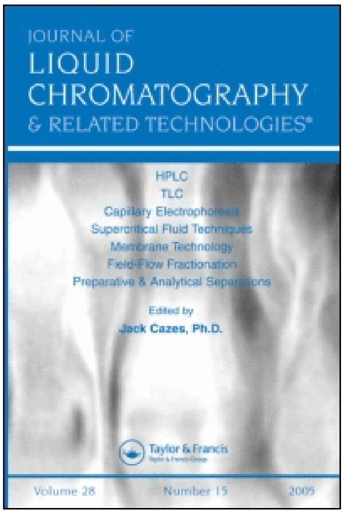

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THIN-LAYER CHROMATOGRAPHIC SEPARATION OF SOME ALLIED METAL IONS AND THEIR DETERMINATION BY RING COLORIMETRY

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ABSTRACT

Suitable methods have been worked out for the separation and determination of various groups of similar metal ions in mixtures, employing a combination of thin-layer chromatography and ring colorimetry. Solvent mixtures employed were : n-butanol + 12N HCl + dioxan (5:1:4); n-butanol + 6N HCl + dioxan (5:1:4); hexanol + dioxan + acetic acid + water (160:10:2:40); methanol + water (9:1 and 7:3). The following mixtures of cations were separated by TLC and the separated constituents were subsequently determined by ring colorimetry : Fe(III)- Co(II)- Cu(II)- Pb(II)- Ni(II); Pt(IV)- Co(II)- Cu(II)- Pd(II)- Ni(II); Ag(I)- Ni(II)- Co(II)- Fe(III); Cu(II)- Ni(II)- Bi(III); Cu(II)- Bi(III)- Hg(II).

INTRODUCTION

The work on the applications of thin-layer chromatography (TLC) in quantitative inorganic analysis has been sparse (1). Here, the separation and determination of some inorganic ions have been achieved by using a combination of TLC and ring colorimetry (2). The procedure has been found to be useful and has an

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added advantage that only inexpensive equipment is needed.

The cations studied in the present communication were : Al(III), Ag(I), Cu(II), Co(II), Ni(II), Cd(II), Hg(II), Bi(III), Fe(II), Fe(III), Mn(II), Zn(II), Mg(II), Pd(II), Pt(IV), Rh(III), Ru(III), and UO_2(VI), and the following combinations of developing solvents were used :

(a) n-Butanol + 12N HCl + dioxan (5:1:4)
(b) n-Butanol + 6N HCl + dioxan (5:1:4)
(c) Hexanol + dioxan + acetic acid + water (160:10:2:40)
(d) Methanol + water (9:1)
(e) Methanol + water (7:3)

A number of solvents and acid in various concentration were employed and only the above mentioned combinations have been found to be satisfactory.

EXPERIMENTAL

Metal Solutions :

0.1 Mol dm^{-3} stock solutions of the following were prepared using reagent grade chemicals (BDH or Johnson Matthey, London, England), standardized by the estimation of the metal contents and diluted as necessary:

Nitrates of silver(I), mercury(II), bismuth(III), uranyl(VI), and magnesium(II); chlorides of nickel(II), cobalt(II), copper(II), iron(II), iron(III), platinum (IV), cadmium(II), zinc(II), aluminium(III), manganese(II), palladium(II), ruthenium(III) and rhodium(III).

Chromogenic Reagents :

Diethyldithiocarbamate (DDTC) (BDH AnalaR); 0.1% w/v in ethanol

p-Dimethylaminobenzylidene rhodamine (BDH AnalaR): 0.1% w/v in ethanol

1-(2-pyridylazo)-2-naphthol (PAN; Koch-Light, Coinbrook, England): 0.1% w/v in ethanol

8-Hydroxyquinoline (BDH AnalaR): 2% w/v in chloroform.

Developing Solvents :

Suitable mixtures of n-butanol, dioxan, hexanol, methanol, acetic acid and hydrochloric acid (all BDH AnalaR).

Adsorbents :

Silica gel G (E. Merck, Darmstadt, FGR) and cellulose (Joseph Crosfield and Sons, Coinbrook, England).

Apparatus and Procedure :

TLC equipment kit (Toshniwal, New Delhi, India) was used. The adsorbents were spread on the glass plates (20 X 20 cm^2) as a slurry using an applicator supplied with the equipment. The plates were kept horizontally in the drying racks, dried in air and finally at 110° for 2 hr. They were then stored in desiccators. The plates were examined before use and those with uniform layers were used.

