

CHROM. 4061

THE SEPARATION OF CERTAIN METAL IONS BY SOLUBILIZATION
THIN-LAYER CHROMATOGRAPHY

K. OGUMA

Laboratory for Analytical Chemistry, Faculty of Engineering, University of Chiba, Yayoi-cho, Chiba (Japan)

(Received March 14th, 1969)

SUMMARY

The thin-layer chromatographic behaviour of a number of metal ions in methyl alcohol, ethyl alcohol, acetone, or dioxan-nitric acid media on silica gel-cellulose (5:2) thin-layer plates impregnated with a polysulphide polymer has been investigated. Cu(II), Bi(III), Hg(II) and Ag(I) form precipitates with the polysulphide polymer in the thin-layer and remain at or near the starting points. Thus they can be easily separated from the other metal ions (Tl(I), Pb(II), Co(II), Zn(II), Cd(II), Al(III), etc.), which move with the solvent. Mixtures of various metal ions can also be separated.

INTRODUCTION

In a previous paper¹, we reported the effective separation of Ni(II), Cu(II), Pb(II), Fe(III), and Bi(III) utilizing the differences in the solubility of their salts in various developing solvents. In order to create pronounced differences in solubility among the ions concerned, disodium hydrogen arsenate was incorporated into the thin-layer as a precipitant, so that dilute HNO₃ as well as mixtures of HNO₃ and ethyl alcohol served as good developing solvents. This technique was termed "solubilization thin-layer chromatography" by us.

The present work was undertaken to extend further the use of the solubilization thin-layer chromatographic technique for the separation of metal ions. A liquid polysulphide polymer which terminated in reactive thiol (-SH) groups was used as the precipitant. The behaviour of fifteen metal ions on a silica gel-cellulose thin-layer plate impregnated with the polymer was investigated; developing solvents consisting of an organic solvent (methyl alcohol, ethyl alcohol, acetone or dioxan) and HNO₃ were also investigated. Among the solvent systems tested, a mixture of methyl alcohol (or ethyl alcohol) -HNO₃ gave the best results for most metal ion separations. In this solvent system Bi(III), Hg(II), Cu(II) and Ag(I) were retained at or near the origin thus providing a good basis for their specific separation.

EXPERIMENTAL

Reagents

Analytical reagent grade chemicals were used throughout, with the exception of the polysulphide polymer, "Thiokol LP-32", which was of a technical grade, manufactured by the Thiokol Chemical Corporation (Trenton, New Jersey, U.S.A.). The approximate structural formula for this polymer, as given by the manufacturer, was $\text{HS}-(\text{C}_2\text{H}_4-\text{O}-\text{CH}_2-\text{O}-\text{C}_2\text{H}_4-\text{S}-\text{S})_{23}-\text{C}_2\text{H}_4-\text{O}-\text{CH}_2-\text{O}-\text{C}_2\text{H}_4-\text{SH}$; in addition some of the polymer segments are branched. The polymer is a viscous liquid which may be converted to a rubber at room temperature without shrinkage upon addition of a curing agent. Basic information² on the polymer is as follows: colour, light amber; specific gravity 25°C/25°C, 1.28–1.30; viscosity at 80°F, 350–450 P; average mol. wt., 4000.

A commercially available silica gel for thin-layer chromatography was purified as described by SEILER³. Cellulose powder was used without further purification.

Test solutions

Test solutions of the metal ions were prepared by dissolving appropriate amounts of the respective metal, oxide or nitrate in 1 M HNO₃. The metal ion concentration of each solution was 0.1 M. The metal ions studied were: Ag(I), Al(III), Bi(III), Cd(II), Ca(II), Co(II), Cu(II), Fe(III), Hg(II), In(III), Mg(II), Ni(II), Pb(II), Tl(I), and Zn(II).

