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THIN-LAYER CHROMATOGRAPHIC BEHAVIOR OF A NUMBER OF METAL IONS ON DEAE-CELLULOSE IN THIOCYANIC ACID-ORGANIC SOLVENT MIXTURES

K. OGUMA AND R. KURODA

Laboratory for Analytical Chemistry, Faculty of Engineering, University of Chiba, Chiba (Japan)

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SUMMARY

The thin-layer chromatographic behavior of 48 metals was investigated on a weakly basic anion exchanger, DEAE-cellulose, in binary solvent mixtures consisting of HSCN (0.1 to 2.1 *M*) and an organic solvent such as methanol, acetic acid, acetone, dioxane, etc. For the sake of comparison, the R_F values for the same metals on a microcrystalline cellulose, Avicel SF, in three solvent mixtures involving methanol, acetic acid and acetone are also presented. The addition of a protic solvent to the aqueous HSCN solution enhances the adsorption of many metals, in so far as the metals form stable thiocyanato-complexes and their R_F values may be controlled predominantly by the ion-exchange mechanism. This is not the case for the nonprotic acetone-HSCN system, where mechanisms other than ion exchange may prevail to influence the R_F values of the metals. Useful multicomponent separations on DEAE-cellulose are presented to demonstrate the use of R_F measurements for predicting separations in these solvent systems.

INTRODUCTION

DEAE-cellulose along with other substituted celluloses has been extensively investigated in inorganic paper chromatography by LEDERER and his colleagues¹⁻⁸ and others⁹⁻¹³. Most of these works were carried out in aqueous acid or salt solutions, although LEDERER AND MOSCATELLI² investigated the influence of some organic solvents on the ion-exchange behavior of several metals on cellulose ion-exchange papers.

We have previously reported the thin-layer chromatographic (TLC) behavior of a number of metals on DEAE-cellulose in binary solvent systems consisting of HCl (or HNO₃) and an organic solvent^{14,15}, demonstrating the usefulness of DEAE-cellulose as an adsorbent in inorganic TLC. This work has been extended to obtain information about the chromatographic behavior of metals on DEAE-cellulose in binary solvent systems consisting of HSCN and an organic solvent. Generally, most metals exhibited a stronger adsorption on DEAE-cellulose in the mixed solvents than that in aqueous thiocyanate media^{9,12}, in the case where ion exchange is the mechanism involved in controlling the behavior of the metals. The solvent systems inves-

tigated allow a number of useful multicomponent separations to be conducted, particularly in methanolic HSCN media.

EXPERIMENTAL

Test solutions

For most metals 0.1 to 0.01 *M* stock solutions (0.1 *M* in HCl) were prepared from the chloride, oxide or metal. For Bi(III), Sb(III), Sn(IV), Zr and Hf, the acidity of the stock solutions was raised to 3 *M* HCl to prevent hydrolysis. 6 *M* HCl solutions were prepared for As(III) and Ti(IV) using the oxide and chloride, respectively. AgNO₃, Pb(NO₃)₂ and TlNO₃ were dissolved in 0.1 *M* HNO₃ to prepare 0.1 *M* stock solutions. Ammonium or sodium salts of Mo(VI), W(VI), Re(VII), Se(IV) and Te(IV) were each dissolved in deionized water to give 1–10 mg/ml. For niobium *ca.* 120 mg of Nb₂O₅ was fused with 3 g of K₂S₂O₇, and the resulting melt was taken up into 10 ml of 1 *M* tartaric acid.

Preparation of HSCN solution

A cation-exchange method⁶ was used to prepare approximately 2.4 *M* HSCN solution, which was standardized both argentometrically and alkalimetrically and stored at 2° right up until use. This solution was used after an appropriate dilution with deionized water.

