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USE OF DEAE-CELLULOSE IN INORGANIC THIN-LAYER CHROMATOGRAPHY

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SUMMARY

R_F values for 52 metals obtained on DEAE-cellulose in binary solvent systems were surveyed to evaluate the use of DEAE-cellulose in inorganic thin-layer chromatography. R_F values were measured as a function of hydrochloric acid concentration in binary solvent systems consisting of hydrochloric acid and an organic solvent (1:20) such as methanol, *n*-butanol, acetone, tetrahydrofuran, acetic acid and cyclohexanone. Useful multicomponent separations are presented to demonstrate the use of R_F measurements for predicting separations in these solvent systems. All the solvent systems tested also afford separations of particular metals when the organic solvent and hydrochloric acid concentrations are specifically selected; thus, As (III) and Ge can be separated from fifty metals specifically as well as from each other. Ion-exchange and partition distribution were proposed as the mechanisms controlling the metal behavior on DEAE-cellulose for the methanolic acid system and for the other five solvent systems, respectively.

INTRODUCTION

An increasing number of papers have recently been published on the subject of thin-layer chromatography (TLC). The growth and acceptance of inorganic TLC have been noted in reviews of LEDERER¹ and NICKLESS². A bibliography of paper and thin-layer chromatography covering the period 1961-1965 has also appeared³. Most work on inorganic TLC has been done on silica gel or alumina as adsorbent. Other materials have been used for a few separations.

Work in our laboratory using dilute aqueous chloride-thiocyanate solutions has shown that DEAE-cellulose (diethylaminoethylcellulose) can be successfully used for the consecutive separation of Re, Mo and W⁴, separation of noble metals from base metals⁵ and a specific separation of Hg(II)⁶. However, few metals show adsorption on DEAE-cellulose in aqueous solutions.

In order to extend the application of DEAE-cellulose for inorganic separation and to investigate a new adsorbent for inorganic TLC, we have examined the chromatographic behavior of a number of metals on DEAE-cellulose in binary solvent systems consisting of hydrochloric acid and an organic solvent. The solvent systems

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investigated allow a number of useful multi-component separations to be conducted. Specific separation methods can also be developed for particular metals by selecting a proper concentration of organic solvent and hydrochloric acid.

EXPERIMENTAL

Stock solutions of metals

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

Preparation of plates

A weakly basic cellulose anion exchanger, DEAE (diethylaminoethylcellulose, Serva, for TLC), was used as adsorbent. For comparison microcrystalline cellulose Avicel SF (Avicel Sales Division, FMC Corp., Marcus Hook, Pa.) was also used as adsorbent. About 10 g of DEAE-cellulose were slurried with 200 ml of 0.5 *M* NH₄Cl solution, adjusted to pH 1 with HCl, and stirred mechanically for 1 h. DEAE-cellulose then was washed with a sufficient amount of 0.1 *M* HCl and finally with deionized water; after each wash the aqueous phase was removed by centrifugation. A 5-g portion of DEAE-cellulose in the chloride form thus prepared was slurried with 15 ml of water and spread to a 250- μ m thickness on 31 mm \times 200 mm glass plates. The plates were allowed to dry at 40° for 24 h and were stored in a desiccator over a saturated KBr solution for at least one week.

For the preparation of microcrystalline cellulose plates, a 5-g portion of the adsorbent was blended with 15 ml of deionized water, and the mixture was spread on 31 mm \times 200 mm glass plates to a thickness of 250 μ m. Avicel plates were dried and stored as above.

Application

A sample or stock solution, usually 1 μ l, was applied to the dry plate 1.5 cm from one edge by using a micropipette, and the plate was allowed to dry for 30 min before insertion into a chromatographic tank. The plate then was placed in the tank (24.0 cm \times 23.0 cm \times 12.5 cm) containing a solvent boat (21.5 cm \times 2.5 cm \times 2.0 cm) holding 21 ml of the developing solvent and allowed to stand for 1 h to equilibrate. Then the plate was immersed in the solvent and developed until the solvent front had risen 17 cm. All the developments were conducted at a constant temperature of 30.0 \pm 0.1°.

Solvent systems

All solvent systems tested were binary, consisting of an organic solvent and hydrochloric acid, and the ratio of 20:1 was kept constant throughout the work. Six organic solvents, including methanol, *n*-butanol, acetone, tetrahydrofuran, acetic

acid and cyclohexanone were used; each was mixed with 1, 6 and 12 *M* HCl, thus making eighteen developing solvent systems. The liquid phase was usually homogeneous, except for the cyclohexanone-1 *M* HCl system, from which the upper organic layer was taken as the developing solvent.

