.1 and 1N. For convenience,  $R_F$  values on Avicel SF shifted the abscissa arbitrarily to the right.

metals known to exhibit some adsorption on the strongly basic resin in H<sub>2</sub>SO<sub>4</sub> solutions particularly at concentrations less than 1 N. There are marked differences in the  $R_F$  values obtained on DEAE and Avicel SF for the following metals: Zr, Hf, Nb, Mo(VI), W(VI), Re(VII), Rh(III), Ir(IV), Pt(IV), Au(III), Se(IV), Th and U(VI). All of these belong to the group of metals adsorbing on the strongly basic resin.

In the case of Re(VII), Pt(IV) and Au(III) no information is available about their adsorption on the strongly basic resin from H<sub>2</sub>SO<sub>4</sub> or sulfate solutions, but obviously it can be assumed that those metals which exhibit pronounced differences in  $R_F$  between DEAE and Avicel SF adsorb on DEAE by ion exchange in aqueous H<sub>2</sub>SO<sub>4</sub> media.

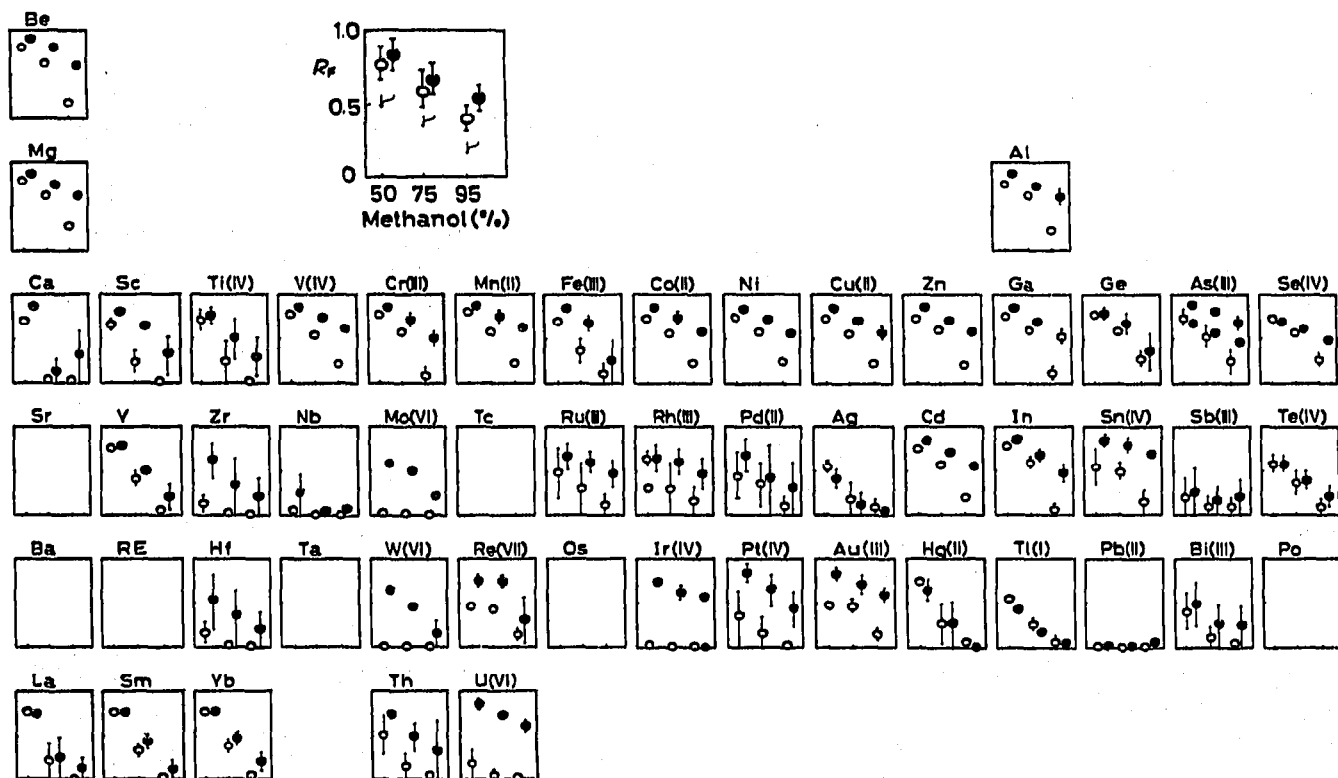


Fig. 2. Variation of  $R_F$  values of metals on DEAE and Avicel SF with the concentration of methanol in methanol-1N  $H_2SO_4$  media.  $\circ$  = DEAE;  $\bullet$  = Avicel SF. All the  $R_F$  measurements were conducted at 50, 75 and 95% methanol concentrations. For convenience  $R_F$  values on Avicel SF shifted the abscissa arbitrarily to the right.

