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Chanchal Kumar Pal[a]; Amiya Kumar Chakraburtty[a]
[a] DEPARTMENT OF CHEMISTRY, JADAVPUR UNIVERSITY, CALCUTTA, INDIA

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NOTE

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CHANCHAL KUMAR PAL and
AMIYA KUMAR CHAKRABURTTY

DEPARTMENT OF CHEMISTRY
JADAVPUR UNIVERSITY
CALCUTTA-32, INDIA

Abstract

Use of organic hydroxamic acids for detection and separation of metals by circular paper chromatography was successfully applied to various metals. Salicylhydroxamic acid in the presence of isopropyl and isobutyl alcohols was found to give the best results. No developer to process the chromatograms is necessary because the metal hydroxamic acid complexes separate as distinctly colored bands.

INTRODUCTION

The extensive complex forming capabilities of the organic hydroxamic acids with metallic elements have been thoroughly utilized for the separation and estimation of metals by gravimetric, colorimetric, titrimetric, and solvent extraction methods (*1–5*). The wide variety of distinctly colored complexes (Table 1) which the hydroxamic acids form with different transition elements opens up the possibility of using these reagents as suitable single spraying and developing agents for the transitional metal ions after their separation on circular filter paper chromatograms. But a better and more fruitful application of the hydroxamic acids in the chromatographic separation of transitional metals has been made by using them in the presence of suitable solvent mixtures for the effective

TABLE 1

Specific Detecting Reagents for Common Metal Ions

Metal ion	Alizarin	$(NH_4)_2S_x$	Dithizone	Diphenyl carbazone	Oxine	Rubeanic acid	Salicyl hydroxamic acid
Cu(II)	Dark brown	—	—	Red violet	Yellow brown	Green	Green (ammonia)
Fe(III)	Violet	Black	—	—	Black	—	Pink (acid)
Mn(II)	—	Brown black	—	—	Brown	—	Dark brown (ammonia)
Ti(IV)	—	—	—	—	Yellow brown	—	Orange yellow (acid)
Cr(III)	Red violet	—	—	Violet	—	Dark green	Greenish (ammonia)
Co(II)	—	Brown black	—	Pale	Brown yellow	Yellow	Brownish (ammonia)
U(VI)	—	—	—	—	Brown	—	Orange (ammonia)
V(V)	—	—	—	—	Brown	—	Violet (acid)
Mo(VI)	—	Yellow	—	—	Yellow	—	Yellow (ammonia)

migration and separation of the metals by utilizing the properties of the metal chelates formed on the chromatogram. The rate of migration of metal ions in the presence of hydroxamic acids has been found to be greater than for free metal ions, making the R_F values in the former case greater and yielding better separation. The characteristic colors of the various complexes proved to be an additional advantage because the use of separate developing agents could be done away with and this resulted, not only in minimizing the time required for particular experiment but also in producing sharp and distinct color bands. Faster and clearer separations were also possible because the metal chelates that formed on the paper caused differences in separation rates which made it possible to eliminate irregular color development, overlapping and background coloration, etc.

Of the several different hydroxamic acids which were employed, salicylhydroxamic acid proved to be most effective with respect to separation and detection. The aliphatic hydroxamic acids were found to be unsuitable owing to their insolubility in organic solvents.

Mention may be made in this connection of the use of the chelating agents, *N*-benzoyl-*N*-phenyl hydroxamic acid (*6*) and pyridine-2-aldehyde-2-quinolyl hydrazone (*7*), in the similar chromatographic separation of transition metals.

EXPERIMENTAL

Reagents

Stock solution of the metals Ti(IV), V(V), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), U(VI), and Mo(VI) were prepared from their corresponding analytical grade reagents.

Solvents used for chromatographic separation were all reagent grade. The reagents salicylhydroxamic acid (*8*) and benzohydroxamic acid (*9*) were prepared in the laboratory, crystallized several times, and their melting points were checked. Doubly distilled water was used throughout. Whatman No. 1 circular filter paper was used for chromatogram.

Apparatus

Petri dishes and glass cover.

Procedure

The technique used by Rutter (*10*) was adopted with some minor modifications.