In these studies, solutions of 0.01 mol dm^{-3} concentration were used. In the cases of mixtures, equal volumes of solutions 0.01 mol dm^{-3} were mixed.

The spots of the mixtures were applied to the plates with the help of a self-filling micropipette and allowed to dry in air. The plates were placed with an edge dipped about 2 cm in the solvent and placed vertically in a rectangular glass chamber (21 X 21 X 9 cm^3) covered with ground glass. The chamber had been previously saturated with the vapour of the corresponding solvent.

After the desired migration of ions, the plates were dried in air, examined in visible and ultraviolet light after spraying the appropriate chromogenic reagents. The distances were measured to obtain L_E (leading edge) and T_E (tailing edge). R_f values were obtained from :

$$R_f = \frac{L_E + T_E}{2 \times \text{distance moved by the solvent}}$$

The various ions were identified on the plates as indicated in Table 1.

TABLE 1

Reagents for Identification

Treatment	Observation	Metal Ion
Sprayed with 8-hydroxyquinoline, exposed to NH_3 and held under ultraviolet light.	Dark Spot	UO_2(VI)
	Yellow fluorescent spot	Al(III)
Sprayed with a 1:1 mixture of PAN and p-dimethylaminobenzylidene rhodamine and viewed in :		
(i) Visible light	Red Spot	Mn(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II).
	Blue Spot	Co(II), Pd(II), Pt(IV).
	Gray Spot	Fe(II), Fe(III).
	Yellow Spot	Ag(I).
(ii) Ultraviolet light	Dark Spot	Ru(III), Rh(III).
Sprayed with DDTC and viewed in visible light	Green Spot	Pb(II), Bi(III).

For the solvent mixture (a) and (b), the coating material was cellulose, while for the other combinations of solvents i.e. (c), (d) and (e), silica gel was employed. The thickness of the adsorbent layer was 0.2 mm, which was found suitable. The developing time of run was 45 min with solvents (a) and (b), while with (c) the plates were developed for 1.45 hr. The time of development with mixtures (d) and (c) were 30 min. In all the cases, one drop of 0.01 mol dm^{-3} metal solution was used. The R_f values for the individual metal ions are reported in Table 2.

Quantitative Separation by Ring Colorimetry (3)

Table 2 helped in finding the suitable possible combinations of metal ions for quantitative separa-

TABLE 2

R_f values of Various Metal Ions

Metal Ion	Solvent mixture				
	(a)*	(b)*	(c)†	(d)†	(e)†
Al(III)	0.19	0.14	...	...	...
Ag(I)	0	0	...	...	...
Cu(II)	0.78	0.67	0.38	0	0
Co(II)	0.66	0.27	0.07	0	0.09
Ni(II)	0.13	0.13	0.95	0.06	0.10
Cd(II)	...	...	...	0.15	0.17
Hg(II)	...	...	...	0.91	0.15
Bi(III)	...	...	...	0.37	...
Fe(II)	0	0	0	0	0
Fe(III)	0.96	0.89	0	...	...
Mn(II)	0.26	0.22	...	...	...
Zn(II)	0.91	0.87	...	...	...
Mg(II)	0.12	0.095	...	...	...
Pd(II)	...	...	0.62	...	0.16
Pt(IV)	...	...	0	...	...
Rh(III)	...	...	0	...	...
Ru(III)	...	...	0	...	...
UO_2(VI)	...	...	0	...	0.47

*Adsorbent : Cellulose

†Adsorbent : Silica Gel

tions. In the following mixtures, the metal ions were quantitatively estimated by ring colorimetry after they were separated on thin layer chromatograms. They were:

1. Fe(III)- Co(II)- Cu(II)- Pd(II)- Ni(II)
2. Pt(IV)- Co(II)- Cu(II)- Pd(II)- Ni(II)
3. Ag(I)- Ni(II)- Co(II)- Fe(III)
4. Cu(II)- Ni(II)- Bi(III)
5. Cu(II)- Bi(III)- Hg(II).