#### Adsorption from a mixture of $H_2SO_4$ and a protic solvent

The  $R_F$  variation of metals on DEAE and Avicel SF with increasing additions of methanol to 1N  $H_2SO_4$  is shown in Fig. 2. The addition of methanol to the  $H_2SO_4$  solution generally lowers the  $R_F$  values on DEAE and Avicel SF to some extent in the case of nearly all the metals tested. The exception is Au(III); the  $R_F$  of Au(III) on DEAE starts at 0.15 in the aqueous 1N  $H_2SO_4$ , and passes through a broad maximum at 50-75% methanol, and then reaches around 0.15 on going to 95% methanol. The same exceptional behavior of  $AuCl_4^-$  on DEAE-paper in HCl-ethanol mixtures was also noted by LEDERER AND MOSCATELLI<sup>2</sup>.

It is worth noting that metals forming sulfatocomplexes and adsorbing on the strongly basic resin increase their retention on DEAE very rapidly as compared to Avicel SF with increasing methanol concentration, see for example Zr, Hf, Mo(VI), W(VI), Ir(IV), Th and U(VI).

The  $R_F$  values on DEAE and Avicel SF in 1:1 methanol- $H_2SO_4$  mixtures are plotted as a function of  $H_2SO_4$  concentration in Fig. 3. A pronounced lowering of  $R_F$  values on DEAE, as compared to Avicel SF, is particularly marked at lower concentrations of  $H_2SO_4$  for metals which show adsorption on the strongly basic resin. To explain these observations, ion exchange can reasonably be assumed to be the mechanism controlling the  $R_F$  values for sulfatocomplex-forming metals in methanol- $H_2SO_4$  media.