All the experiments were carried out, as far as possible, under similar conditions. The temperature, solvent mixture, width of the filter paper, width of the tail, the distance of the solvent from the external edges, etc. were kept identical. The tail was placed exactly at the center of the disk and equal quantities of the reagents for the different concentrations of each of the ions were used. The chromatograms were very prominent after being placed in ammonia or in acid vapor. The different colors of the individual metals, as obtained on the chromatograms after spraying with hydroxamic acids and developing, are tabulated together with the colors given by other important developing reagents in Table 1. This immediately shows that the number of metals which can be detected because of their distinct coloration with hydroxamic acid exceeds the number of those which have important single developing agents.

The chromatographic properties of the following metal ions have been studied: Ti(IV), V(V), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), and Cu(II). The behaviors of these elements have been studied with the following solvent systems:

(i) 1 *M* HCl (10 ml): $CH_3CHOH—CH_3$ (90 ml)

(ii) $C_7H_7O_3N$ (0.01 *M*): $(CH_3)_2—CH—CHOH$ (90 ml): 1 *M* HCl (5 ml): H_2O (5 ml)

(iii) $C_7H_7O_3N$ (0.01 *M*): $CH_3—CHOH—CH_3$ (90 ml): 1 *M* HCl (5 ml): H_2O (5 ml)

(iv) $C_7H_7O_3N$ (0.01 *M*): C_2H_5OH (90 ml): 1 *M* HCl (5 ml): H_2O (5 ml)

(v) $C_7H_7O_3N$ (0.01 *M*): CH_3OH (90 ml): 1 *M* HCl (5 ml): H_2O (5 ml)

(vi) $C_7H_7O_2N$ (0.01 *M*): $(CH_3)_2CH—CHOH$ (90 ml): 1 *M* HCl (5 ml): H_2O (5 ml)

(vii) $C_7H_7O_2N$ (0.01 *M*): $CH_3—CHOH—CH_3$ (90 ml): 1 *M* HCl (5 ml): H_2O (5 ml)

(viii) $C_7H_7O_2N$ (0.01 *M*): C_2H_5OH (90 ml): 1 *M* HCl (5 ml): H_2O (5 ml)

(ix) $C_7H_7O_2N$ (0.01 *M*): CH_3OH (90 ml): 1 *M* HCl (5 ml): H_2O (5 ml)

It is observed that the metal hydroxamic acid complexes have distinct rates of migration, and the color intensity of the bands formed on the chromatogram are also different for different metal complexes. The rates of migration of these complexes in the different solvent systems are shown in Tables 2 and 3. It is evident that the separation of mixtures of different metal ions without using a developing agent is quite feasible. On the basis

TABLE 2

Rates of Migration (time, 1 hr)

Metal	Color	R_F values for solvent mixtures				
		i	ii	iii	iv	v[a]
Ti(IV)	Orange yellow	0.35	0.60	0.80	0.57	0.62
V(V)	Violet	0.30	0.87	0.51	0.81	0.57
Cr(III)	Greenish	0.28	0.10	0.71	0.56	0.66
Mn(II)	Dark brown	0.37	—	0.34	0.18	0.62
Fe(III)	Pinkish	0.35	0.50	0.64	0.79	0.76
Co(II)	Brownish	0.27	0.10	0.41	0.61	0.62
Ni(II)[b]	Red	0.23	0.18	0.29	0.52	0.55
Cu(II)	Green	0.28	—	0.32	0.21	0.57

[a] Time required, 0.5 hr.

[b] Dimethyl glyoxime used as a developing agent.

TABLE 3

Rates of Migration (time, 1 hr)

Metal	Color	R_F values for solvent mixtures			
		vi	vii	viii	ix[a]
Ti(IV)	Orange yellow	0.84	0.80	0.80	0.68
V(V)	Violet	0.16	0.80	0.65	0.62
Cr(III)	Greenish	—	0.32	0.59	0.65
Mn(II)	Dark brown	0.75	0.28	0.27	0.57
Fe(III)	Pinkish	0.58	0.80	0.67	0.73
Co(II)	Brownish	0.20	0.35	0.13	0.68
Ni(II)[b]	Red	0.51	0.17	0.43	0.55
Cu(II)	Green	—	0.34	0.37	0.55

[a] Time required, 0.5 hr.

