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THE THIN-LAYER CHROMATOGRAPHIC PROPERTIES OF TRACE METALS

II. SEPARATION OF SOME CATIONS ON COMMERCIALY PRECOATED SHEETS*

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SUMMARY

The effect of seven solvent systems on the separation of several metals on commercially precoated cellulose and silica gel sheets was investigated. Suggestions are made for the separation of metals such as Ni, Co, Mn, Cu, Bi, Pb, V(V), and U(VI) in the presence of Zn and Fe(III). Silica gel sheets appear to be very useful for the separation of a number of cations.

The detection was carried out with reagents discussed previously¹. Detection limits of 0.1 to 0.01 μg per spot were reported. Some of the suggested separation schemes show good promise for further evaluation by *in situ* diffuse reflectance spectroscopy.

INTRODUCTION

In the preceding publication the solvent systems acetone-6 N HCl (9:1) and isopropanol-glacial acetic acid-6 N HCl-water (8:1:1:1) were recommended for the separation of Ni, Co, Mn, Cu and Bi on cellulose and silica gel layers¹. The system methanol-25% HNO₃-water (8:1:1) was suggested for the separation of lead from other cations on cellulose sheets¹. Already during this phase of the investigation it became apparent that commercially precoated Chromagram sheets perform more satisfactorily for the separation of complex mixtures of metal ions. The major advantage is the reproducibility of the well-defined layer thickness, which enables good reproduction of separation patterns and therefore makes the chromatogram particularly suitable for *in situ* quantitative evaluation of the sheet. Other advantages are reduced migration time, improved resolution, simplicity of use, *e.g.*, the elimination of chamber presaturation if sandwich-type developing chambers were used (a great advantage for field work in connection with pollution monitoring), and the possibility of storing the sheets for later reference and cutting out spots for a quantitative determination of the ions.

* For Part I, *cf.* ref. 1.

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Although the use of precoated sheets is very common for the separation of organic compounds, only a few papers have been published on the use of sheets for inorganic systems²⁻⁵. KIRK *et al.*⁶ used TLC sheets coated with different adsorbents for the investigation of various Cr(III) complexes. They also successfully used diffuse reflectance spectroscopy for the identification of the complexes directly on the chromatogram⁶.

In this part of the investigation, the behaviour of Bi³⁺, Cd²⁺, Co²⁺, Cu²⁺, Fe³⁺, Mn²⁺, Ni²⁺, Pb²⁺, U⁶⁺, V⁵⁺, and Zn²⁺ was further studied on precoated cellulose and silica gel sheets with a large number of solvent systems. Particular care was taken to find separation procedures suitable for a quantitative *in situ* reflectance spectroscopic determination of these metals.

EXPERIMENTAL

Reagents and materials

Stock solutions were prepared as described previously¹. Eastman precoated cellulose sheets No. 6061 without binder, and silica gel sheets No. 6064 containing a solvent-resistant polyvinyl alcohol binder (Eastman Organic Chemicals, Eastman-Kodak Co., Rochester, N.Y.) were used for chromatographic separations. Before development of the chromatograms the sheets were purified by prewashing with the solvent systems used subsequently for the separation procedure.

Chromatography and detection

The chromatographic and detection steps were carried out as described previously¹. The seven solvent systems used for the development of the chromatograms in this study are listed in Table I (S₂-S₄ and S₆-S₉).

RESULTS AND DISCUSSION

Isopropanol-containing solvent systems have shown excellent separation characteristics¹, but the major drawback of these mixtures is the long time needed for separation. Therefore it was decided to completely or partially substitute the isopropanol with the faster-flowing solvents acetone or methyl ethyl ketone.

The results obtained on cellulose and silica gel sheets with solvents S₂, S₃, and S₄ (Table I) are presented in Table II. For all three solvent mixtures the *R_F* values

TABLE I
CHROMATOGRAPHIC SOLVENT SYSTEMS DISCUSSED

S ₁	= acetone-6 N HCl (9:1)
S ₂	= acetone-acetic acid-6 N HCl-H ₂ O (8:1:1:1)
S ₃	= acetone-25 % HNO ₃ -6 N HCl-H ₂ O (8:1:1:1)
S ₄	= methyl ethyl ketone-acetic acid-6 N HCl-H ₂ O (8:1:1:1)
S ₅	= isopropanol-acetic acid-6 N HCl-H ₂ O (8:1:1:1)
S ₆	= acetone-isopropanol-6 N HCl-H ₂ O (6:2:1:1)
S ₇	= acetone-isopropanol-6 N HCl-H ₂ O (4:4:1:1)
S ₈	= acetone-isopropanol-6 N HCl-acetic acid-H ₂ O (4:4:1:1:1)
S ₉	= methanol-acetic acid-6 N HCl-H ₂ O (8:1:1:1)
S ₁₀	= methanol-32 % HCl-H ₂ O (8:1:1)
S ₁₁	= methanol-25 % HNO ₃ -H ₂ O (8:1:1)