Preparation of thin-layer plates

A cellulose anion exchanger, MN-cellulose powder 300 DEAE (diethylaminoethylcellulose, Macherey, Nagel & Co.) was used as the adsorbent. Microcrystalline cellulose, Avicel SF (Avicel Sales Division, FMC Corp.) was also used. About 11 g of DEAE-cellulose were slurried with 100 ml of 1 *M* NH₄SCN solution, adjusted to pH 1.3 with dilute HSCN and stirred mechanically for 40 min. DEAE-cellulose was then washed with deionized water three times, each wash solution being removed by centrifugation. The DEAE-cellulose thus prepared was slurried with 73 ml of water and spread to a 250- μ m thickness on five sheets of 200 \times 200 mm glass plates. The plates were allowed to dry at 40° for 3 h after air-drying for 1 h and stored in a desiccator over a saturated KBr solution.

For the preparation of the microcrystalline cellulose plates, 20 g of Avicel SF was mixed with 75 ml of water and spread on 200 \times 200 mm glass plates at a thickness of 250 μ m. Avicel SF plates were dried and stored as above.

Application

A sample or stock solution, usually 0.5 μ l, was applied to the plate 2.5 cm from one edge using a micropipette, and the plate was air-dried for 15 min before placing it in the chromatographic tank. The plate was then placed in the rectangular tank (21.5 \times 21.5 \times 10.5 cm) containing a solvent boat (20.5 \times 2.2 \times 1.8 cm) holding 40 ml of developing solvent and allowed to stand for 1 h to come to equilibration. Then the plate was immersed in the solvent and developed at room temperature until the solvent front had risen 15 cm from the start. All the solvent systems tested were binary, consisting of an organic solvent and HSCN of varying concentration. Among others, three organic solvents, *viz.*, methanol, acetic acid and acetone were tested in detail.

Detection

After development, the plate was dried under an IR lamp and metals were detected by spraying with the reagents below:

Hf, the rare earths, Sc, Th, U(VI), Y and Zr: 0.1 % aqueous arsenazo III solution.

Ag, Bi(III), Cd, Co(II), Cu(II), Fe(III), Hg(II), Ni, Pb(II) and Tl(I): dilute aqueous Na_2S solution.

Au, Ir(IV), Mo(VI), Pd(II), Pt(IV), Re(VII), Rh(III), Se(IV), Te(IV), and W(VI): 10 % SnCl_2 in 3 *M* HCl.

As(III), Mn(II) and W(VI): 10 % AgNO_3 in 10 % NH_4OH .

Al, Be, Ca, In and Mg: 0.1 % alizarin in 1 *M* NaOH.

Cd and Zn: 0.1 % PAN in ethanol followed by 1 *M* NaOH.

Ge, Sb(III) and Sn(IV): 0.05 % phenylfluorone in 95 % ethanol.

Ga: 0.5 % rhodamine B in 6 *M* HCl.

Sr and Ba: 0.1 % aqueous sodium rhodizonate followed by exposure to ammonia.

Nb: 0.1 % aqueous tannic acid.

Cr(III): 1 *M* NaOH followed by 10 % aqueous H_2O_2 .

Ti(IV) and Ru(III): not used.

RESULTS AND DISCUSSION

R_F values for 48 metals chromatographed on DEAE-cellulose in methanol-HSCN media are illustrated in Fig. 1 as a function of HSCN concentration. The variation of the R_F values of the same metals with the volume concentration of methanol are shown in Fig. 2, where the HSCN concentration was kept constant at 1 *M*. The R_F values for the metals on DEAE-cellulose and on Avicel SF in methanol-, acetic acid-, and acetone-1 *M* HSCN media are given in Table I; the volume ratio of organic to aqueous was maintained constant at 3:1.