Preparation of the thin-layer plates

The silica gel (20 g) and the cellulose powder (8 g) were mixed thoroughly with 4 g of the polysulphide polymer in 70 ml of benzene. Benzene was evaporated under an I.R.-lamp. The mixture was slurried with 98 ml of deionized water and spread (thickness 250 μ) on 5 glass plates (20 × 20 cm) with an applicator. The plates were dried first in air for 1 h and then in a dryer with a fan at about 50°C for 1.5 h. The prepared plates were further purified as described below, since the cellulose powder and the polysulphide polymer contained so many impurities which would interfere with the detection of the metal ions after development. The plates were developed by an ascending technique for 16 cm with 0.01 M HNO₃ and dried in a dryer at about 50°C for 1 h. The plates were then developed with 0.001 M NH₄OH to neutralize a residual amount of HNO₃ and dried as before. The plates processed this way were stored in a desiccator over silica gel until ready for use.

Procedure

About 0.5 μl of a test solution was spotted with a micropipette 2 cm from one end of the plate, and dried under an I.R.-lamp for 5 min. The plate was then inserted in the tank which had already been conditioned with solvent vapour for 30 min, and immediately developed to 10 cm by an ascending technique at room temperature. The developing solvents used were the mixtures of HNO₃ and methyl alcohol, ethyl alcohol, acetone or dioxan. Subsequently, the plate was dried in air and the spots of metal ions were located with the following reagents:

Ammonium sulphide. Dilute colourless solution. Ag(I), Hg(II), Bi(III), Pb(II), Tl(I), Ni(II), Co(II), Cu(II), Fe(III), Cd(II) formed coloured spots.

8-Hydroxyquinoline. 1% solution in ethyl alcohol, followed by exposure to ammonia. Mg(II), In(III), Zn(II), Al(III), and Ca(II) showed up in U.V. light.

All R_F values are the average of two replicates and are given for the leading and trailing edges of spots.

RESULTS AND DISCUSSION

In conventional systematic qualitative analysis of inorganic cations, hydrogen sulphide has been used as an effective precipitating reagent for the copper-arsenic and the nickel-aluminium groups.

Some organic reagents having -SH group(s) (*e.g.*, dithiol, rubeanic acid, 8-mercaptoquinoline, 2-mercaptobenzothiazole, thionalide, etc.), also react with many

TABLE I

R_F VALUES OF METAL IONS IN A METHYL ALCOHOL-HNO₃ SYSTEM

Developing time: *ca.* 30 min.

Ions	MeOH-0.1 M HNO ₃ (8:2)	MeOH-0.5 M HNO ₃ (8:2)	MeOH-1 M HNO ₃ (8:2)
Co(II)	0.84-0.95	0.80-0.95	0.79-0.95
Cu(II)	0.01-0.27	0.02-0.29	0.03-0.28
Hg(II)	0.00-0.06	0.00-0.06	0.00-0.05
Tl(I)	0.34-0.65	0.38-0.59	0.37-0.54
Pb(II)	0.45-0.82	0.61-0.79	0.61-0.77
Bi(III)	0.00-0.18	0.00-0.28	0.02-0.34
Fe(III)	0.00-0.17	0.02-0.34*	0.19-0.51
Ag(I)	0.00-0.04	0.00-0.04	0.00-0.04
Ni(II)	0.86-0.95	0.84-0.95	0.82-0.94
Cd(II)	0.87-0.93	0.86-0.94	0.84-0.92
Al(III)	0.00-0.95	0.77-0.97	0.77-0.97
Ca(II)	0.84-0.91	0.82-0.91	0.79-0.88
Zn(II)	0.85-0.94	0.84-0.96	0.82-0.94
Mg(II)	0.85-0.94	0.85-0.97	0.81-0.93
In(III)	0.00-0.93	0.87-0.96	0.84-0.95

* A small portion of Fe(III) was detected at R_F 0.88-0.92.

metal ions of the "sulphide groups" to form complexes insoluble in dilute acids or weak alkaline solutions. These organic reagents have long been used as organic precipitants. In addition most of these complexes can be extracted in suitable organic solvents, so that the proper choice of the analytical conditions may sometimes offer a very specific solvent extraction separation system for a particular metal ion.

Based on these observations, it should be of interest to see how metal ions behave when developed on thin-layer plates, impregnated with a compound containing reactive thiol (-SH) group(s), by mixtures of organic solvents and dilute acid. The separation of the metal ions may depend primarily on the difference in the solubility of the compounds formed by the reaction of the metal ions with the precipitant in the thin-layer plates, though partition would not be excluded completely as a working mechanism of the separation.