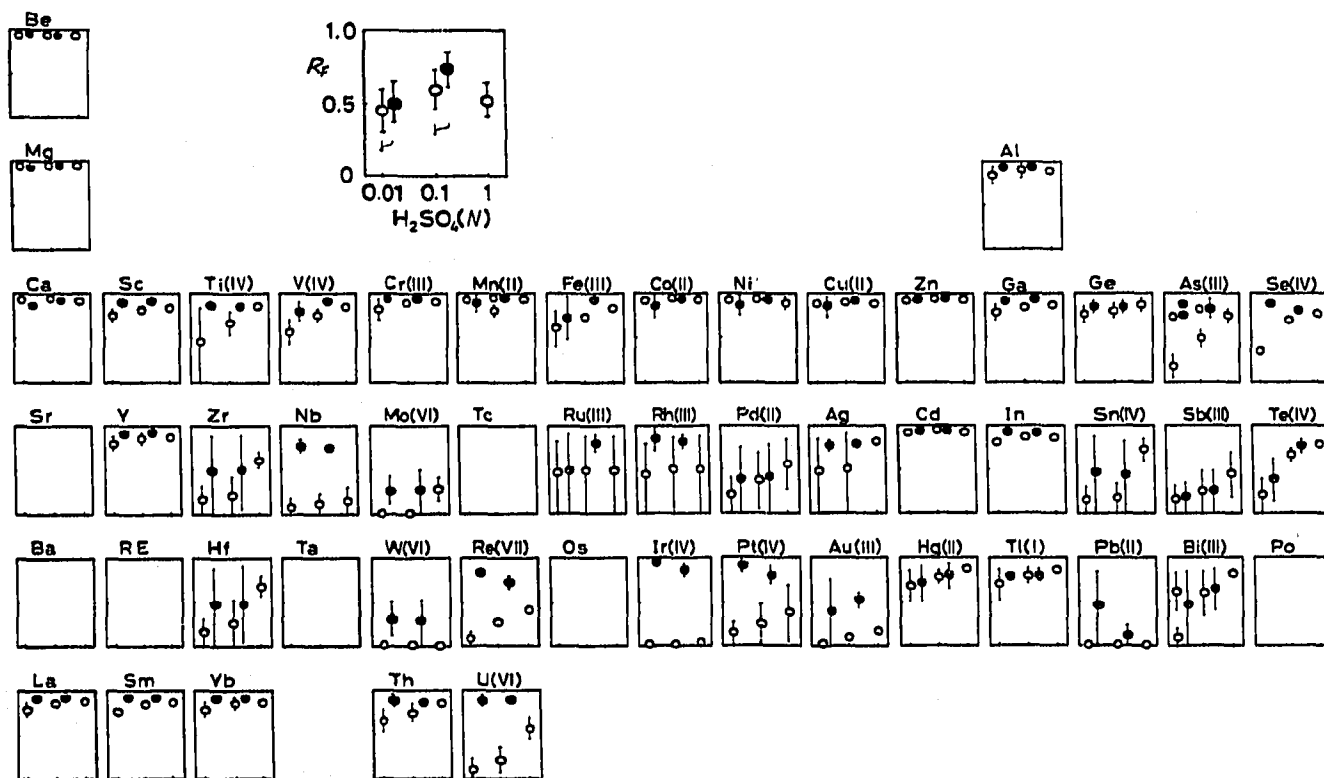


Fig. 3. Variation of  $R_F$  values on DEAE and Avicel SF with the concentration of  $H_2SO_4$  in methanol- $H_2SO_4$  media (1:1).  $\circ$  = DEAE;  $\bullet$  = Avicel SF. All the  $R_F$  measurements were conducted at the three  $H_2SO_4$  concentrations, 0.01, 0.1 and 1N. For convenience  $R_F$  values on Avicel SF shifted the abscissa arbitrarily to the right.

$R_F$  values for metals on DEAE and Avicel SF in 1:1 and 3:1 (DEAE only) acetic acid- $H_2SO_4$  media are given in Table I as the function of  $H_2SO_4$  concentration. There are no marked differences in the  $R_F$  values on DEAE and Avicel SF for most of the metals over the  $H_2SO_4$  concentration range tested, except for Sc, Zr, Hf, Nb, Mo(VI), W(VI), Re(VII), Ir(IV), Pt(IV), Au(III), Pb(II), Th and U(VI). With increasing acetic acid concentration the  $R_F$  values for these metals on DEAE decrease rapidly, almost remaining near the start, although Re(VII) and Au(III) maintain about the same chromatographic distribution regardless of the amounts of acetic acid added. As indicated by LEDERER AND MOSCATELLI<sup>2</sup>, the hydration is perhaps already very poor for the complexes of Au(III) and Re(VII). The differences in  $R_F$  values between DEAE and Avicel SF can be explained on the same basis as the mechanism in the methanol- $H_2SO_4$  mixtures.

#### Adsorption from a mixture of $H_2SO_4$ and an aprotic solvent

The trends of the  $R_F$  values of metals on DEAE and Avicel SF were investigated when acetone or dioxane was added as the aprotic solvent to  $H_2SO_4$  solutions of varying concentration. Results for the  $R_F$  measurements are given in Tables II and III.

In most cases the addition of increasing amounts of the aprotic solvent to  $H_2SO_4$  solutions causes the  $R_F$  values on DEAE to be lower in both the acetone- and dioxane- $H_2SO_4$  media. However, this is not always the case.  $R_F$  values for Au(III) and Re(VII) in aqueous  $H_2SO_4$  solutions increase with the addition of acetone or dioxane,

TABLE I

 $R_F$  VALUES ( $\times 100$ ) ON DEAE AND AVICEL SF IN ACETIC ACID- $H_2SO_4$  MIXTURESD = DEAE; A = Avicel SF; w = weak tailing, difference between  $R_{F \text{ front}}$  and  $R_{F \text{ rear}} = 0.3 \sim 0.5$ ; s = strong tailing, difference between  $R_{F \text{ front}}$  and  $R_{F \text{ rear}} > 0.5$ .

