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THIN-LAYER CHROMATOGRAPHIC SEPARATION OF NOBLE METALS ON DIETHYLAMINOETHYLCELLULOSE IN AQUEOUS CHLORIDE SOLUTIONS

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SUMMARY

The thin-layer chromatographic behaviour of the noble metals on diethylaminoethylcellulose was investigated in aqueous chloride solutions of Li, Na, Mg, Ca and Al. The R_F values increase in the order Ir(III)=Rh(III) > Ru(III) > Pd(II) > Pt(IV) > Ir(IV) > Au(III) in all of the salt solutions tested. The solutions of higher chloride concentrations ($\geqslant 5\ M$) yield sufficiently large differences in R_F values of two adjacent metals to permit good separations. Typical chromatograms for multi-component separations of the noble metals are presented.

INTRODUCTION

Recent advances in separations of the noble metals have been reviewed by Beamish[1] and Beamish and Van Loon[2]. However, there is little information available on multi-component chromatographic separations of the noble metals in a single run, probably because of irreversible adsorption and the formation of anomalous zones, resulting from hydrolysis, polymerization and changes in oxidation state before or during chromatography.

Many papers[3-8] have been published on the thin-layer chromatographic (TLC) behaviour and separation of noble metals, covering a limited number of the metals (generally gold, platinum and palladium) and usually excluding ruthenium, rhodium and iridium, which have more complicated solution chemistry. In addition, most procedures for these separations require either the formation of noble metal–organic complexes before development or the use of developing solvents that contain organic complexing agents. Thus, effective methods for the separation of the noble metals are still lacking.

Although the chromatographic behaviour of a number of metals on diethylaminoethylcellulose (DEAE-cellulose) has already been explored in various aqueous acids and binary solvent systems consisting of an acid and an organic solvent, little

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attention has been paid to the use of DEAE-cellulose and of aqueous salt solutions for the separation of the noble metals from each other. The adsorption behaviour of gold and the platinum-group metals on DEAE-cellulose paper in lithium chloride–0.1 and 1 M hydrochloric acid media has been studied by Lederer[9] and Bagliano et al.[10], but separations were not described. We have also demonstrated the chromatographic behaviour and separation of platinum and palladium on DEAE-cellulose columns in ammonium thiocyanate and potassium chloride media[11].

In order to extend the application of DEAE-cellulose in inorganic separations and to find simpler and more effective chromatographic systems for the separation of the noble metals, we have examined the TLC behaviour of gold and the platinum-group metals (except osmium, which is readily separated by distillation), on DEAE-cellulose in hydrochloric acid and various aqueous chloride solutions. The chloride media investigated permit a number of useful multi-component separations of analytical interest to be conducted effectively.

EXPERIMENTAL

Materials

Stock solutions of noble metals. Analytical-reagent grade chemicals were used. To prepare stock solutions of noble metals, the following compounds were used: sodium chloroaurate, chloroplatinic acid, palladium chloride, ruthenium trichloride ($RuCl_3 \cdot xH_2O$, $x = 1$–3), rhodium trichloride ($RhCl_3 \cdot 3H_2O$), sodium chlororhodate ($Na_3RhCl_6 \cdot 2H_2O$), sodium chloroiridate(III) ($Na_3IrCl_6 \cdot 10H_2O$) and sodium chloroiridate(IV) (Na_2IrCl_6). The last three compounds were obtained from Mitsuwa (Osaka, Japan) and the others from Wako (Osaka, Japan). Individual stock solutions of the noble metals were prepared by dissolving an appropriate amount of the compounds in 3 M and occasionally 0.1 M hydrochloric acid to give 0.025 M solutions and allowing them to stand at room temperature. Test solutions for the examination of the chromatographic behaviour were prepared by diluting the stock solutions with the same concentration of hydrochloric acid to give 0.005 M metal solutions. Sample solutions for the separation of the metals were prepared by mixing an equal volume of the individual stock solutions in 3 M hydrochloric acid, just before application on a plate.

Solvents. Developing solvents were prepared by dissolving each of the chlorides of lithium, sodium, magnesium and calcium in de-ionized water. Aluminium chloride was dissolved in 0.1 M hydrochloric acid to prevent hydrolysis. For the separation of mixtures containing iridium, salt solutions containing bromine were also used as the solvent. These solutions were prepared by mixing in varying proportions a salt solution with a chloride concentration of 5 M or 7 M and a saturated bromine solution with the same chloride concentration.