Detection

After development the plate was dried under an infrared lamp, and the positions of metals were located by spraying with one of the agents summarized as follows:

For Cr(III) and Ti — 10 % aq. H₂O₂. Cr(III) was first sprayed with 1 *M* NaOH, followed by H₂O₂.

For Se(IV) and Te(IV) — 10 % SnCl₂ in 3 *M* HCl.

For Al, Be and In — 0.1 % alizarin in 1 *M* NaOH.

For Ca and Mg — 0.1 % thymolphthalein complexone in dilute ammonia.

For Bi(III), Mo(VI), Re(VII), Sb(III), Sn(IV) and W(VI) — 0.1 % dithiol in 0.25 *M* NaOH. Mo(VI), Re(VII) and W(VI) were first sprayed with dithiol, followed by HCl.

For Hg(II), Tl(I) and Zn — 0.1 % dithizone in chloroform.

For Ga — 0.5 % Rhodamine B in 6 *M* HCl.

For Nb(V) — 0.1 % aqueous tannic acid.

For Hf, rare earths, Sc, Th, U(VI), Y and Zr — 0.05 % aqueous arsenazo III.

For Ag, Au, Cd, Co, Cu(II), Fe(III), Ir(IV), Ni, Pb(II), Pd(II), Pt(IV), Rh(III) and Ru(III) — dilute colorless sodium sulfide solution.

For Ba and Sr — 0.1 % aqueous sodium rhodizonate. Rhodizonate was first applied, followed by exposure to ammonia.

For Ge — 100 mg of phenylfluorone dissolved in 1 ml of HCl and diluted to 100 ml with ethanol.

For As(III), Mn(II) and V(IV) — 2 % silver nitrate-ammonia solution (3:1).

RESULTS AND DISCUSSION

Adsorption behavior and separation of metals

R_F values of 52 metals on DEAE-cellulose in six solvent systems (organic solvent-HCl) are listed in Figs. 1 and 2 and in Table I. For comparison in Table II *R_F* values are given for the same metals chromatographed on microcrystalline cellulose Avicel SF using three organic solvent-6 *M* HCl systems. The use of microcrystalline cellulose has been previously reported⁷⁻⁹ for separations by inorganic TLC. However, only limited information is available, and systematic study is still lacking for a number of metals.

R_F values for metals chromatographed on DEAE-cellulose in the methanol-HCl system (Fig. 1) suggest that many analytical separations may be possible by selecting a proper concentration of HCl. One distinctive feature of this solvent system is that the first transition elements, except for Zn, indicate high *R_F* values, while the second transition elements, except for Mo(VI), show very low *R_F* values over the HCl concentration range tested. Platinum group metals actually remained at the start. A great advantage of the methanol-HCl system is that the spots remain small, except for those of Ru(III) and Rh(III). In all the other solvent systems *R_F* values increase with increasing concentration of HCl or have a constant value near