[b] Dimethyl glyoxime used as a developing agent.

of this, it has been possible to work out separations of the individual metal ions from a mixture, especially those metals which form colored complexes with hydroxamic acids. These separations are achieved in the presence of suitable solvent mixture. The following mixtures of metal ions have been separated and their constituents identified:

(a) U(VI), Fe(III), Ti(IV)
(b) U(VI), V(V), Fe(III), Ti(IV)
(c) Co(II), V(V), Fe(III), Ti(IV)
(d) Co(II), Cu(II), V(V), Ti(IV)

TABLE 4

Separation of Mixtures of Metal Ions (time, 1 hr)[a]

	No. of metals	Color	R_F	Remarks
(a)	U(VI)	Orange	0.46	Clear and distinct color bands
	Fe(III)	Pinkish	0.76	
	Ti(IV)	Yellow	0.88	Only a portion migrated
(b)	U(VI)	Orange	0.44	Separation is not clear and distinct, diffusion of the colors on the chromatogram
	V(V)	Violet	0.50	
	Fe(III)	Pinkish	0.71	
	Ti(IV)	Yellow	0.88	
(c)	Co(II)	Dirty brown	0.30	Clear and distinct distinct color bands
	V(V)	Violet	0.42	
	Fe(III)	Pinkish	0.61	
	Ti(IV)	Yellow	—	No migration
(d)	Co(II)	Dirty brown	0.25	Clear and distinct color bands
	Cu(II)	Green	0.35	
	V(V)	Violet	0.45	
	Fe(III)	Pinkish	0.60	
	Ti(IV)	Yellow	—	Only a portion migrated
(e)	Co(II)	Dirty brown	0.28	Clear and distinct color bands
	U(VI)	Orange	0.42	
	V(V)	Violet	0.48	
	Fe(III)	Pinkish	0.68	
	Ti(IV)	Yellow	—	Only a portion migrated

[a] In all cases the solvent mixture was isopropanol (40 ml), salicylhydroxamic acid (0.076 g), water (5 ml), and 1 *M* hydrochloric acid (5 ml). The developing agent was ammonia vapor.

(e) Co(II), U(VI), V(V), Fe(III), Ti(IV)

by utilizing the salicylhydroxamic acid–isopropanol–hydrochloric acid–water system. The results are given in Table 4.

RESULTS AND DISCUSSION

In the course of our studies with different solvent mixtures it was observed that no developing reagent is required to identify the metal ions, except nickel, where dimethyl glyoxime has been used, because hydroxamic acids form complexes with the metals which separate as distinctly colored bands. A look at the results (Tables 2 and 3) reveals that best results with respect to separation are obtained with the isopropanol–salicylhydroxamic acid system. The migration rates of the different elements are quite different and the bands are very sharp. This system can be utilized for the separation of the metal ions from their mixtures (Table 4). In the butyl alcohol–salicylhydroxamic acid system the rates of migration of the different elements are not satisfactory, even with iron, titanium, and vanadium, which separated nicely in the previous system. With butyl alcohol–benzohydroxamic acid the nature of the migration of the different elements is very poor and diffused in nature. The isopropanol–benzohydroxamic acid mixture and the isobutanol–benzohydroxamic acid mixture, on the other hand, show a sharp separation of bands. The salicylhydroxamic acid–isopropanol system, however, has been found to be very effective for the separation of metals from their mixtures.

Although fast migrations for the different elements have been observed with the ethyl alcohol–salicylhydroxamic acid and ethyl alcohol–benzohydroxamic acid systems, they are observed to keep a tail during their movement on the chromatogram, especially with iron(III), titanium(IV), manganese(II), cobalt(II), and vanadium(V). Similiar disadvantages have also been observed with methyl alcohol–salicylhydroxamic acid and methyl alcohol–benzohydroxamic acid systems.

In course of our study it has been observed that mixtures of metal ions migrate slowly on the chromatograms after forming colored complexes with hydroxamic acids. Some of the colored metal hydroxamic acid complexes have been found to interfere with each other. When both iron and manganese, for example, are present, they become diffused and it is difficult to identify manganese. As has been observed before, titanium in the above solvent mixture shows two different bands, one in the spotted zone and the other near the solvent front. The partial immobility of titanium could be due to the separation of the solid titanium–salicylhydroxamic acid complex, the precipitation of which is quantitative (*2*) in the pH range 2.6 to 6.0. Other color-forming metal hydroxamic acid complexes are very distinct and their chromatograms are very sharp.

This technique for identification of different metals has been successfully applied to various ores, minerals, and alloys.

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