Thin-layer plates. A cellulose anion exchanger, DEAE-cellulose (for TLC, Serva, Heidelberg, G.F.R.) was used as adsorbent. A 10-g portion of DEAE-cellulose was shaken mechanically for 1 h with a 1 M sodium chloride solution adjusted to pH 1 with 1 M hydrochloric acid. The DEAE-cellulose thus treated was washed with 0.1 M hydrochloric acid and then three times with de-ionized water, being separated each time by centrifugation. The pH of the final supernatant liquid should be about 3. The purified DEAE-cellulose (chloride form) was slurried with 23 ml of de-ionized

water and spread to a thickness of 0.25 mm on glass plates (20×20 cm²) with an applicator. The plates were allowed to stand for 30 min at room temperature and then dried in an oven at *ca.* 40° for 5 h. After cooling, they were stored in a desiccator containing saturated sodium chloride solution until ready for use.

Procedure

A test or sample solution (*ca.* 0.5 μl) was applied to the plate at a point 2.5 cm from one end by means of a micropipette and the spots were dried in air for 30 min. The plate was placed in a chromatographic tank ($22 \times 11 \times 22$ cm³) containing about 120 ml of a developing solvent and allowed to stand for 30 min to equilibrate with the tank atmosphere. Ascending development was conducted at a constant temperature of $25 \pm 1°$ until the solvent front had travelled 10 cm.

After development, the plate was dried under a heat lamp. Iridium and ruthenium were first detected by spraying with saturated bromine water. The other metals, after expelling bromine by heating, were located by spraying with a 2% tin(II) chloride–2% potassium iodide solution in 3 M hydrochloric acid, followed by gentle heating. The tin(II) chloride solution should be freshly prepared.

RESULTS AND DISCUSSION

Adsorption behaviour

The R_F values of gold and the platinum-group metals except osmium on DEAE-cellulose (chloride form) in hydrochloric acid and aqueous lithium chloride and sodium chloride media are given as a function of a total chloride concentration in Table I, which also gives the R_F values of the same metals on DEAE-cellulose in 2.5 M magnesium chloride, 2.5 M calcium chloride and 1.6 M aluminium chloride–0.1 M hydrochloric acid media for comparison. The metals are arranged in order of increasing R_F values at a total chloride concentration of 5 M, and this order is the same for all of the salt solutions tested. The valence states recorded are those of the metals before contacted with DEAE-cellulose. The adsorption function of iridium(IV) is tentative because of its partial reduction to iridium(III). The other metals give a well defined spot at higher chloride concentrations, although ruthenium(III), rhodium(III) and iridium(III) show two spots, tailing or heading only with lower chloride concentrations.

In hydrochloric acid media, all of the metals tested show a tendency for their R_F values to increase with increasing concentration of chloride ion. This is not always so with the aqueous lithium chloride and sodium chloride media, there being a considerable decrease in the R_F values of the metals that form stable anionic chloro complexes, such as gold, iridium(IV) and platinum(IV), at higher concentrations of the chlorides, and a slight decrease for palladium(II). In these media, the R_F values of gold decrease with increasing chloride concentration and those of iridium(IV), platinum and palladium first increase with increasing chloride concentration, pass through a broad maximum near 5 M for the lithium chloride media and near 4 M for the sodium chloride media, and then decrease gradually with further increase in the chloride concentration. Thus, the higher is the concentration of the chlorides, the larger are the differences in the R_F values between one of the salt solutions and hydrochloric acid. This has also been found with the paper chromatographic system[10] com-

TABLE I

$R_F \times 100$ VALUES OF NOBLE METALS ON DEAE-CELLULOSE (CHLORIDE FORM) IN VARIOUS CHLORIDE MEDIA

Medium	Total chloride concentration (M)	$R_F \times 100$							Time of run (min)
		Au(III)	Ir(IV) [a]	Pt(IV)	Pd(II)	Ru(III)	Rh(III)	Ir(III)	
HCl	1	26–32	16– 25---38[***] 53– 61	20–27	21–28	16–23---35 35–46	47– 60---63 63– 73	30– 37 51– 60	55
	2	31–36	26– 34---50 58– 65 68– 75	31–39	34–42	35–55	63– 77	57– 63 67– 76	67
	3	33–39	27– 37---70 70– 81	36–45	40–49	50–66	74– 85	75– 82	70
	4	38–43	29– 38 74– 85	40–48	44–52	57–74	78– 89	80– 86	90
	5	45–50	39– 45 83– 93	44–57	50–56	69–75	85– 93	86– 94	100
LiCl	1	20–26	13– 22---35 50– 58	16–24	18–27	0–71	45– 73	26– 33 53– 61	65
	3	21–25	25– 32---80	29–38	36–44	44–55	67– 82	71– 80	70