The mixtures were spotted on the plates as usual and chromatograms were run using the following solvents (Table 3) :

After the run, the duplicates (or guides) were treated with detecting reagents to locate the spots, while the original chromatogram (not treated with reagent) was used for the determinations. The separated substances (located by comparison with the guide) were scarpped off quantitatively, with the help of a spatula, into a sintered glass funnel (porosity G4). Each lot of scrapping was washed carefully with 1 cm^3 of 0.5 mol dm^{-3} HCl using a few drops each time and received on a circular Whatman No.1 filter paper (diameter 55 mm), and treated as usual on the ring oven for the transportation to the ring zone. The standard rings were obtained separately for comparison by ring colorimetry. The amount of metal ion separated

TABLE 3

Solvents Employed

Solvent Mixture	Mixture of Ions
(c)	Fe(III)- Co(II)- Cu(II)- Pd(II)- Ni(II) Pt(IV)- Co(II)- Cu(II)- Pd(II)- Ni(II)
(a)	Ag(I)- Ni(II)- Co(II)- Fe(III)
(e)	Cu(II)- Ni(II)- Bi(III)
(d)	Cu(II)- Bi(III)- Hg(II).

on the TLC plate was known by using the visual comparison of the test rings with standard scales as usual.

Some of the typical results of determinations are shown in Tables 4 to 8.

It has been found that the determinations were possible down to the following limits when present in a few drops of the solutions : Fe(II) 0.84 µg; Ni(II) 0.88 µg; Co(II) 0.89 µg; Cu(II) 0.95 µg; Ag(I) 1.06 µg;

TABLE 4

Quantitative Separation of the Mixture :
Fe(III)- Co(II)- Ni(II)- Cu(II)- Pd(II)

Ion	Taken µg	Found µg	No. of determinations	Error(%)	Standard deviation(%)
Fe(III)	1.68	1.60	4	-4.7	0.60
Co(II)	1.77	1.72	4	-2.9	0.38
Ni(II)	1.76	1.77	4	+0.5	0.17
Cu(II)	1.90	1.90	4	0	0.24
Pd(II)	3.19	3.19	4	0	0.14

Developing Solvent : Hexanol + dioxan + acetic acid + water (160:10:2:40)

Adsorbent : Silica Gel Time of Run : 1.45 h.

TABLE 5

Quantitative Separation of the Mixture :
Ni(II)- Co(II)- Cu(II)- Pd(II)- Pt(IV)

Ion	Taken µg	Found µg	No. of determinations	Error(%)	Standard deviation(%)
Ni(II)	1.76	1.78	4	+1.1	0.16
Co(II)	1.77	1.75	4	-1.1	0.10
Cu(II)	1.90	1.90	4	0	0.08
Pd(II)	3.19	3.20	4	+0.30	0.08
Pt(IV)	5.85	5.80	4	-0.85	0.21

Developing Solvent : Hexanol + dioxan + acetic acid + water (160:10:2:4)

Adsorbent : Silica Gel Time of Run : 1.45 h.

TABLE 6

Quantitative Separation of the Mixture :

Fe(III)- Co(II)- Ni(II)- Ag(I)

Ion	Taken µg	Found µg	No. of determinations	Error (%)	Standard deviation (%)
Fe(III)	1.68	1.63	4	-2.9	0.24
Co(II)	1.77	1.75	4	-1.1	0.08
Ni(II)	1.76	1.78	4	+1.1	0.19
Ag(I)	3.24	3.21	4	-0.92	0.20

Developing Solvent : n-Butanol + 12N HCl + dioxan (5:1:4)

Adsorbent : Cellulose Time of Run : 45 min

TABLE 7

Quantitative Separation of the Mixture :

Ni(II)- Cu(II)- Bi(III)

Ion	Taken µg	Found µg	No. of determinations	Error (%)	Standard deviation (%)
Ni(II)	1.76	1.78	4	+1.1	0.14
Cu(II)	1.90	1.91	4	+0.52	0.12
Bi(III)	6.27	6.23	4	-0.63	0.19

Developing Solvent : Methanol + water (9:1)

Adsorbent : Silica Gel Time of Run : 35 min

TABLE 8

Quantitative Separation of the Mixture :

Cu(II)- Hg(II)- Bi(III)

Ion	Taken µg	Found µg	No. of determinations	Error (%)	Standard deviation (%)
Cu(II)	1.90	1.90	4	0	0.08
Hg(II)	6.03	6.06	4	+0.5	0.36
Bi(III)	6.27	6.23	4	-0.63	0.16

Developing : Methanol + water (7:3)

Adsorbent : Silica Gel Time of Run : 30 min

Pd(II) 1.6 µg; Pt(IV) 2.93 µg; Bi(III) 3.1 µg; U(VI) 3.6 µg.

The total time required for separation and determination of the constituents in the above combinations was about 50-90 min including the time required for the preparation of the standard scales.

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