Metal	0.01N $H_2SO_4$			0.1N $H_2SO_4$			1N $H_2SO_4$		
	Adsorbent			Adsorbent			Adsorbent		
	D	D	A	D	D	A	D	D	A
	Acetic acid (%)			Acetic acid (%)			Acetic acid (%)		
	75	50	50	75	50	50	75	50	50
Ag	39s	84	71	39s	84	63	37	67	59
Al	35	95	90	45	95	91	38	95	86
As(III)	{16 56	{22 72	{67 83	{24 57	{37 73	{66 86	54	70	{66 86
Au(III)	3	6	82	8	16	81	31	41	79
Be	88	94	90	88	94	93	76	92	90
Bi(III)	76	82	84	78	86	82	61	84	80
Ca	4	69	80	0	73	85	0	86	85
Cd	86	92	81	83	93	84	46	90	79
Co(II)	85	92	88	81	93	85	{48 89	93	84
Cr(III)	24	99	97	13	57	86	33	94	{80 96
Cu(II)	87	93	86	87	93	84	{48 89	92	84
Fe(III)	99	96	92	98	93	93	{30 99	{74 99	83
Ga	64s	89	86	60s	84w	88	39	95	84
Ge	{28 58	67	76	59	63w	78	61	78	80
Hf	6	14	41s	6	12	42s	7	29	64w
Hg(II)	92	94	81	92	85	82	89	86	80
In	45	96	{84 93	58w	94	{88 95	42	88	82
Ir(IV)	0	4	74	0	5	68	5	4	65
La	22	74	79	21w	72w	82	31w	83	84
Mg	84	95	89	49s	91	90	80	94	84
Mn(II)	86	91	88	84	92	87	89	93	86
Mo(VI)	0	0	18	0	0	24	3	4	{15 39
Nb	5	6	66	4	7	72	6	9	67
Ni	83	93	86	80	93	83	{45 86	92	84
Pb(II)	0	0	80	0	0	15	0	0	0
Pd(II)	0	36s	70	0	31s	69	16w	34w	67
Pt(IV)	0	9	72	4	3	77	5	15	76
Re(VII)	4	9	78	12	24	79	38	50	78
Rh(III)	6	{25s 90	56	31	24w	59	16w	29s	55
Ru(III)	0	48s	67w	0	27s	67	20w	38s	61w
Sb(III)	52	47	55w	44	46w	47w	41	35	48w
Sc	14	50	80	11	46	79	22	67	82
Se(IV)	47	59	71	46	56	71	54	74	68
Sm	29	74w	77	17	73w	80	33	82	81
Sn(IV)	25	29w	77	20	27w	78	31	59	80
Te(IV)	17	27s	25s	27	36w	37w	22	59	59
Th	21	38	76	14	15	75	{7 22	61	78
Ti(IV)	7	35s	41s	0	18w	49s	13	64	72

TABLE I (continued)

Metal	0.01 N H <sub>2</sub> SO <sub>4</sub>			0.1 N H <sub>2</sub> SO <sub>4</sub>			1 N H <sub>2</sub> SO <sub>4</sub>					
	Adsorbent			D			D					
	Acetic acid (%)			D	D	A	D	D	A	D	D	A
				75	50	50	75	50	50	75	50	50
Tl(I)				83	89	73	84	89	69	86	90	63
U(VI)				5	7	80	4	6	82	5	21	82
V(IV)				57 <sup>w</sup>	87	81	47 <sup>s</sup>	86	81	{40 65	{78 87	80
W(VI)				0	0	25 <sup>w</sup>	0	0	0	0	0	{0 30
Y				30	76 <sup>w</sup>	78	26	75 <sup>w</sup>	82	39	82	83
Yb				29	77 <sup>w</sup>	78	23	74 <sup>w</sup>	81	35	82	82
Zn				80	93	83	79	92	85	44	91	79
Zr				5	9	42 <sup>s</sup>	5	9	43 <sup>s</sup>	5	23	72

and then do not vary appreciably with further addition of acetone or dioxane. Insensitive variation of  $R_F$  values with increasing additions of acetone or dioxane can also be seen for the platinum group of metals, Ge, Sn(IV), As(III), Sb(III), etc.