5	17–22	29–35, 90–100	34–43	44–53	63–71	74–94	86–98	135
7	16–21	26–32, 97–100	33–41	47–55	70–80	89–100	93–100	205
9	12–18	18–25, 98–100	25–33	39–46	73–83	96–100	98–100	370
NaCl 1	23–27	15–24---67	17–23	21–29	35–73	60–72---75, 75–83	33–43, 60–67	55
2	22–26	11–26---80	24–32	29–38	33–70	78–89	73–83	65
3	18–22	23–28---86	28–36	39–48	59–75	75–90	79–88	70
4	16–20	23–27---94	26–35	44–52	66–80	78–91	89–96	92
5	13–17	21–26---100	26–35	47–57	67–79	82–100	90–100	115
Satd.	12–16	18–23---100	22–31	44–53	64–77	83–100	93–100	120
MgCl$_2$ 5	18–23	25–30, 90–99	28–37	40–50	58–69	90–97	91–99	230
CaCl$_2$ 5	21–24	25–31, 88–95	33–40	45–53	61–73	85–96	90–98	190
AlCl$_3$** 5	24–29	31–37, 91–100	36–46	49–59	69–81	85–99	95–100	360

* A 0.025 M stock solution was used.
** A 1.6 M AlCl$_3$–0.1 M HCl solution was used.
*** ---, Weak streak.

posed of DEAE-cellulose and lithium chloride media, in which the R_F values of gold, iridium(IV) and platinum are considerably decreased in comparison with pure hydrochloric acid media, although not affected by variations in the lithium chloride concentration. As can be seen from a comparison of the data for the five salt solutions with those for hydrochloric acid, at a total chloride concentration of 5 M, any of these salt solutions cause appreciable decreases in the R_F values of gold, iridium(IV), platinum and palladium, almost independent of the nature of the salts concerned.

On the contrary, ruthenium(III), iridium(III) and rhodium(III) exhibit a decreasing adsorption with increasing chloride concentration in the aqueous lithium chloride and sodium chloride media, and there are no substantial differences in the R_F values of these metals between one of the salt solutions and hydrochloric acid. In addition, it can be seen from the data for the salt solutions with a total chloride concentration of 5 M that the adsorption of these metals is hardly affected by the nature of the cations of the chlorides used, although ruthenium always has lower R_F values than the others, which have R_F values of nearly unity at higher chloride concentrations in all of the media tested.

Separation

A survey of the TLC behaviour of the noble metals on DEAE-cellulose in the aqueous chloride solutions should permit the development of many effective methods for their separation. One of the outstanding features of the present chromatographic system is that there are sufficiently large differences in the R_F values of two adjacent metals in various salt solutions of higher chloride concentrations to permit good resolutions to be achieved.

Fig. 1 shows thin-layer chromatograms for the consecutive separation of the five metals except iridium at a development distance of 10 cm with various salt solutions with a total chloride concentration of 5 M. With all of the developing solvents, the R_F values of the metals in the mixture were identical with those when chromatographed alone and there was no marked tailing. Although not shown in Fig. 1, a
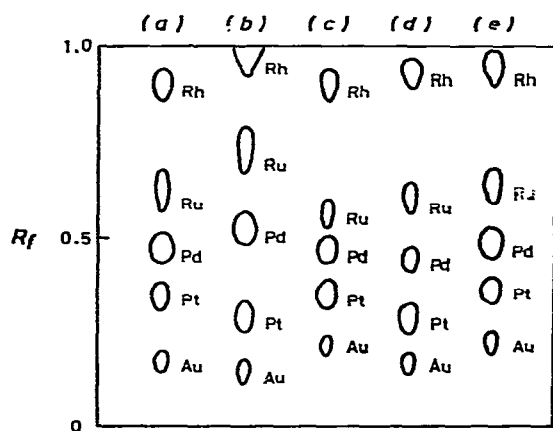

Fig. 1. Separation of Au(III), Pt(IV), Pd(II), Ru(III) and Rh(III) on DEAE-cellulose (chloride form). Solvent: (a) 5 M LiCl solution; (b) 5 M NaCl solution; (c) 2.5 M MgCl$_2$ solution; (d) 2.5 M CaCl$_2$ solution; (e) 1.6 M AlCl$_3$–0.1 M HCl solution.

five-component mixture containing iridium(III) instead of rhodium was also separated under the same experimental conditions. As can be seen from Table I, the higher the concentration of chloride in any salt solution, the shorter is the developed zone but the longer is the development time. Therefore, salt solutions with a total chloride concentration of 5 M were used for the separation of the noble metals; in particular, 5 M sodium chloride solution is regarded as the best for general purposes because it offers more convenient and faster separations.