Adsorption behavior of metals

Among the metals tested, those which form stable thiocyanatocomplexes exhibit strong adsorption on the DEAE-cellulose over the HSCN concentration range tested (Fig. 1). Thus the R_F values for Zr, Hf, V(IV), Nb, Mo(VI), W(VI), Re(VII), U(VI), (Fe(III)), Co(II), the platinum group metals, Cu(II), Ag, Au, Zn, Cd, Hg(II), Ga, In, Sn(IV), Sb(III), and Bi(III) are generally low and mostly near or at start. Even metals which have comparatively high R_F values, *e.g.*, Re(VII), Fe(III), Co(II), Au, and Cd show increasing adsorption when the volume ratio of organic to aqueous is increased, their R_F values becoming almost zero in 95 % methanol media (Fig. 2). An exception is Ga, whose R_F values are less sensitive to the alcohol concentration. Obviously, the increasing alcohol concentration reduces the concentration of the competitive thiocyanate ions and may facilitate the formation of thiocyanatocomplexes, thus allowing the thiocyanatocomplexes of the metals to be adsorbed easily on the ion-exchange sites of DEAE-cellulose¹⁵.

The above mentioned metals have been shown to adsorb well on a strongly basic anion-exchange resin^{16,17} and resin paper⁸ from aqueous chloride-thiocyanate and pure HSCN solutions, respectively. In addition, the trends of the R_F values as