TABLE II

 R_F VALUES OF METAL IONS IN AN ETHYL ALCOHOL-HNO₃ SYSTEMDeveloping time: *ca.* 55 min.

Ions	EtOH-0.5 M HNO ₃ (8:2)	EtOH-1 M HNO ₃ (8:2)	EtOH-3 M HNO ₃ (8:2)	EtOH-5 M HNO ₃ (8:2)
Co(II)	0.73-0.85	0.66-0.80	0.63-0.79	0.56-0.74
Cu(II)	0.01-0.24	0.01-0.23	0.02-0.24	0.03-0.29
Hg(II)	0.00-0.04	0.00-0.05	0.00-0.06	0.00-0.06
Tl(I)	0.26-0.46	0.24-0.40	0.25-0.39	0.22-0.38
Pb(II)	0.31-0.58	0.30-0.52	0.33-0.52	0.33-0.53
Bi(III)	0.00-0.19	0.00-0.24	0.02-0.34	0.03-0.55
Fe(III)	0.05-0.31*	0.18-0.47*	0.53-0.76	0.57-0.74
Ag(I)	0.00-0.05	0.00-0.04	0.00-0.03	0.00-0.04
Ni(II)	0.73-0.84	0.66-0.78	0.62-0.75	0.57-0.71
Cd(II)	0.79-0.86	0.73-0.81	0.71-0.79	0.67-0.78
Al(III)	0.75-0.90	0.69-0.85	0.73-0.86	0.65-0.81
Ca(II)	0.68-0.79	0.61-0.71	0.57-0.67	0.48-0.61
Zn(II)	0.73-0.84	0.68-0.79	0.66-0.78	0.59-0.74
Mg(II)	0.73-0.84	0.68-0.78	0.64-0.78	0.56-0.72
In(III)	0.78-0.91	0.74-0.88	0.78-0.91	0.70-0.86

* A small portion of Fe(III) was detected at R_F 0.80-0.85 in EtOH-0.5 M HNO₃ (8:2) and at R_F 0.71-0.87 in EtOH-1 M HNO₃ (8:2).

In Tables I to IV, the R_F values of fifteen metal ions in developing systems consisting of HNO₃ and four organic solvents are given.

As can be seen from the tables, the silver and copper group metal ions like Ag(I), Hg(II), Cu(II), and Bi(III) are retained near the starting point. It is of interest to note that Cd(II), Pb(II) and Tl(I) show moderately high R_F values in all the solvent systems tested. The presence of organic solvents in the developing solvent

TABLE III

 R_F VALUES OF METAL IONS IN AN ACETONE-HNO₃ SYSTEMDeveloping time: *ca.* 30 min.

Ions	Acetone-0.5 M HNO ₃ (8:2)	Acetone-1 M HNO ₃ (8:2)	Acetone-3 M HNO ₃ (8:2)
Co(II)	0.82-0.94	0.81-0.93	0.62-0.76
Cu(II)	0.00-0.29	0.00-0.17	0.00-0.21
Hg(II)	0.00-0.14	0.00-0.12	0.00-0.11
Tl(I)	0.44-0.62	0.43-0.61	0.38-0.50
Pb(II)	0.56-0.81	0.68-0.77	0.52-0.66
Bi(III)	0.00-0.28	0.00-0.29	0.02-0.58
Fe(III)	0.59-0.95	0.79-0.94	0.64-0.80
Ag(I)	0.00-0.07	0.00-0.05	0.00-0.05
Ni(II)	0.82-0.92	0.78-0.90	0.61-0.73
Cd(II)	0.86-0.93	0.84-0.91	0.71-0.80
Al(III)	0.86-0.97	0.84-0.94	0.68-0.81
Ca(II)	0.83-0.91	0.82-0.91	0.66-0.77
Zn(II)	0.81-0.92	0.81-0.91	0.65-0.77
Mg(II)	0.85-0.93	0.82-0.93	0.69-0.79
In(III)	0.89-0.97	0.87-0.97	0.75-0.87

and the steric effects of the polymer used as a precipitant, either both or one of these, seem to have some effect on the behaviour of these three metal ions.