LEDERER AND MOSCATELLI<sup>2</sup> found that the adsorption of Zn and Cd on DEAE-paper from acetone-HCl and ethanol-HCl mixtures increases with the concentration of ethanol and decreases with the increasing concentration of acetone. This kind of difference between a protic solvent and acetone or dioxane was not found in this work for those metals which form strong sulfatocomplexes, because of the strong retention of these complexes on DEAE in different media. Perhaps this difference between two kinds of solvents can be reflected by the principal mechanism controlling the  $R_F$  values. The retention of metals forming sulfatocomplexes on DEAE in acetone- and dioxane-H<sub>2</sub>SO<sub>4</sub> media may not only be controlled by ion exchange proper, but partition may also play an important role in determining the  $R_F$  values. The rather higher  $R_F$  values of the platinum group of metals, Mo(VI), W(VI), U(VI), etc. on Avicel SF as compared to those of metals exhibiting no evidence of sulfatocomplex formation indicate an appreciable participation of the partition mechanism in the case of sulfatocomplexes in acetone- and dioxane-H<sub>2</sub>SO<sub>4</sub> media.

Acetone and dioxane are sufficiently non-polar and not so effective as protic solvents in destroying the hydration clouds around the metal ions. This may account for the inadequate participation of the ion-exchange mechanism in acetone- and dioxane-H<sub>2</sub>SO<sub>4</sub> media.

## SEPARATIONS

Inspection of the  $R_F$  values of metals chromatographed on DEAE in methanol-, acetic acid-, acetone-, and dioxane-H<sub>2</sub>SO<sub>4</sub> mixtures will allow many useful separations of analytical interest to be conducted effectively. Typical chromatograms involving multicomponent separations are illustrated in Fig. 4.

The time necessary for the separation is dependent on the volume ratio, concentration of sulfuric acid, and the type of organic solvent and adsorbent. When

TABLE II

 $R_F$  VALUES ( $\times 100$ ) ON DEAE AND AVICEL SF IN ACETONE- $H_2SO_4$  MIXTURES

See Table I for symbols, s, w, D and A.

Metal	Adsorbent	0.01 N $H_2SO_4$			0.1 N $H_2SO_4$			1 N $H_2SO_4$		
		D	D	A	D	D	A	D	D	A
		Acetone (%)			Acetone (%)			Acetone (%)		
		75	50	50	75	50	50	75	50	50
Ag		13	40	48	13	46	54	12	50	38
Al		0	38	53	3	43	66	10	72	72
As(III)		{14 49	{13 66	{66 88	{19 43	{29 62	{62 84	46	68	{61 87
Au(III)		51s	43	83w	31	57	97	63	75	98
Be		5	38	68	12	43	78	41	80	82
Bi(III)		7	5	13	5	6	11	7	22w	37w
Ca		0	18w	43w	6	20w	26s	0	14	6
Cd		0	28	50	4	41	64	20	74	71
Co(II)		0	26	48	5	43	65	18	73	67
Cr(III)		0	15	47	0	28	64	8	67	70
Cu(II)		0	26	44	3	44	64	18	75	67
Fe(III)		0	20w	28s	4	17	67	13	58	69
Ga		3	31w	30	3	38	64	11	70	70
Ge		27s	36s	68w	31	59	73	56	74	77
Hf		0	4	8	0	4	12	3	11	45s
Hg(II)		24w	52	59	30	56	72	45	78	74
In		3	20	53	3	29	66	20	65	69
Ir(IV)		0	0	65	4	5	67	14	6	64
La		0	11	32	0	18	40	3	52	46
Mg		3	48	57	8	46	67	22	76	71
Mn(II)		0	34	58	4	46	66	23	80	70
Mo(VI)		0	0	45	0	0	{34 98	0	0	{55 99
Nb		0	0	22w	0	0	21w	4	6	28s
Ni		0	28	47	4	43	63	16	73	64
Pb(II)		0	0	23w	0	0	12	0	0	0
Pd(II)		11	22w	48s	18	27s	76w	48	58w	83w
Pt(IV)		{4 20	14	90	13	14	89	15	36s	93
Re(VII)		{3 57	{21 72	93	43	{43 64	95	61	78	94
Rh(III)		12	27s	64w	12	23w	56w	17	34s	58
Ru(III)		12	27s	34s	13	23w	57w	20	38s	57w
Sb(III)		19	11	32w	16	13	38w	15	25w	53s
Sc		0	8	50w	0	16	64	7	50	68
Se(IV)		11	20	61	21	43	70	58	44	69
Sm		0	9	34	0	17	45	4	51	49
Sn(IV)		37w	27s	57s	32w	38s	47s	39w	54s	84
Tc(IV)		0	5	8	0	12	23w	10	74	43
Th		3	6	42w	0	13	57	4	33	59
Ti(IV)		0	5	10	0	14	33s	9	39w	56
Tl(I)		5	26	32	6	42	37	10	45	33
U(VI)		0	4	66	0	5	70	5	14	74
V(IV)		0	24	51	3	41	68	22	71	72
W(VI)		0	0	98	0	0	98	0	0	{89 99
Y		0	13	40	0	23	50	4	52	54
Yb		0	14	35	0	23	48	4	52	51
Zn		0	28	48	4	43	62	17	73	68
Zr		0	4	12	0	4	15	3	11	49s