TABLE II

R_F VALUES OF THE CATIONS ON CELLULOSE (c) AND SILICA GEL (s) WITH SOLVENT SYSTEMS S_2 , S_3 , AND S_4

For abbreviations of solvent systems, cf. Table I. C = comet; T = tailing; ST = strong tailing.

Metal	$R_F \times 100^a$					
	S_2		S_3		S_4	
	c	s	c	s	c	s
Bi(III)	89	81	94	90	68	64
Cd(II)	94	82	98	90	61	66
Co(II)	15	30	17	46	5	15
Cu(II)	54	70	53	74	27	48
Fe(III)	97	97	95	98	61	95
Mn(II)	10	36	24	62	6	20
Ni(II)	6	13	15	42	4	11
Pb(II)	ST	ST	ST	ST	ST	ST
U(VI)	67	75	94	89	40 C	55
V(V)	ST ^b	ST	ST		SC	21 T
Zn(II)	94	88	96	90	63	71
Wet front	—	79	95	—	61	62
Time for 14 cm	51 min	2 h 25 min	70 min	3 h 25 min	60 min	2 h 55 min
Temperature (°C)	26	25	25	22	24	25

^a Average of six to ten determinations.

^b Yielded clear tailing double spots.

generally increased in the order $Ni < Co < Mn < Cu < U(VI) < Bi < Cd$ on both silica gel and cellulose. Exceptions were Mn, which precedes Co when separated on cellulose with the system S_2 , and Cd which, when separated on cellulose with the system S_4 , had a lower R_F value than Bi (see also Fig. 1). Fe and Zn were in most cases close to the solvent front, and had higher R_F values than Bi and Cd. Only in the system which contained methyl ethyl ketone on cellulose layers did both Fe and Zn lag behind Bi. Vanadium(V) and lead appeared as long tailing spots in all three systems. In the mixture S_2 vanadium(V) yielded clear double spots. In the less polar system containing methyl ethyl ketone, a much lower migration was observed for all the cations on cellulose as well as silica gel. Substituting the acetic acid in system S_3 for nitric acid resulted in higher R_F values on silica gel, without improving the separation. The mobility of Ni, Co, and Mn on cellulose remained much lower, and hence Cu can be separated from other metals, except from larger amounts of lead and vanadium(V) where the tailing spots may interfere.

In general it was observed that on silica gel more efficient separations could be obtained for all the metals investigated. Some good examples are the resolution of Ni-(Co or Mn) and Cu (R_F 0.13-0.30-0.36, and 0.70) with the system S_2 .

The solvent system isopropanol-glacial acetic acid-6 N HCl-water (8:1:1:1) yielded good results for the separation of (Ni or Co)-Cu and Bi on silica gel¹, but the time of development was about 8 h. Substituting the isopropanol with the faster-flowing acetone (S_2) resulted in a good resolution of Ni, Co, and Cu, but unfortunately