However, there is a simple guide, which enables us to predict the behaviour of the metal ions: in all the solvent systems studied, the ions forming less soluble sulphides than copper(II) sulphide^{4,5} are retained near the starting point. Fe(III), however, in spite of the low solubility of its sulphide in water, begins to migrate with increasing nitric acid concentration.

TABLE IV

R_F VALUES OF METAL IONS IN A DIOXAN-HNO₃ SYSTEM

Developing time: *ca.* 50 min.

<i>Ions</i>	<i>Dioxan-0.1 M HNO₃ (7:3)</i>	<i>Dioxan-0.5 M HNO₃ (7:3)</i>	<i>Dioxan-1 M HNO₃ (7:3)</i>
Co(II)	0.89-1.00	0.89-1.00	0.88-1.00
Cu(II)	0.03-0.38	0.02-0.30	0.06-0.41
Hg(II)	0.00-0.23	0.00-0.15	0.00-0.29
Tl(I)	0.49-0.75	0.63-0.78	0.67-0.79
Pb(II)	0.76-0.94	0.83-0.94	0.82-0.93
Bi(III)	0.00-0.19	0.00-0.37	0.02-0.55
Fe(III)	0.02-1.00	0.85-1.00	0.87-1.00
Ag(I)	0.00-0.05	0.00-0.07	0.00-0.10
Ni(II)	0.90-1.00	0.87-0.98	0.85-0.97
Cd(II)	0.90-0.98	0.89-0.96	0.85-0.96
Al(III)	0.68-1.00	0.88-1.00	0.86-1.00
Ca(II)	0.89-0.98	0.89-0.98	0.83-0.92
Zn(II)	0.89-1.00	0.87-0.99	0.85-0.96
Mg(II)	0.90-1.00	0.88-0.99	0.85-0.97
In(III)	0.80-1.00	0.91-1.00	0.89-1.00

Some brief comments on each solvent system may be of value in planning a separation. Al(III) and In(III) give pronounced tailing in the methyl alcohol-0.1 *M* HNO₃ (8:2) system. This tailing seems to be due to the hydrolysis of Al(III) and In(III), and can be eliminated by increasing the acid concentration.

In ethyl alcohol-HNO₃ and acetone-HNO₃ systems, the R_F values of Co(II), Tl(I), Pb(II), Ni(II), Cd(II), Al(III), Ca(II), Zn(II), Mg(II) and In(III) decrease with increasing acid concentration. In particular, the rate at which the R_F value of Ca(II) decreases with the increase of acid concentration in the ethyl alcohol-HNO₃ system is higher than that of the other nine metal ions. This suggests the possibility of a useful method for the separation of Ca(II) from the other metal ions using a mixture of ethyl alcohol and HNO₃ with a high acid concentration. Because of the undesirable diffuse front of Bi(III) at 5 *M* HNO₃ (R_F 0.03-0.55), the optimum solvent system for the specific separation of Ca(II) is probably a mixture of ethyl alcohol-3 *M* HNO₃ (8:2).

The mixture of dioxan and HNO₃ with the volume ratio of 8:2 dissolved the precipitant incorporated in the adsorbent and carried away most of the precipitant to the solvent front. In addition, the solvent front did not move up horizontally. Both the leading and trailing edges of the spots of all the metal ions studied were