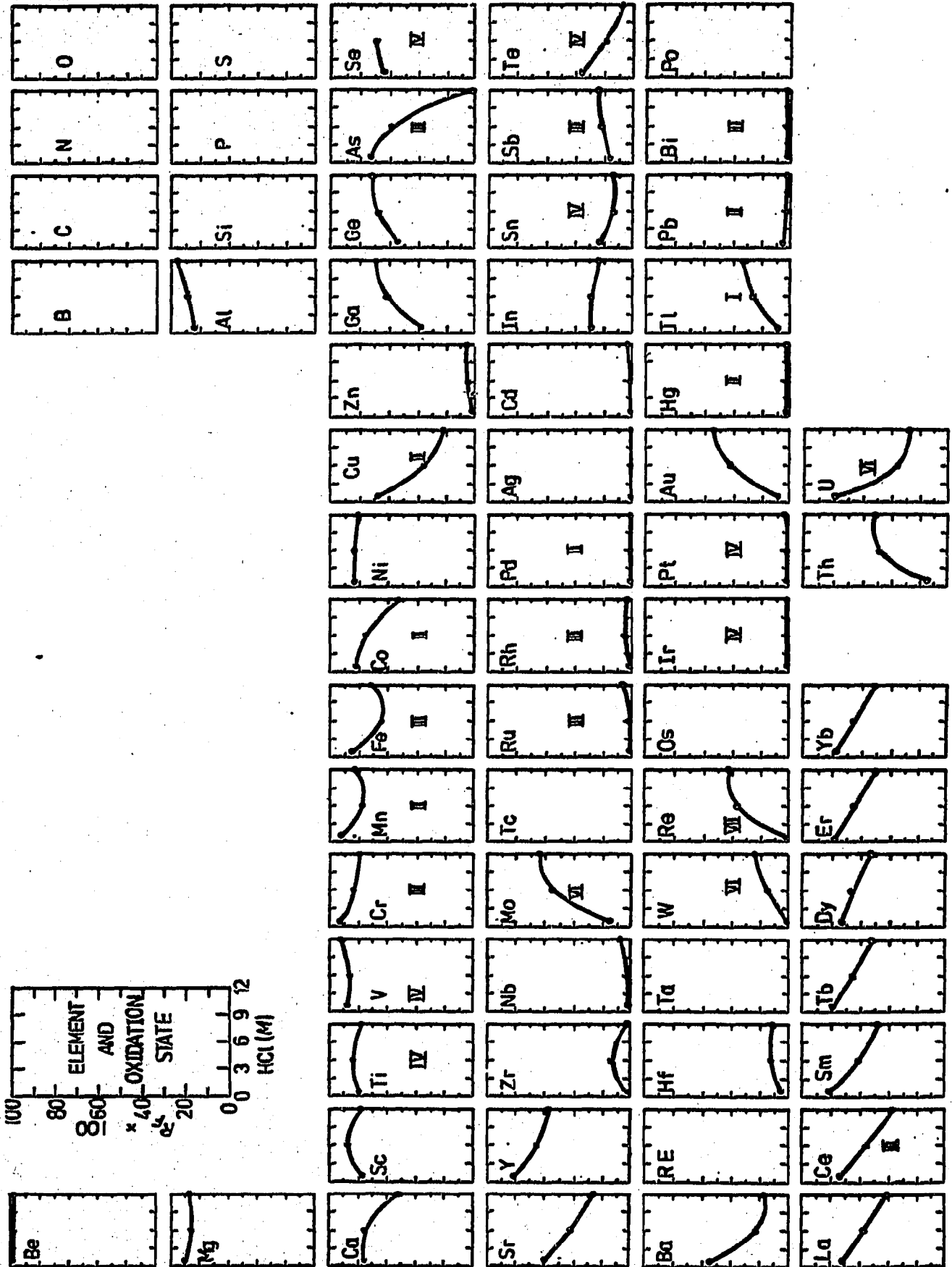


Fig. 1. R_f spectra of metals chromatographed on DEAE-cellulose in methanol-HCl (20:1).