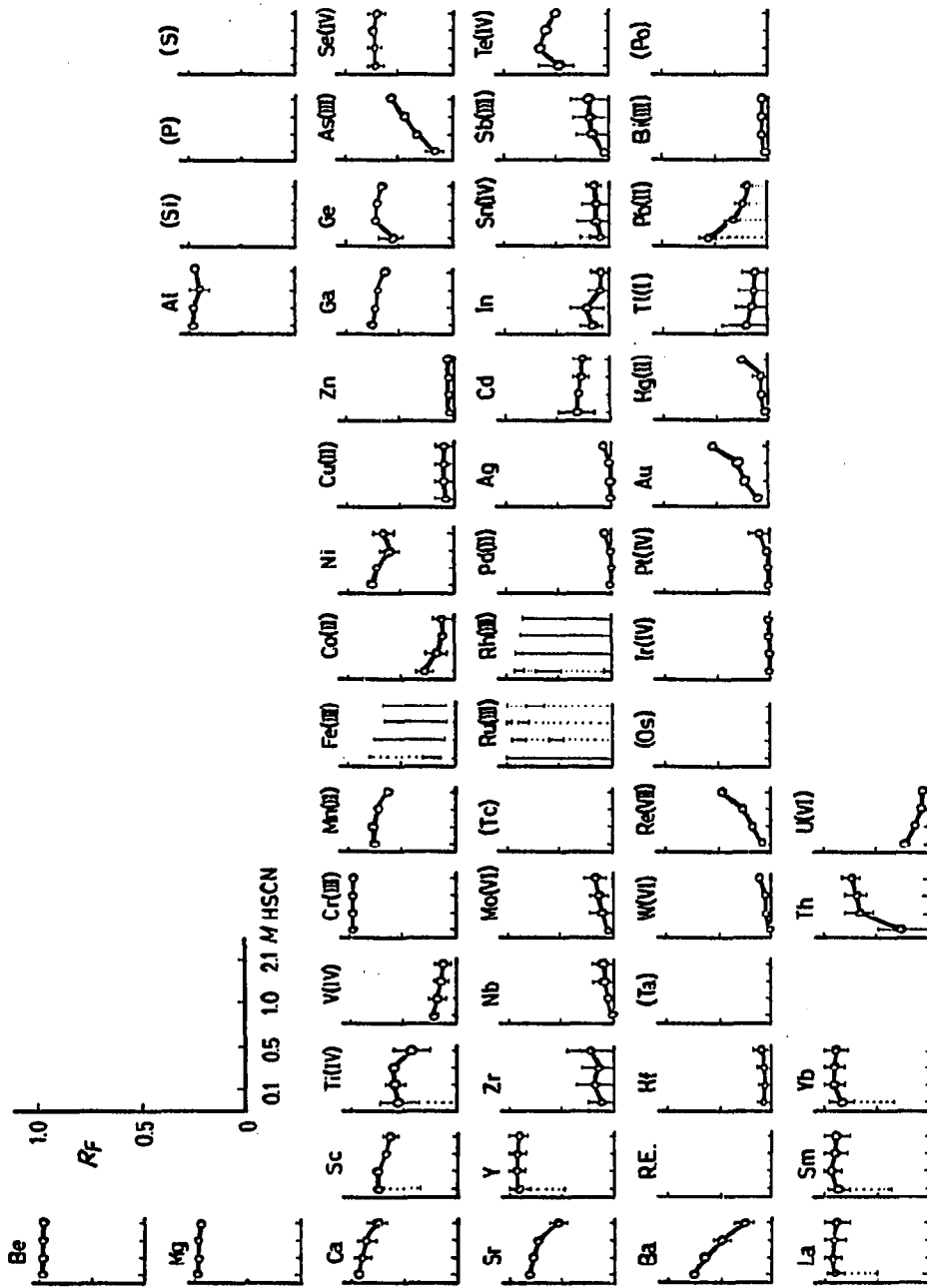


Fig. 1. R_f spectra of metals chromatographed on DEAE-cellulose in methanol-HSCN (3:1).