TABLE V

SEPARATION OF TERNARY MIXTURES OF METAL IONS

<i>Solvent system and developing time</i>	<i>Mixture* separated and R_F values</i>
MeOH-1 M HNO ₃ (8:2) 30 min	Tl (0.38-0.54)-Pb(0.64-0.77)-Co (0.86-0.97) Bi (0.01-0.23)-Tl (0.39-0.54)-Pb(0.64-0.78) Tl (0.39-0.53)-Pb(0.64-0.77)-Zn (0.86-0.97) Tl (0.39-0.54)-Pb(0.64-0.78)-Cu (0.83-0.92) Hg(0.00-0.06)-Tl (0.39-0.54)-Pb(0.64-0.78) Hg(0.00-0.06)-Pb(0.65-0.78)-Ni (0.87-0.96) Ag(0.00-0.04)-Pb(0.65-0.78)-Al (0.88-0.98) Hg(0.00-0.06)-Pb(0.65-0.77)-In (0.89-0.98) Ag(0.00-0.05)-Tl (0.39-0.53)-Mg(0.88-0.99) Hg(0.00-0.06)-Tl (0.39-0.54)-Ca (0.83-0.91)
EtOH-3 M HNO ₃ (8:2) 55 min	Ag(0.00-0.04)-Ca(0.52-0.62)-Cd (0.73-0.81) Hg(0.00-0.06)-Pb(0.35-0.50)-Cd (0.72-0.81) Hg(0.00-0.06)-Tl (0.25-0.38)-Fe (0.52-0.76) Cu (0.02-0.12)-Pb(0.34-0.50)-In (0.78-0.89) Hg(0.00-0.07)-Pb(0.34-0.50)-Ni (0.65-0.75) Cu (0.02-0.13)-Ca(0.54-0.63)-Al (0.73-0.84) Ag(0.00-0.04)-Pb(0.34-0.50)-Ca (0.55-0.63) Cu (0.04-0.15)-Tl (0.28-0.37)-Ca (0.54-0.62) Cu (0.04-0.14)-Pb(0.34-0.49)-Zn (0.66-0.77) Ag(0.00-0.05)-Tl (0.26-0.38)-Co (0.67-0.77)
Acetone-1 M HNO ₃ (8:2) 33 min	Cu (0.00-0.21)-Pb(0.61-0.75)-Co (0.79-0.89) Bi (0.00-0.35)-Tl (0.45-0.60)-Fe (0.76-0.91) Bi (0.00-0.34)-Pb(0.60-0.73)-Fe (0.76-0.90) Hg(0.00-0.20)-Pb(0.60-0.74)-Cd (0.81-0.89) Hg(0.00-0.20)-Pb(0.60-0.73)-Al (0.83-0.91) Bi (0.00-0.32)-Pb(0.59-0.73)-In (0.84-0.94) Ag(0.00-0.08)-Pb(0.60-0.74)-Zn (0.81-0.90) Cu (0.00-0.19)-Tl (0.45-0.59)-Ca (0.80-0.88) Ag(0.00-0.08)-Tl (0.44-0.60)-Ni (0.79-0.87) Cu (0.00-0.20)-Pb(0.59-0.74)-Mg(0.81-0.90)
Dioxan-0.5 M HNO ₃ (7:3) 50 min	Bi (0.02-0.35)-Tl (0.62-0.74)-Pb(0.80-0.92) Bi (0.02-0.34)-Tl (0.61-0.73)-Co (0.86-0.98) Bi (0.02-0.33)-Tl (0.61-0.73)-Fe (0.77-0.98) Cu (0.03-0.21)-Tl (0.62-0.72)-Co (0.86-0.98) Hg(0.00-0.23)-Tl (0.61-0.71)-Al (0.86-1.00) Hg(0.00-0.22)-Tl (0.61-0.72)-In (0.87-1.00) Cu (0.02-0.22)-Tl (0.62-0.71)-Mg(0.86-0.98) Ag(0.00-0.07)-Tl (0.61-0.72)-Zn (0.86-0.98) Cu (0.02-0.21)-Tl (0.62-0.72)-Cd (0.86-0.95) Cu (0.02-0.19)-Tl (0.62-0.72)-Ni (0.87-0.96)

* The amount of each metal applied in each separation was :Ag, 3.6 μ g; Al, 0.9 μ g; Bi, 7.0 μ g; Ca, 1.3 μ g; Cd, 3.7 μ g; Co, 2.0 μ g; Cu, 2.1 μ g; Fe, 1.9 μ g; Hg, 6.6 μ g; In, 3.8 μ g; Mg, 0.8 μ g; Ni, 2.0 μ g; Pb, 6.9 μ g; Tl, 6.8 μ g; Zn, 2.2 μ g.

very irregular and the R_F values could not be measured accurately.

Nothing was gained by decreasing the volume ratio of organic solvents tested to HNO₃ from 8:2 to 6:4 or from 7:3 to 5:5.