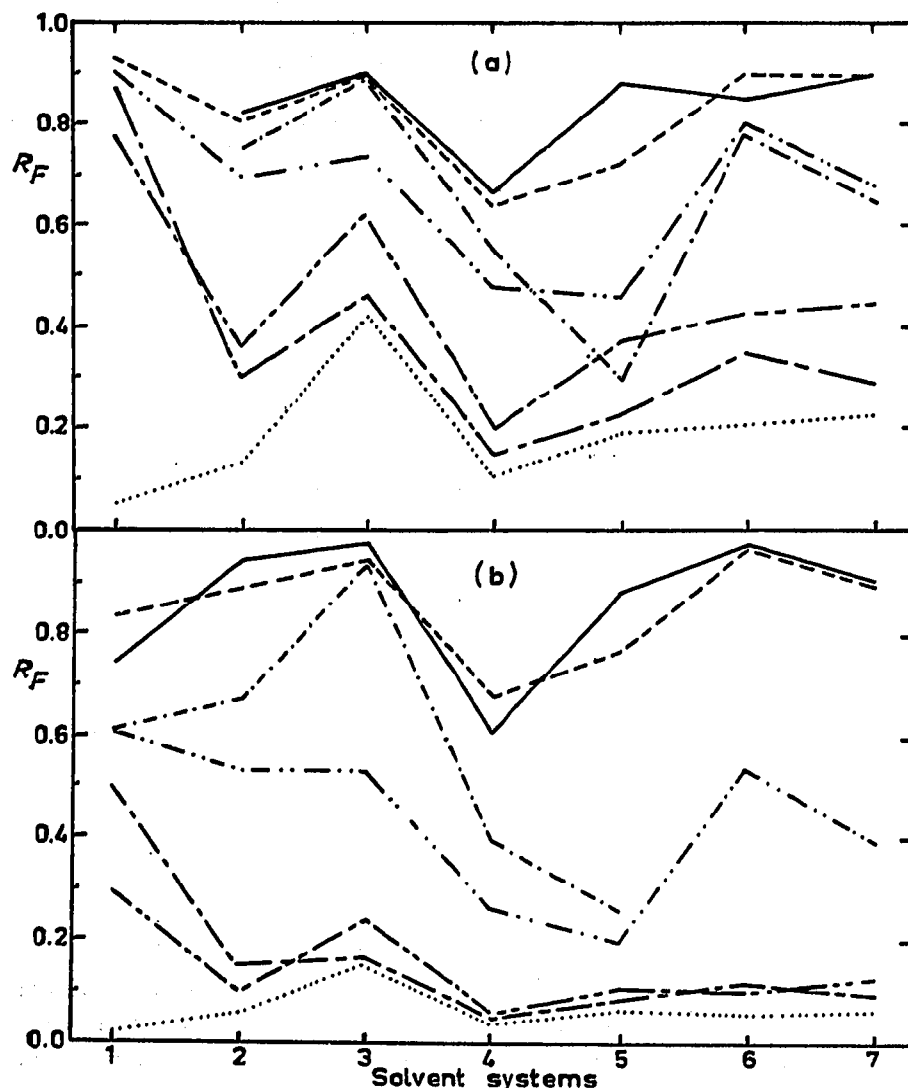


Fig. 1. Variation of R_F values of the metals as a function of different solvent mixtures on silica gel (a) and cellulose (b) sheets (see Table I for a description of solvent systems S_1 - S_7). - - - -, Bi^{3+} ; —, Cd^{2+} ; — · —, Co^{2+} ; — · · —, Cu^{2+} ; — · · · —, Mn^{2+} ; · · · · ·, Ni^{2+} ; — · — · —, UO_2^{3+} .

Cu was running close to the wet front ($R_F \text{ Cu} = 0.70$; $R_F \text{ wet front} = 0.79$). In order to combine the advantages of the two systems, solvent mixtures of acetone, isopropanol and HCl were investigated in various proportions. The results are summarized in Table III. In the system S_7 the R_F values increase on silica gel in the order $\text{Ni} < \text{Co} < \text{Mn} < \text{U(VI)} < \text{Cu} < \text{Bi-Cd}$, while in the solvent system S_6 , where the ratio of acetone and isopropanol was 6:2, Cd slightly precedes Bi. On cellulose, in solvent systems S_5 , S_6 , and S_7 , a very low migration for Ni, Co, and Mn was observed (see also Fig. 1). From this it seems that the acetone in systems S_6 and S_7 has no effect on the separation of Ni, Co, and Mn on cellulose, even though in S_6 acetone is present in much larger quantity. Only the migration of Cu was observed to increase considerably. This effect is rather astonishing, particularly since it occurs only on cellulose layers (Fig. 1) and must have been brought about by the presence of isopropanol which

TABLE III

R_F VALUES OF THE CATIONS ON CELLULOSE (c) AND SILICA GEL (s) WITH SOLVENT SYSTEMS S_0 - S_9 . For abbreviations of solvent systems, cf. Table I. C = comet; T = tailing; ST = strong tailing.

Metal	$R_F \times 100^a$					
	S_0		S_7		S_8	S_9
	c	s	c	s	c	c
Bi(III)	97	90	90	90	90	88
Cd(II)	98	85	91	90	83	90
Co(II)	12	35	10	29	6	73
Cu(II)	54	80	40	68	31	70
Fe(III)	98	95	87	94	81	95
Mn(II)	11	43	13	45	9	74
Ni(II)	6	21	7	23	5	72
Pb(II)	ST	ST	ST	ST	ST	ST
U(VI)	T	78	T	65	T	82
V(V)	ST ^b	ST	25 C	ST	17	82
Zn(II)	98	91	94	93	93	93
Wet front	—	94	87	95	81	—
Time for 14 cm	70 min	3 h 25 min	88 min	4 h 20 min	90 min	65 min
Temperature (°C)	27	25	27	24	25	25

^a Average of six to ten determinations.