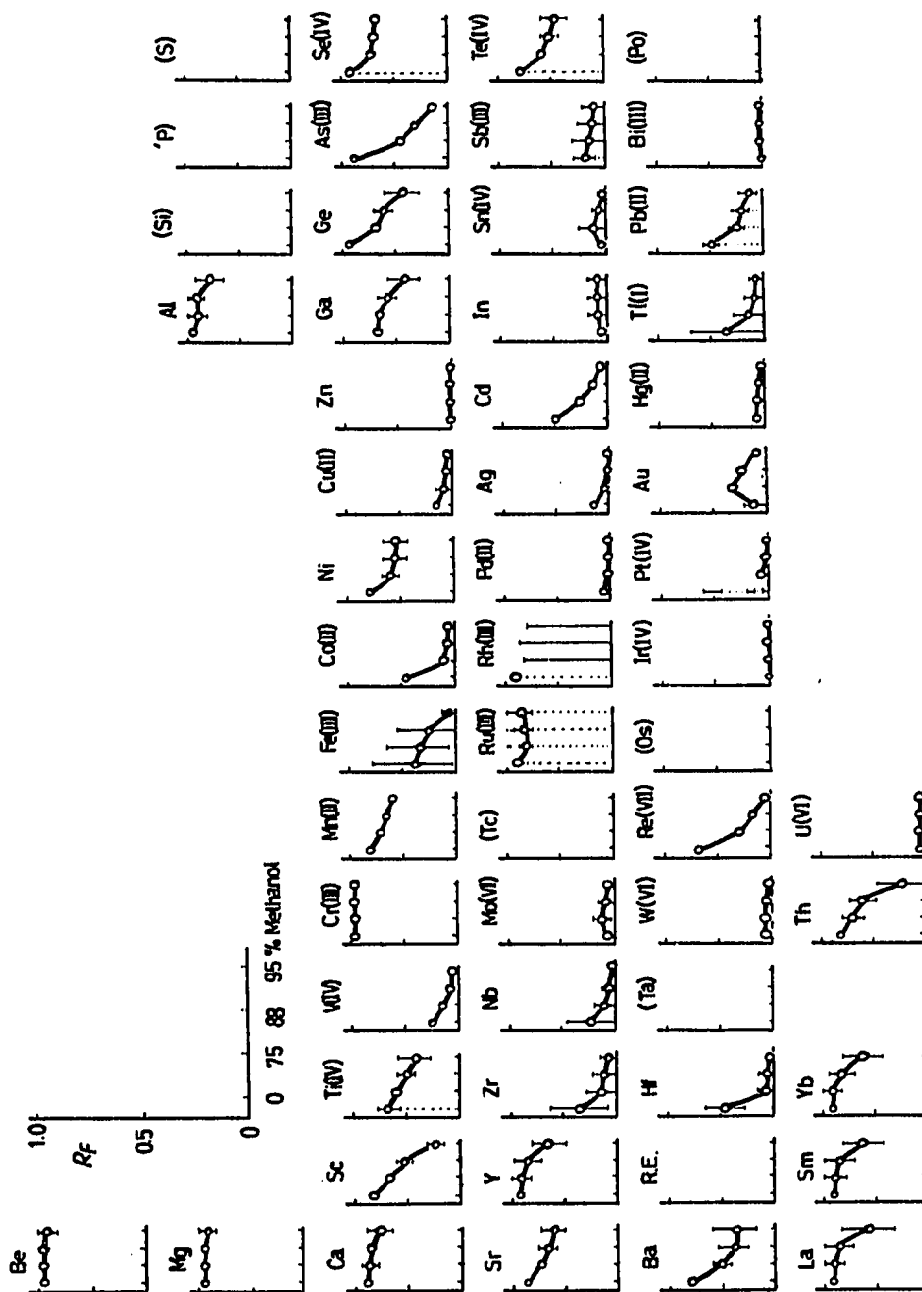


Fig. 2. R_f spectra of metals chromatographed on DEAE-cellulose in methanol-1 M HSCN.

TABLE I

R_F VALUES (× 100) ON DEAE-CELLULOSE AND AVICEL SF IN THREE DIFFERENT SOLVENT SYSTEMS

Metal	Methanol-1 M HSCN (3:1)		Acetic acid-1 M HSCN (3:1)		Acetone-1 M HSCN (3:1)	
	DEAE- cellulose	Avicel SF	DEAE- cellulose	Avicel SF	DEAE- cellulose	Avicel SF
Ag	0-5	61..93-96 ^a	0-3	0-1..77	7-20	95-100
Al	82-100	89-97	39-53	49-59	89-100	58-91
As(III)	40-49		31-46..53	27-51	13-33, 41-51	43-51, 69-78
Au	27-36	92-97	7-42	81-90	89-97	95-100
Ba	41-57	45-61	47-60	58-66	23-63	36-54
Be	93-100	91-99	54-65	62-68	90-100	89-100
Bi(III)	0-5	77-87	0-3	0-3..15-29	7-16	45-63
Ca	77-93	75-83	49-61	54-61	89-100	45-69
Cd	19-33	81-89	0-5	43-53	59-91	95-100
Co(II)	3-15	87-97	0-3	49-57	87-96	97-100
Cr(III)	97-100	88-96	37-47	46-53	87-92	55-68..75-85
Cu(II)	0-15	87-96	0-32	0-4..64	30-41..91	95-100
Fe(III)	6-65	86-97	0-5	37-68	63-87	96-100
Ga	64-73	84-96	5-23	55-65	89-95	93-100
Ge	65-75	70-77	50-67	55-65	49-58	59-67
Hf	0-14	0-71	0-18	0-49	0-46, 89-94	0-74
Hg(II)	0-13	95-99	0-7	83-91	48-57..	95-100
					74-85	
In	1-18	90-99	0-5	61-69	69-89	96-100
Ir(IV)	0-2		0-6		0-1	
La	78-100	77-87	35-51	35..41-54	62-91	46-78
Mg	95-100	81-91	55-67	52-60	86-91	45-73
Mn(II)	68-75	85-94	13-22	47-55	89-92	75-97
Mo(VI)	3-21	84-91	0-7	68-87	81-96	98-100
Nb	0-19	0-63	0-9	0-37	0-1..15	0-45
Ni	50-69	85-95	6-25	31-41	58-73	74-88
Pb(II)	0..18-32	39-53	0-10	0..49-56	0..43-56	94-100
Pd(II)	1-4	90-97	0-5	56..72-79	31-45	93-100
Pt(IV)	0-7	41-97	0-3	0-87	0-11..47	73-100
Re(VII)	24-35	77-88	19-27	65-73	55-72	91-98
Rh(III)	0-85	25-97	0-33	0-69	0-5..19-37	0-100
					..59-77	
Ru(III)	0-2..77-89	61-97	0-35	0-75	0-2..69-81	20-100
	..95-100				..88-92	
Sb(III)	0-34	0-61	15-24	62-71	22-31..	68-77, 91-100
					73-92	
Sc	61-71	86-93	5-15	58-65	87-92	97-100
Se(IV)	69-79	69-76	6-64	33-57	56-63	71-100
Sm	77-100	77-87	30-45	31..38-52	62-93	41-69
Sn(IV)	0-25	87-97	0-5	70-87	85-92	77-100
Sr	67-75	65-75	49-62	59-64	47-74	40-50
Te(IV)	53-65	55-64	0-23	2-37	32-55	40-47
Th	59-80	75-87	26-38	44-56	79-93	43-88
Ti(IV)	55-63	82-89	0-7..12	38-50	35..59-89	74-90
Tl(I)	0-29	0-27	0-33	0-3..49	0-37	0-32
U(VI)	3-10	91-97	0-2	51-58	44-55	97-100
V(IV)	7-20	88-97	0-5	51-60	57-72	96-100
W(VI)	7-11	81-87	0-1	67-72	0-1	99-100
Y	82-100	77-88	32-49	33..37-52	75-93	43-84
Yb	81-100	79-87	30-41	28..33-47	77-93	46-70
Zn	0-5	91-97	0-5	77-85	88-98	87-100
Zr	0-29	0-70	0-33	0-51	0-92	0-68