Chromatograms for the separation of a six-component mixture are given in Fig. 2, together with the developing solvents used. For the separation of mixtures containing iridium(IV), it is essential to add bromine to the solvents in order to preserve the quadrivalent state, as iridium(IV) produces two spots even at higher chloride concentrations. Usually, a 40-ml portion of a saturated bromine solution with a total chloride concentration of 5 M was added to an 80-ml portion of a solution with the same chloride concentration but free from bromine. With such solutions containing bromine, the R_F values of the metals in the mixture were also identical with those when chromatographed alone and the overall pattern of the zones was reproducible on repeated runs. However, the R_F values of gold and ruthenium decreased by 0.08 in comparison with those for the 5 M chloride solutions free from bromine, but this did not adversely affect the separations of the noble metals because there were still adequate differences in the R_F values of adjacent metals.
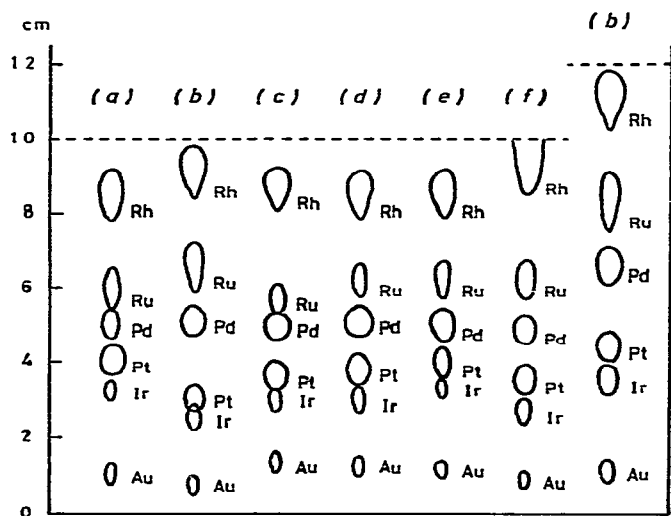

Fig. 2. Separation of Au(III), Ir(IV), Pt(IV), Pd(II), Ru(III) and Rh(III) on DEAE-cellulose (chloride form). Solvent: (a) solution of 5 M LiCl (80 ml) and 5 M LiCl saturated with Br$_2$ (40 ml); (b) solution of 5 M NaCl (80 ml) and 5 M NaCl saturated with Br$_2$ (40 ml); (c) solution of 2.5 M MgCl$_2$ (80 ml) and 2.5 M MgCl$_2$ saturated with Br$_2$ (40 ml); (d) solution of 2.5 M CaCl$_2$ (80 ml) and 2.5 M CaCl$_2$ saturated with Br$_2$ (40 ml); (e) solution of 1.6 M AlCl$_3$–0.1 M HCl (80 ml) and 1.6 M AlCl$_3$–0.1 M HCl saturated with Br$_2$ (40 ml); (f) solution of 7 M LiCl (80 ml) and 7 M LiCl saturated with Br$_2$ (40 ml). – – –, Solvent front.

As can been seen in Fig. 2, the iridium(IV)–platinum and palladium–ruthenium separations are difficult with a development distance of 10 cm with some of the salt solutions containing bromine. Better resolutions were obtained by making the

development distance 2 cm longer or by increasing the total chloride concentration to 7 M, but these techniques led to slower separations. On the other hand, it is worth noting that such salt solutions containing bromine also permit the excellent resolution of rhodium and iridium(III) or iridium(IV), which is one of the most difficult aspects of platinum-group metal analyses.

Hence this chromatographic system provides satisfactory resolutions of all of the pairs of adjacent metals, thus allowing multi-component separations to be conducted simply and effectively.

Ageing and acidity of stock solutions

In order to separate successfully the platinum-group metals from each other, it is essential to have an intimate knowledge of the character of their stock solutions, which may affect their separations. The solution chemistry of iridium(III), ruthenium(III) and rhodium(III) in dilute hydrochloric acid has already been studied by paper chromatographic or electrophoretic methods[12,13]. We examined the effects of ageing and acidity of the stock solutions of the same metals on the chromatographic behaviour to ensure the validity of the present method of separation.

When each of the solutions of sodium chloroiridate(III) dissolved in 0.1 and 3 M hydrochloric acid was chromatographed with the various salt solutions, DEAE-cellulose always yielded only a single spot over a wide range of total chloride concentrations. This has also been found with a DEAE-cellulose paper–hydrochloric acid system[12].