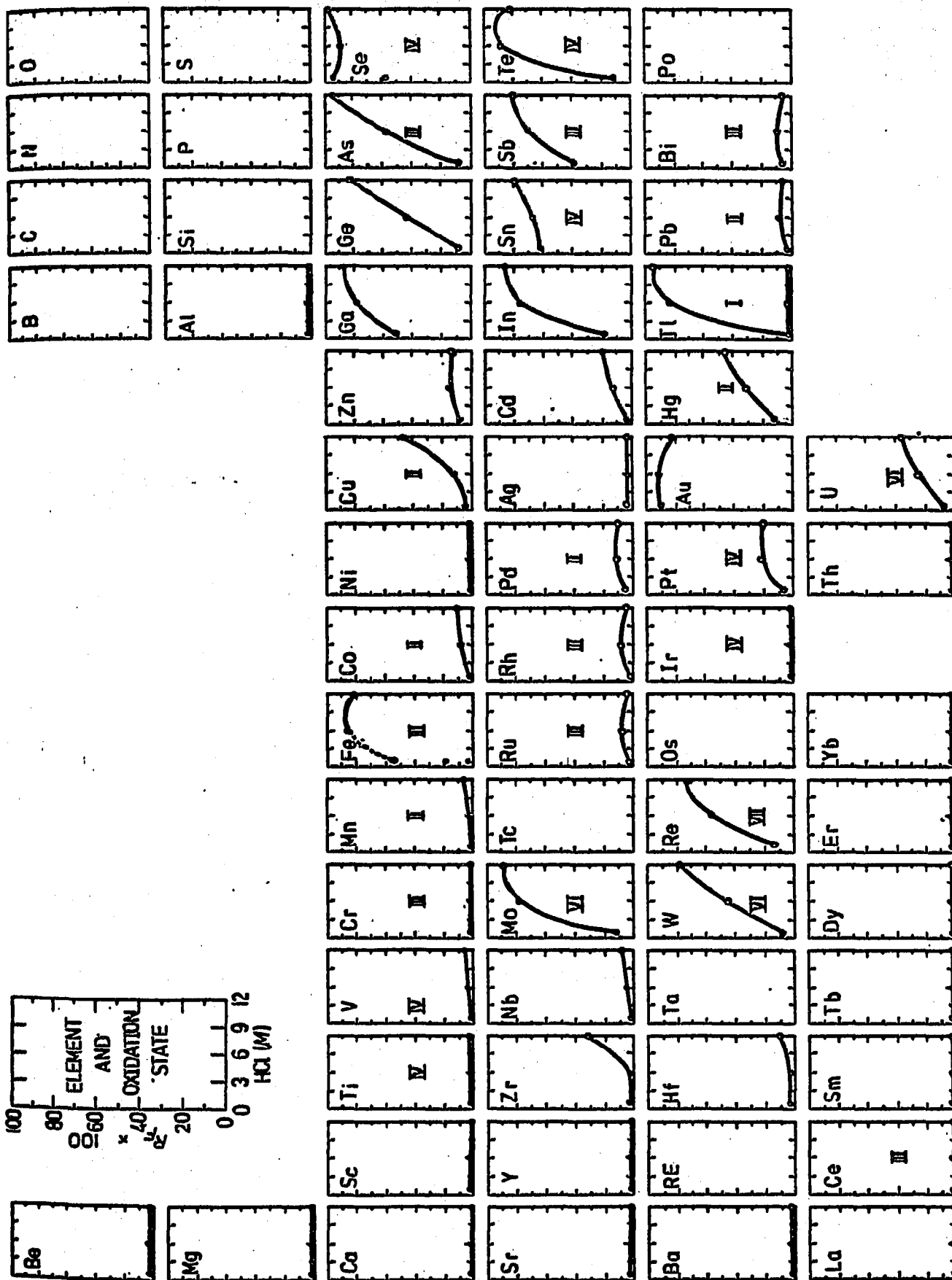


Fig. 2. R_f spectra of metals chromatographed on DEAE-cellulose in cyclohexanone-HCl (20:1).

TABLE I

R_F VALUES (X 100) ON DEAE-CELLULOSE USING SOLVENT SYSTEMS OF DIFFERENT MOLAR HCl CONCENTRATION

	n-Butanol-HCl (20:1)			Acetone-HCl (20:1)			Tetrahydrofuran-HCl (20:1)			Acetic acid-HCl (20:1)		
	I	6	12	I	6	12	I	6	12	I	6	12
Ag	1-3	1-10	1-2	3-39	27-61	5-51	1-19	33-61	0-70	2-4	1-2	0-3
Al	1-7	1-10	0-11	0-4	0-5	0-5	0-4	1-8	1-8	0-5	0-6	0-11
As(III)	50-64	61-67	57-78	30-40	76-83	93-10	11-16 30-38	57-60	69-75 90-96	32-46	46-52	—
Au	50-65	82-94	98-100	89-99	88-94	95-10	94-99	93-100	95-100	5-17	14-33	27-45
Ba	0-5	0-5	0-3	0-4	0-4	0-5	0-4	1-6	0-4	11-33	20-42	19-59
Be	4-17	0-22	7-18	0-7	0-10	6-11	0-6	11-20	9-21	1-9	2-10	11-27
Bi(III)	0-5	0-9	0-6	0-17	0-17	0-14	9-29	17-47	7-38	1-4	0-8	2-4
Ca	0-4	0-4	0-4	0-4	0-5	0-5	0-4	0-6	0-6	3-14	7-20	17-46
Cd	1-4	0-9	1-6	26-36	73-79	74-83	16-20	56-67	67-70	1-4	0-4	0-5
Ce(III)	0-3	0-4	0-4	0-4	0-5	0-5	0-4	0-4	0-9	1-8	2-13	0-15
Co(II)	0-7	0-8	1-5	10-16	31-38	48-58	1-5	29-36	40-58	0-4	0-4	0-7
Cr(III)	0-6	0-4	0-4	0-6	0-6	0-5	0-5	2-9	3-7	1-6	3-11	1-7
Cu(II)	4-9	3-13	3-8	31-38	54-60	49-55	23-27	65-69	58-68	0-6	0-5	0-7
Dy	0-3	0-4	0-4	0-4	0-5	0-5	0-4	0-4	0-5	1-7	0-9	0-10
Er	0-3	1-5	0-4	0-4	0-5	3-7	0-4	0-4	0-5	1-6	0-7	0-8
Fe(III)	1-39	0-90	1-78	95-100	92-99	97-100	80-85	85-96	90-100	2-12	4-21	31-52
Ga	35-77	62-100	76-100	93-100	98-100	92-100	89-99	92-100	95-100	3-18	12-31	47-65
Ge	18-31	35-53	27-37	36-40	67-76	93-100	15-20	61-63	64-67	57-71	—	—
Hg(II)	0-7	0-15	1-10	29-37	70-75	67-76	34-42	65-70	91-92	1-5	2-9	0-8
Hf	0-3	0-4	0-4	0-4	0-11	0-6	0-4	0-9	1-46	1-9	0-9	1-6
In	1-14	1-17	1-11	57-70	67-72	76-85	45-65	62-71	94-100	0-5	0-6	2-15
Ir(IV)	1-3	1-6	1-4	0-24	0-30	0-39	1-13	38-48	23-47	2-3	1-2	1-3
La	0-3	0-4	0-4	0-4	0-5	0-5	0-4	0-4	0-5	1-11	0-17	0-18