TABLE III

 $R_f$  VALUES ( $\times 100$ ) ON DEAE AND AVICEL SF IN DIOXANE-H<sub>2</sub>SO<sub>4</sub> MIXTURES

See Table I for symbols, s, w, D and A.

Metal	0.01 N H <sub>2</sub> SO <sub>4</sub>			0.1 N H <sub>2</sub> SO <sub>4</sub>			1 N H <sub>2</sub> SO <sub>4</sub>		
	Adsorbent			D	D	A	D	D	A
	Dioxane (%)			75	50	50	75	50	50
Ag	6	30	49	9	39	58	16	52	50
Al	10	30w	82	11	45	85	35	72	89
As(III)	{13	{20	{71	{19	{28	{69	{40	64	{63
	{47	{63	{90	{49	{67	{86	{54		{83
Au(III)	28	37	95	28	44w	93	60	74	96
Be	4	24	62	13	40	81	51	73	91
Bi(III)	14	14	37s	15	15	{38s	20w	41	{76
						{89			{94
Ca	0	13	44s	6	20w	33s	19w	36s	12
Cd	0	22	56	7	39	76	44	72	86
Co(II)	0	21	56	10	38	75	42	70	85
Cr(III)	0	13	52s	4	32	77	29	72	87
Cu(II)	0	23	53	9	38	76	41	69	86
Fe(III)	0	7	48w	0	19	77	22	61	87
Ga	12	29w	83	8	45	85	35	72	88
Ge	28s	45	72w	38	58w	82	54	77	85
Hf	5	7	25w	6	9	30s	7	21	65w
Hg(II)	16w	{8	0	18	{0	74	{0	{0	97
		{47			{48		{11	{88	
In	12	31w	83	10	40w	83	26	72	88
Ir(IV)	3	0	81	0	0	77	0	0	83
La	4	22w	52	4	31	66	12	62	71
Mg	7	35	72	12	42	80	50	73	89
Mn(II)	0	27	65	10	42	79	44	72	85
Mo(VI)	0	0	99	0	0	99	{0	7	{75
							{6		{99
Nb	0	5	20w	0	6	48	8	0	42s
Ni	0	21	55	10	39	74	40	70	83
Pb(II)	0	0	24w	0	0	21w	0	0	5
Pd(II)	14	14	43s	14	21w	{0	38w	{0	87
						{80		{54w	
Pt(IV)	7	13	92	9	21w	91	29w	42	94
Re(VII)	0	{13	92	22	{39	91	51	72	95
		{56			{61				
Rh(III)	34s	38s	81	{20	{9	79	34s	73	83
				{63	{55				
					{73				
Ru(III)	24w	30s	44s	21w	21w	75	28s	73	85
Sb(III)	22	15	47s	27	21	52s	34	41w	80
Sc	6	19w	66	7	26	78	18	57	80
Se(IV)	{0	15	63	18	41	71	51	71	75
	{8								
Sm	3	18w	52	0	26	68	13	60	72
Sn(IV)	35w	39w	57s	45w	41w	82	51	69	88
Tc(IV)	0	5	14	4	23w	40w	37	63	71
Th	6	9	73w	6	15	79	9	45	81
Ti(IV)	0	9	26s	5	33s	70	19w	63	81
Tl(I)	0	23	40	8	38	49	18	50	48
U(VI)	0	4	83	0	5	84	7	19	86
V(IV)	3	27	62	11	41	79	46	72	85
W(VI)	0	0	37	0	0	97	0	0	98
Y	7	26w	61	6	39w	72	16	65	76
Yb	6	29	58	5	39w	71	15	65	75
Zn	0	21	54	8	37	76	40	72	86
Zr	4	6	32s	4	8	44s	6	17	74

compared on the same basis, the developing time in each solvent system is in the order:

Aqueous > acetone  $\cong$  methanol > dioxane > acetic acid.