The R_F values listed in Tables I to IV indicate many useful separation procedures for the metal ions studied. Inspection of the relevant R_F values will show whether a separation is feasible and what the most favourable developing system

TABLE VI

SEPARATION OF DIFFERENT RATIOS OF METAL IONS

<i>Mixtures (μg)</i>	<i>R_F values</i>
<i>MeOH-1 M HNO₃ (8:2), 26 min</i>	
Bi(0.1)-Pb(10)	Bi (0.01-0.04) ; Pb(0.60-0.77)
Bi(10)-Pb(1)	Bi (0.01-0.26) ; Pb(0.64-0.72)
Bi(0.1)-Tl(10)	Bi (0.01-0.04) ; Tl (0.37-0.52)
Bi(10)-Tl(1)	Bi (0.01-0.28) ; Tl (0.39-0.45)
Tl(10)-Pb(1)	Tl (0.38-0.52) ; Pb(0.63-0.71)
Tl(1)-Pb(10)	Tl (0.38-0.46) ; Pb(0.59-0.76)
Hg(0.1)-Pb(10)	Hg(0.02-0.04) ; Pb(0.60-0.75)
Hg(10)-Pb(1)	Hg(0.00-0.06) ; Pb(0.65-0.72)
Hg(10)-Tl(1)	Hg(0.00-0.06) ; Tl (0.40-0.49)
Hg(0.1)-Tl(10)	Hg(0.02-0.05) ; Tl (0.40-0.54)
<i>EtOH-3 M HNO₃ (8:2), 50 min</i>	
Tl(10)-In(0.1)	Tl (0.24-0.37) ; In (0.81-0.87)
Tl(1)-In(10)	Tl (0.26-0.34) ; In (0.79-0.91)
Cu(10)-Zn(1)	Cu (0.02-0.43) ; Zn(0.68-0.76)
Cu(1)-Zn(10)	Cu (0.02-0.08) ; Zn(0.65-0.80)
Ca(1)-Al(10)	Ca (0.53-0.61) ; Al (0.64-0.86)
Ca(10)-Al(1)	Ca (0.52-0.70) ; Al (0.73-0.84)
Cu(10)-Pb(1)	Cu (0.02-0.34) ; Pb(0.37-0.47)
Cu(1)-Pb(10)	Cu (0.02-0.08) ; Pb(0.33-0.49)
Hg(10)-Cd(1)	Hg(0.00-0.05) ; Cd(0.71-0.78)
Hg(1)-Cd(10)	Hg(0.02-0.05) ; Cd(0.70-0.79)

should be. Typical separations accomplished are given in Table V. Separations of some metal ions present in varying proportions are also feasible: 10:1 and 1:100 mixtures of Bi(III)-Pb(II), Bi(III)-Tl(I), Hg(II)-Pb(II), In(III)-Tl(I) and Hg(II)-Cd(II), and 10:1 and 1:10 mixtures of Zn(II)-Cu(II), Al(III)-Ca(II) and Pb(II)-Cu(II) could be separated very easily from each other (Table VI).

ACKNOWLEDGEMENTS

Our sincere thanks are due to Prof. R. KURODA, of this laboratory, for his helpful discussions and comments, and to Dr. F. AOKI and Dr. M. KOJIMA, Government Chemical Industrial Research Institute, Shibuya-ku, Tokyo, for their encouragement through the investigation. We are indebted also to Nomura Jimusho, Inc., Minato-ku, Tokyo, for free samples of some of the polysulphide polymers.

REFERENCES

- 1 N. IKEDA AND K. OGUMA, *J. Chromatog.*, 31 (1967) 289.
- 2 *Thiokol Chemical Corporation Technical Bulletin LP-32*, Clifton, N. J., ca. 1967.
- 3 H. SEILER, in E. STAHL (Editor), *Thin-Layer Chromatography*, Academic Press, New York, 1965.
- 4 A. SEIDEL AND W. F. LINKE, *Solubilities of Inorganic and Metal Organic Compounds*, Van Nostrand, New York, 1960.
- 5 H. STEPHEN AND T. STEPHEN, *Solubilities of Inorganic and Organic Compounds*, Vol. 1, Pergamon Press, London, 1963.