Mn(II)	1-5	0-6	1-8	0-7	24-28	49-63	0-5	13-17	35-45	0-6	2-8	2-13
Mo(VI)	1-24	25-63	1-52	31-39	56-61	95-99	24-50	72-85	70-91	2-15	26-35	22-35
Nb	0-5	0-4	0-4	0-5	0-28	0-5	0-5	0-17	0-63	0-4	1-14	4-11
Ni	1-6	0-8	0-5	0-6	0-5	0-5	0-4	2-7	2-9	3-9	5-13	9-27
Pb(II)	0-4	0-6	0-3	0-6	0-34	0-21	2-30	7-50	9-41	1-4	1-3	0-3
Pd(II)	0-7	0-20	1-11	0-18	6-20	4-18	2-17	13-32	5-25	1-5	1-4	0-5
Pt(IV)	1-10	0-24	0-12	6-28	12-32	13-36	6-18	31-54	24-55	1-5	0-3	0-5
Re(VII)	31-45	71-82	59-65	57-66	51-70	96-100	26-47	51-57	77-83	8-13	39-47	43-51
Rh(III)	0-19	0-17	0-10	0-15	0-11	0-14	0-54	0-36	1-30	0-4	0-4	0-5
Ru(III)	1-19	0-26	0-12	0-17	0-39	0-42	0-38	0-63	0-79	1-5	0-4	0-6
Sb(III)	10-25	11-38	5-21	45-59 85-91	95-97	87-94	26-78	83-99	92-100	1-10	6-18	4-18
Sc	0-3	0-5	0-4	0-4	0-10	11-21	0-4	1-5 15-20	5-9 28-40	3-10	2-10	2-10
Se(IV)	67-73	68-75	57-64	27-29	70-85	96-100	41-58	49-52	63-67	30-44	52-56	56-61
Sm	0-3	0-4	0-4	0-4	0-4	0-5	0-4	0-4	0-5	0-10	0-13	0-15
Su(IV)	0-22	1-25	3-13	93-100	92-97	77-89	88-99	93-99	92-100	0-4	0-10	0-4
Sr	0-5	0-5	0-3	0-4	0-4	0-5	0-4	0-5	0-4	13-21	18-29	37-56
Tb	0-3	0-4	0-4	0-4	0-5	0-5	0-4	0-4	0-5	0-7	0-9	0-7
Te(IV)	2-8	10-24	2-17	38-43	35-39	86-94	25-36	49-55	71-84	0-4	0-7	0-4
Th	0-3	1-5	0-4	0-4	0-5	0-5	0-4	0-4	0-10	2-8	0-8	1-9
Ti(IV)	0-17	1-25	14-25	0-6	0-5	0-5	1-9	6-18	22-30	1-5	0-2	0-6
Tl(I)	2-79	76-92	0-5	97-100	97-99	92-97	91-100	95-100	98-100	3-9	25-36	41-46
U(VI)	3-10	1-9	1-8	23-26	55-57	70-87	15-17	52-54	58-59	1-4	0-3	1-4
V(IV)	1-10	1-10	1-13	0-7	6-13	12-25	9-25	34-54	80-91	0-6	3-11	12-21
W(VI)	1-3	0-15	0-8	0-50	0-51	88-96	1-25	58-81	64-73	1-2	0-20	1-22
Y	0-3	1-5	0-4	0-4	0-5	0-9	0-4	0-4	1-5	1-7	0-9	1-10
Yb	0-3	0-5	0-4	0-4	0-5	0-6	0-4	0-4	0-5	1-6	0-7	0-8
Zn	0-8	0-13	0-9	42-47	48-51	54-63	34-46	67-74	38-60	0-4	0-9	0-6
Zr	0-3	0-4	1-5	0-4	0-11	0-4	0-4	0-7	0-44	1-9	0-7	1-5