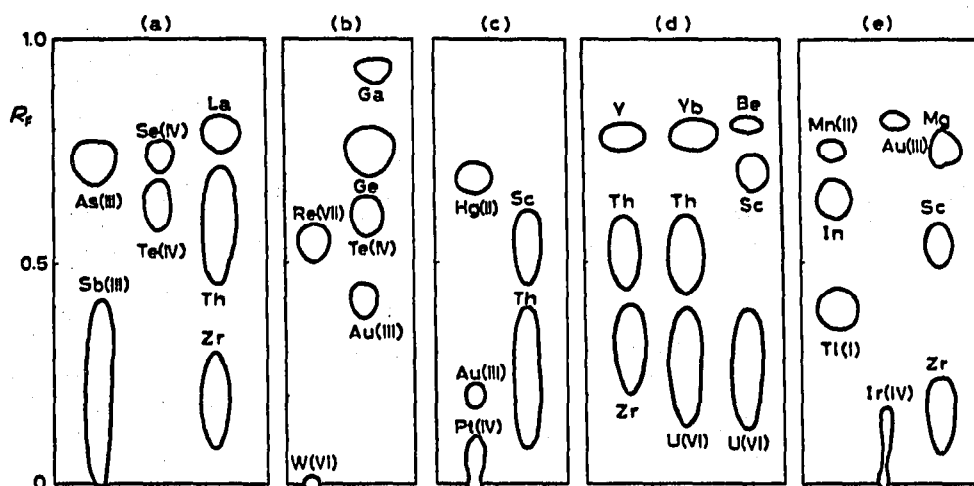


Fig. 4. Various separations, DEAE used throughout. (a) Methanol-1*N* H<sub>2</sub>SO<sub>4</sub> (1:1); (b) acetic acid-1*N* H<sub>2</sub>SO<sub>4</sub> (1:1); (c) acetic acid-0.1*N* H<sub>2</sub>SO<sub>4</sub> (1:1); (d) dioxane-1*N* H<sub>2</sub>SO<sub>4</sub> (1:1); (e) acetone-1*N* H<sub>2</sub>SO<sub>4</sub> (1:1).

Decreasing the concentration of H<sub>2</sub>SO<sub>4</sub> also helps to shorten the time of separation. Development on Avicel SF usually needs about twice the time of development on DEAE in the same solvent mixture. Although not illustrated, the following separations were also feasible:

*DEAE-aqueous 1 N H<sub>2</sub>SO<sub>4</sub> (time: 1 h 30 min)*

Nb(0.00-0.25)-Zr(0.28-0.87)-Y(0.91-0.98)

Zr(0.72-0.88)-Ti(IV)(0.90-0.95)

W(VI)(0.00-0.22)-Re(VII)(0.47-0.57)

*DEAE-acetone-1 N H<sub>2</sub>SO<sub>4</sub> (3:1) (time: 1 h 50 min)*

Te(IV) (0.02-0.16)-Ge(0.45-0.65)

Te(IV) (0.03-0.18)-Se(IV) (0.57-0.65)

Sb(III) (0.00-0.05)-As(III) (0.40-0.60)

## REFERENCES

- 1 R. KURODA, N. YOSHIKUNI AND K. KAWABUCHI, *J. Chromatogr.*, 47 (1970) 453.
- 2 M. LEDERER AND V. MOSCATELLI, *J. Chromatogr.*, 13 (1964) 194.
- 3 K. ISHIDA AND R. KURODA, *Bunseki Kagaku*, 19 (1970) 81.
- 4 K. OGUMA AND R. KURODA, *J. Chromatogr.*, 52 (1970) 339.
- 5 M. LEDERER AND L. OSSICINI, *J. Chromatogr.*, 15 (1964) 514.
- 6 L. DANIELSSON, *Acta Chem. Scand.*, 19 (1965) 670.
- 7 F. W. E. STRELOW AND C. T. C. BOTHMA, *Anal. Chem.*, 39 (1967) 595.