^a "... stands for weak streak.

a function of HSCN concentration in our methanol-HSCN system are very similar to those given by BAGLIANO *et al.*⁶ for DEAE-paper in aqueous HSCN media. Taking into consideration the R_F values given by these authors for DEAE-paper and SB-2 resin paper the sequence of adsorption of thiocyanatocomplexes according to the systems involved is: anion exchange resin-aqueous HSCN > DEAE-methanolic HSCN > DEAE-aqueous HSCN.

The enhanced ion-exchange capability of DEAE-cellulose in mixed solvents over purely aqueous solvents has also been observed in methanol-HNO₃ (ref. 14) and methanol-HCl (ref. 15) systems.

Ion-exchange adsorption again seems to be the preponderant mechanism in determining the R_F values for metals forming thiocyanatocomplexes on DEAE-cellulose in acetic acid-HSCN media. As can be seen in Table I there are pronounced differences in the R_F values for metals forming thiocyanatocomplexes on DEAE-cellulose and on Avicel SF in acetic acid-HSCN medium, as is the case for the methanol-HSCN medium. R_F values on DEAE-cellulose are very low, near or equal to zero, while those on Avicel SF are fairly high. This is not the case for those metals, *e.g.*, the alkaline earths, the rare earths and Y, Cr(III), Ge, As(III), Se(IV) and Te(IV), which mostly do not form strong thiocyanatocomplexes. R_F values for the metals of this group do not differ appreciably from each other on DEAE-cellulose and Avicel SF.

In contrast to the protic solvent-HSCN systems, a great number of metals move upwards in acetone-HSCN media (Table I), irrespective of adsorbents, and there are actually no marked differences in R_F values on DEAE-cellulose and Avicel SF for most of the metals. A limited number of metals like W(VI), Ir(IV), Ag and Bi(III) remain at or near the start on DEAE-cellulose. Evidently, the diethylaminoethyl group does not function effectively in acetone-HSCN media, so that other mechanisms may prevail in determining the R_F values in this solvent system. The same observations are applicable in mixed solvent systems involving HCl and HNO₃.