TABLE II

R_F VALUES (X 100) ON AVICEL SF IN USING THREE DIFFERENT SOLVENT SYSTEMS

	<i>Methanol-6 M HCl</i> (20:1)	<i>Acetone-6 M HCl</i> (20:1)	<i>Cyclohexanone-6 M HCl</i> (20:1)
Ag	0- 1	53- 81	0- 5
Al	84- 91	0- 6	0- 5
As(III)	55- 64	73- 77	41- 46
Au	77- 82	85-100	79- 91
Ba	14- 31	0- 4	0- 4
Be	91-100	4- 13	0- 4
Bi(III)	76- 85	74- 82	48- 67
Ca	53- 64	0- 5	0- 4
Cd	71- 77	81- 85	29- 35
Ce(III)	22- 46	0- 4	0- 5
Co(II)	61- 74	51- 61	6- 9
Cr(III)	85- 88	0- 5	0- 4
Cu(II)	57- 59	60- 62	16- 19
Dy	36- 52	0- 4	0- 5
Er	45- 54	0- 5	0- 5
Fe(III)	62- 79	96- 99	66- 97
Ga	83- 98	98-100	82-100
Ge	64- 76	76- 81	42- 51
Hg(II)	92- 97	84- 99	66- 84
Hf	0- 18	0- 32 37- 48	0- 5
In	81- 92	98-100	80- 99
Ir(IV)	47- 53	84- 90	0- 4
La	27- 48	0- 4	0- 5
Mg	74- 89	0- 5	0- 4
Mn(II)	72- 84	26- 35	0- 5
Mo(VI)	60- 69	75- 89	54- 87
Nb	0- 18	0- 5	0- 4
Ni	60- 72	0- 4	0- 5
Pb(II)	1- 32	7- 62	1- 28
Pd(II)	37- 84	75- 96	0- 41
Pt(IV)	74- 80	66-100	24- 31
Re(VII)	81- 91	82- 95	50- 65
Rh(III)	27- 75	0- 67	0- 18
Ru(III)	38- 74	0- 99	1- 28
Sb(III)	72- 81	89- 95	83- 97
Sc	70- 85	0- 19	0- 5
Se(IV)	64- 69	97-100	87- 94
Sm	29- 53	0- 4	0- 5
Sn(IV)	88- 93	88- 90	86- 96
Sr	34- 49	0- 4	0- 4
Tb	38- 53	0- 4	0- 5
Te(IV)	53- 59	93-100	84- 92
Th	24- 45	0- 4	0- 5
Ti(IV)	73- 80	1- 8	0- 4
Tl(I)	98-100	98-100	83- 87
U(VI)	71- 86	98-100	35- 42
V(IV)	81- 93	6- 14	3- 11
W(VI)	0- 42	64- 76	54- 60
Y	40- 59	0- 5	0- 5
Yb	41- 54	0- 5	0- 5
Zn	91- 98	77- 87	38- 65
Zr	0- 14	0- 47	0- 5

zero irrespective of the HCl concentration, although sometimes R_F values pass through a broad maximum. In *n*-butanol-HCl most metals remain at or near the start over the wide HCl concentration range, while only a few metals exhibit high R_F values. As(III), Au, Ga, Ge, Re(VII) and Se(IV) are among the latter, thus being separated specifically from many other metals. This is also the case for acetic acid-HCl, in which only a limited number of metals, including the alkaline earths As(III), Au, Ga, Mo(VI), Re(VII), Se(IV) and Tl(I), exhibit high R_F values. R_F values tend to increase with increasing concentration of HCl.