Fig. 3 shows the chromatograms obtained by developing aged solutions of ruthenium trichloride dissolved in 0.1 and 3 M hydrochloric acid with 5 M sodium chloride solution as solvent. The ruthenium solution in 0.1 M hydrochloric acid shows pronounced tailing and heading, probably due to slow stepwise hydration and subsequent oxidation of ruthenium(III) to ruthenium(IV) by air during ageing[13]. On the other hand, the solution in 3 M hydrochloric acid gives a well defined spot, although it is long. Evidently, the choice of acidity is important for a stock solution
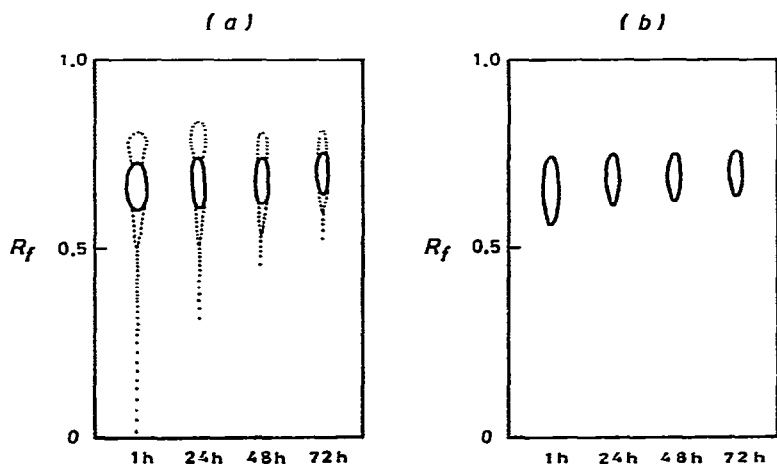

Fig. 3. Ageing of solutions of RuCl$_3$ dissolved in (a) 0.1 and (b) 3 M HCl. – – –, Weak spot.

of ruthenium. All of the data quoted, except for Fig. 3(a), were obtained with a solution of ruthenium trichloride in 3 M hydrochloric acid.

Fig. 4 shows the effect of ageing of solutions of rhodium trichloride and sodium chlororhodate dissolved in 3 M hydrochloric acid on chromatograms developed with 5 M sodium chloride solution as solvent. Almost the same chromatograms were obtained when the solutions of these compounds dissolved in 0.1 M hydrochloric acid were chromatographed with the same solvent. Rhodium trichloride produced two spots in all of the media tested, irrespective of ageing and the acidity of its solution. The stronger spot is in good agreement with that obtained from the solution of sodium chlororhodate but the other remains at the point of application because of partial hydrolysis of rhodium trichloride to insoluble species[12]. On the other hand, a solution of sodium chlororhodate aged for 96 h or more gives only a single spot, although more freshly prepared solutions yield two spots or tailing because of the slowness with which the equilibria between the complexes of rhodium formed in the solutions are established. All of the data quoted for rhodium, except for Fig. 4(a), were obtained from a solution of sodium chlororhodate aged for 96 h or more.
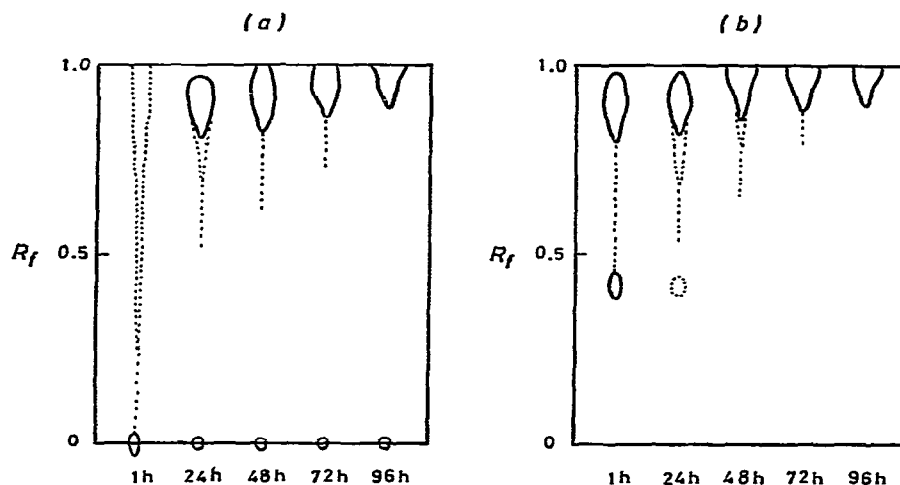

Fig. 4. Ageing of solutions of (a) RhCl$_3$ and (b) Na$_3$RhCl$_6$ dissolved in 3 M HCl. — — —, Weak spot.

There was no abnormal adsorption of the metals other than that already described.

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