Separation of metal ions

Knowledge of the R_F values for metals chromatographed on DEAE-cellulose in mixed solvent media will permit many separations of analytical interest to be conducted effectively. The methanol-HSCN system, particularly, may provide a number of useful separations, if we select a favorable concentration of HSCN and an appropriate volume ratio for a pair or group of metals. Results of multicomponent separations are illustrated in Fig. 3. The R_F value of a metal when chromatographed in a mixture does not differ from that obtained individually.

Even in solvent systems other than methanol- and acetone-HSCN interesting separations are feasible. For example in acetic acid-1 M HSCN (3:1):

W(VI) (0-3)-Re(VII) (22-30),
In(0-3)-Ga(6-17)-Al(42-54),
U(VI) (0-3)-Sc(7-13)-Th(31-41),

and in dioxane-1 M HSCN (3:1):

Ba(42-53)-Sr(67-76)-Ca(79-86)-Be(94-100),
Bi(III) (0-48)-Pb(II) (57-71),
Tl(I) (3-55)-Pb(II) (57-71),
Co(II) (10-28)-Cd(37-54)-Ni(81-89),
In(65-75)-Ga(90-100).

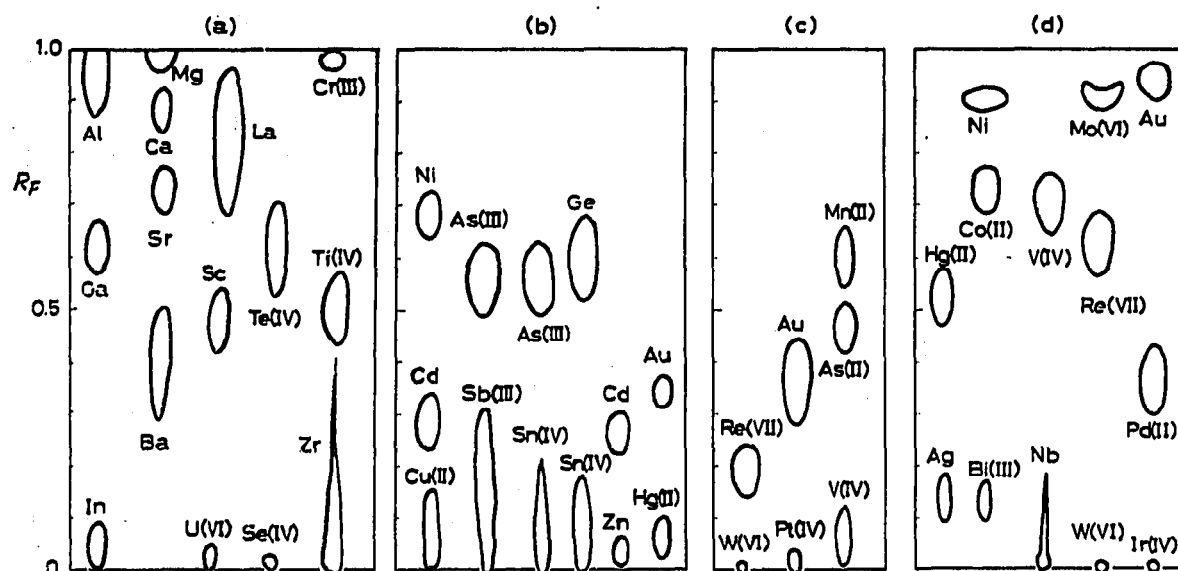


Fig. 3. Separations: (a) methanol-1 *M* HSCN (7:1), development time 30 min; (b) methanol-1 *M* HSCN (3:1), development time 55 min; (c) methanol-2.1 *M* HSCN (7:1), development time 30 min; (d) acetone-1 *M* HSCN (3:1), development time 40 min.

All of these separations were conducted on DEAE-cellulose. The values in parenthesis indicate the range of the R_F values ($\times 100$). When compared on the same volume ratio basis, the time necessary to achieve the separation in each solvent system is in the order: acetone (the most rapid) < dioxane < methanol < acetic acid.

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