R_F values for metals chromatographed in acetone, tetrahydrofuran and cyclohexanone-HCl systems clearly indicate useful separation procedures for many metals studied. Inspection of relevant R_F values will show whether a separation is feasible and what the most favorable concentration of HCl should be. It is noteworthy that these systems also afford very specific separation procedures for particular metals, when a proper concentration of HCl is selected. In cyclohexanone-1 *M* HCl Au, Sb(III), Se(IV) and Sn(IV) can be separated very specifically from a number of metals. A limited number of metals including Au, Fe(III), Ga and Tl(I) exhibit an R_F value of nearly unity in acetone-HCl, irrespective of HCl concentration, thus being separated very specifically. The same metals and Sn(IV) also indicate the highest R_F value of unity in tetrahydrofuran-HCl over the HCl concentration range tested. Thus, specific separation of these metals is also possible.

Solvent systems developed for multi-component mixtures are illustrated in Table III to demonstrate the use of R_F value measurements for separations.

Factors controlling the R_F values

On DEAE-cellulose R_F trends observed as a function of HCl concentration in methanol-HCl generally closely parallel those in the anion-exchange systems reported by KRAUS AND NELSON¹⁰, with some exception for Ga, Ge and Mo(VI). This suggests that the mechanism of metal distribution on DEAE-cellulose in methanol-HCl is dominantly controlled by ion exchange. Except for those metals which show hydrolytic behavior (Zr, Hf, Nb, W(VI)) or which precipitate (Pb(II)), the metals remaining at or near the start on DEAE-cellulose over the HCl concentration range tested are among those which form the strongest chloro-complexes, including Bi(III), Cd, Hg(II), platinum group metals and Zn.

We have previously reported that only an extremely limited number of metals, including Hg(II)⁶, Pd(II) and Pt(IV)⁵ and W(VI)⁴, can adsorb on DEAE-cellulose in pure aqueous media, usually dilute chloride-thiocyanate solutions. This enabled us to develop very specific column procedures for these metals using an aqueous chloride-thiocyanate system. Because of the extremely high affinity of DEAE-cellulose to simple anions like Cl⁻ or SCN⁻, distribution coefficients for these metals decreased rapidly with increasing concentration of Cl⁻ and/or SCN⁻. Therefore, in order to extend the application of DEAE-cellulose to many other metals, reduction of the concentration of Cl⁻ as well as promotion of the formation of chloro-complexes of metals seem to be primary requirements. In the aqueous solution a reduction of Cl⁻ concentration will inevitably cause the dissociation of chloro-complexes. On the contrary, the addition of increasing amounts of methanol will reduce the HCl concentration and also favor reduction of the concentration of water molecules around the cations, thus leading to the destruction of the hydration cloud around

TABLE III

SOLVENT SYSTEMS FOR THE SEPARATION OF MULTI-COMPONENT MIXTURES

Abbreviations: MeOH = methanol, BuOH = *n*-butanol, Ac = acetone, THF = tetrahydrofuran, HOAc = acetic acid, CYCH = cyclohexanone.