^b Yielded clear tailing double spots.

seems to prevent the formation of the chloride complexes of these three metals. In any event, isopropanol exerts a dominating influence in the systems S_5 - S_7 . Lead and vanadium(V) gave strong tailing in solvent mixtures S_0 and S_7 on both adsorbents. Uranium(VI) showed tailing on cellulose. Zinc and iron(III) were running close to the organic front. The time of development on silica gel was now reduced from 8 h to about 4 h per 14 cm of length.

TABLE IV

SOME QUANTITATIVE SEPARATION POSSIBILITIES OF METALS WITH THE SOLVENT SYSTEMS S_1 - S_{11} . For abbreviations of solvent systems, cf. Table I.

	Cellulose sheet	Silica gel sheet
S_1	Ni-Mn-Co-Cu	Ni from the others
S_2	Cu-U(VI) from the others	Ni-(Co or Mn)-Cu
S_3	Cu from the others	Mn-Cu-(Ni or Co)
S_4	Cu-U(VI) from the others	(Ni or Co or Mn)-(Cu or U(VI))
S_5	No good separation	(1) Bi from the others (2) (Ni or Co)-Cu-Bi (3) Ni-Mn-Bi
S_6	Cu from the others	Ni-(Co or Mn)-(Cu or U(VI))
S_7	Cu from the others	(Ni or Co)-Mn-(Cu or U(VI))
S_8	Cu-V(V) from the others	—
S_9	No good separation	—
S_{10}	No good separation	—
S_{11}	Pb from the others	—

A satisfactory resolution of (Ni or Co)-Mn-Cu with R_F values 0.23-0.29-0.45-0.65, respectively, was obtained with solvent mixture S_7 on silica gel sheets. If a higher ratio of acetone to isopropanol (6:2) was used (S_6), the successful separation of Ni-(Co or Mn)-Cu was possible, with R_F values 0.21-0.35-0.43-0.80 (see also Table IV). In the system S_8 on cellulose, slightly lower R_F values were observed for Cd, Co, Cu, Fe(III), Mn, and U(VI) in comparison to R_F values obtained in the same system but without acetic acid (S_7) (Table III). The strong tailing of V(V) on cellulose was suppressed in the presence of acetic acid. With the solvent system S_6 on cellulose, the cations were running close to the dry front with little difference in R_F values.