<i>Elements separated ($R_F \times 100$)</i>	<i>Developing solvent used (20:1)</i>
Mg (93-80)—Ca (56-49)—Sr (38-27)—Ba (21-10)	MeOH-12 M HCl
Ni (76-69)—Au (53-46)—Cu(II) (24-14)—Ag (3-0)	MeOH-12 M HCl
Be (98-88)—Sc (83-72)—Th (51-43)—U(VI) (19-10)—Zr (3-0)	MeOH-12 M HCl
Al (100-94)—Sc (88-75)—Th(59-37)—U(VI) (17-6)	MeOH-12 M HCl
Ni (94-83)—Cu(II) (24-16)—Zn (5-0)	MeOH-6 M HCl
Se(IV) (71-65)—Te(IV) (23-17)	MeOH-6 M HCl
Cr(III) (98-91)—Mo(VI) (72-0)	MeOH-6 M HCl
Th (64-47)—U(VI) (51-47)—Zr (3-0)	MeOH-3 M HCl
Cu(II) (38-26)—Ag, Bi(III), Cd, Hg(II), Pb(II) (12-0)	MeOH-1 M HCl
Rare earths (82-56)—Th (49-23)	MeOH-1 M HCl
Se(IV) (73-67)—As(III) (63-55)—Ge (26-14)—Te(IV) (11-4)	BuOH-1 M HCl
Fe(III) (100-98)—In (79-71)—Cu(II) (64-59)—Co (57-51)— Mn (41-35)—V(IV) (20-16)—Ni (5-0)	Ac-6 M HCl
Fe(III) (94-90)—In (78-69)—Zn (54-49)—Cu(II) (42-37)— Co (12-7)—Ni (5-0)	Ac-1 M HCl
Au (97-92)—Cu(II) (63-57)—Ir(IV) (42-36)—Pd(II) (33-16)	THF-6 M HCl
Ti(I) (99-92)—Zn (68-63)—Co (37-33)—Mn(II) (24-19)—Ni (10-3)	THF-6 M HCl
Sn(IV) (99-90)—Fe(III) (77-49)—Cu(II) (40-31)—Zn (36-33)— Al (4-0)	THF-1 M HCl
Ge (97-92)—As(III) (87-80)—50 elements (17-0)	HOAc-1 M HCl
Au (91-85)—Pt(IV) (17-12)—Rh(III) (8-0)	CYCH-12 M HCl
Au (97-84)—Hg(II) (48-24)—Pb(II) (13-0), Pd(II) (10-0)	CYCH-12 M HCl
Sn(IV) (71-69)—Sb(III) (62-57)—As(III) (20-15)—Pb(II) (10-0)	CYCH-1 M HCl

the cations. This effect allows the chloride complexes to be formed at a lower concentration of HCl and may enhance differences in the tendency of chloride complex to be formed. Because of a low concentration of Cl^- , the chloro-complex anions may easily enter the exchange sites without competing with Cl^- for the sites. Thus, the weakly basic anion exchanger DEAE-cellulose can behave in methanol-HCl as if it were a strongly basic anion exchanger in an aqueous HCl system. There are no substantial differences in R_F values on DEAE-cellulose and Avicel for such metals as the alkaline earths, the rare earths, Al, Th, Ti, etc., which do not form chloro-complexes. In these case the usual partition mechanism may dominate to control the distribution of metals.

R_F values for metal ions chromatographed in much less polar cyclohexanone-HCl systems indicate that there are generally few marked differences in R_F values on DEAE-cellulose and Avicel. In contrast to the methanol-HCl system, metals forming strong chloro-complexes tend to migrate upwards, irrespective of adsorbents, while those forming no chloro-complexes exhibit strong retention at or near the start.

BOSWELL AND BROOKS¹¹ reported that chloro-complexes of many metals are

extracted into cyclohexanone and that trends observed in the solvent extraction systems closely parallel those in the anion-exchange systems reported by KRAUS AND NELSON¹⁰. Consequently, it can be expected that metals forming no chloro-complexes may remain at or near start, while chloro-complexes may advance with the cyclohexanone-HCl solvent. Of the competitive mechanisms, ion exchange and partition, the latter prevails, so that there is no marked difference in R_F values between DEAE-cellulose and Avicel, although the contribution of ion-exchange distribution cannot be completely ignored for some metal ions. Thus, R_F values on DEAE-cellulose are always a little lower than those on Avicel for Cd, Hg(II), platinum group metals, Zn, etc., which form the strongest chloro-complexes.

R_F values for metal ions chromatographed on DEAE-cellulose and Avicel in acetone-HCl rather resemble each other and, on the whole, those in cyclohexanone-HCl. Metals forming chloro-complexes tend to migrate upwards, while the other metals remain at the start for both DEAE-cellulose and Avicel. As before, the partition distribution must have an important role in determining R_F values. Again, for the metals forming the strongest chloro-complexes, much lower R_F values are observed on DEAE-cellulose than on Avicel, probably because of a partial contribution of the ion exchange.

We did not obtain R_F data on Avicel in *n*-butanol, tetrahydrofuran and acetic acid-HCl systems. R_F values for metals on DEAE-cellulose in these solvents are, however, generally close to those in cyclohexanone-HCl so that metals are also thought to be distributed on DEAE-cellulose dominantly by the mechanism of partition in these solvent systems. It may be concluded that the utility of a weakly basic anion exchanger will generally be increased by using it in mineral acid media containing increased amounts of a proper organic solvent like methanol.

Similar results with some ions and some solvent systems have been obtained on DEAE-cellulose paper¹².

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