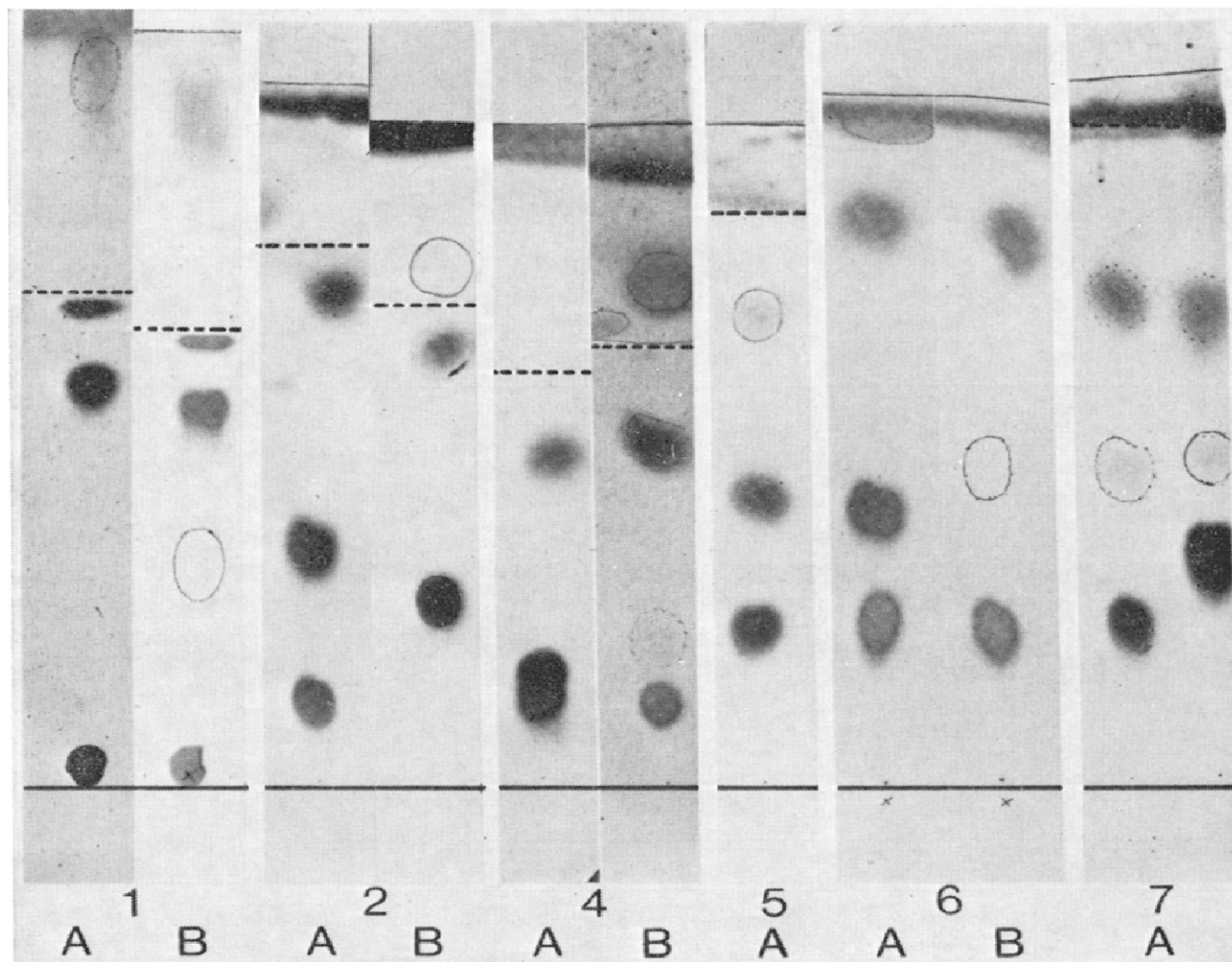


Fig. 2. Examples of good separations of some cations with different solvent systems on silica gel (S_2 and S_4 - S_7) and on cellulose sheets (S_1) (concentration: 1 μ g metal per spot). Solvent systems (see Table I): (S_1) A = Ni < Co < Cu, detection with TAR; B = Ni < Mn < Co < Cu < Zn, detection with TAR. (S_2) A = Ni < Co < Cu; in the front Fe; detection with TAR; B = Co < Cu < Bi; in the front Fe; detection with PAN. (S_4) A = (Ni < Co) < Cu; in the front Fe; detection with PAN; B = Ni < Mn < Cu < Zn; close to the front Fe; detection with PAR. (S_5) A = Co < Cu < Bi; in the wet front Fe; detection with TAR. (S_6) A = Ni < Co < Cu < Zn; in the front Fe; detection with PAN; B = Ni < Mn < Cu; in the front Fe; detection with PAN. (S_7) A = Ni < Mn < Cu; in the front Fe and Zn; detection with PAN and Co < Mn < U (VI); in the front Fe and Zn; detection with PAN. The solvent systems S_1 and S_6 were investigated in Part I, ref. 1.

For a quick selection of optimum conditions for the separation of some metals, the chromatographic "spectra" (R_F values of the cations plotted *versus* solvent systems) (Fig. 1) may be used to advantage.

Fig. 2 shows the thin-layer chromatograms of the best separations of Ni, Co, Mn, Cu, Bi, and Zn with different solvent systems on cellulose and silica gel sheets.

Some quantitative separation schemes of cations with investigated solvent systems are presented in Table IV (see also Part I, ref. 1).

CONCLUSIONS

From the data gathered in this study, it appears that for the separation of trace metals with the solvent systems investigated silica gel is a far more effective adsorbent than cellulose. On the other hand it takes about three times longer to develop a chromatogram on silica gel than on cellulose sheets.

Impurities were found to be present on both types of sheets in sufficient amounts to interfere seriously with the identification of trace amounts of these metals. A prewashing step, usually carried out with the same solvent system used later for separation, is therefore essential. This will eliminate at least the predominant impurities of zinc and iron(III). If this is done, the spots obtained on the Chromagram sheets after detection with the previously mentioned reagents usually appear well resolved and compact. For most metals visual detection limits ranged from 0.1 to 0.01 μg per spot.

The reproducibility of the chromatographic pattern, the reagent background, and the stability of the metal chelates adsorbed on the sheets are such that they make this method suitable for *in situ* diffuse reflectance spectroscopic evaluation of the chromatograms⁶⁻⁹. Investigations to this end are under way and show good promise.

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