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### The thin-layer separation of some metal-EDTA complexes on microcrystalline cellulose

Work in our laboratory has shown that microcrystalline cellulose (Avicel) can be successfully used as an adsorbent in inorganic thin-layer chromatography (TLC)<sup>1</sup>. Its application to the separation of common inorganic anions has been extended by the present work to include anionic transition metal chelates of the EDTA type. Silica gel has been reported as an adsorbent for several Pt(II), Rh(II) and Co(III) EDTA, CyDTA and EDDA complexes<sup>2</sup>. A TLC one-dimensional separation technique on microcrystalline cellulose was developed which allows the separation of nine transition metal-EDTA complexes.

#### *Experimental*

*Preparation of the plates.* The adsorbent was prepared by blending the microcrystalline cellulose (technical grade, Avicel Sales Division, FMC Corp., Marcus Hook, Pa.) with enough distilled water in a Waring blender to make a rather fluid slurry. A ratio of 1 g of microcrystalline cellulose to about 3.8 to 4.3 ml of water blended for 15 to 30 sec at low speed was found to give a fluid slurry. Usually 75 g of Avicel in a blended slurry spread on 20 × 5 cm plates at the thickness of 0.75 mm could prepare 40 plates. The plates were allowed to dry for 24 h and stored in a sodium hydroxide desiccator until ready for use.

*Metal-EDTA complex preparation and application.* The complexes were prepared according to published procedures<sup>3-6</sup>. The complexes of Cr(III), Mn(II), Fe(III), Ni(II), Zn(II), Cd(II) and Hg(II) did not precipitate from the reaction mixture as reported<sup>5</sup>; however, evaporation of the reaction mixture in a vacuum oven at 25° for 24 h to a small volume followed by the addition of absolute alcohol resulted in the precipitation of the desired metal complex. The complexes were prepared in a 1.0% (w/v) aqueous solution except in the case of the Fe, Mn and Zn complexes, where a saturated solution was used.

*Solvent systems.* Reagent-grade chemicals were used to make the solvent systems listed in Table I. The chromatographic tank containing 100 ml solvent was allowed to equilibrate 4 to 5 h with a development time from 1 to 2 h.

*Detection.* Table II summarizes the data of the different detection techniques and reagents used. Except for Co and Cr, which were self-indicating, and Fe, which was detected by UV light, the other complexes were detected by the spraying technique.

#### *Results and discussion*

Twenty-three mixtures of the metal-EDTA complexes (Table II) were separated using seven different solvent systems of varying composition. Solvent systems No. 2 and 3 were reported to give a TLC separation of Mn, Fe, Cr, Co, Ni and Cu using silica gel<sup>7</sup>. On microcrystalline cellulose, these solvent systems did not give an efficient separation for these complexes; however, it did separate the Zn, Cd and Hg complexes. Other solvent systems were developed by taking advantage of the differences in the

TABLE I

SOLVENT SYSTEMS FOR SEPARATION OF METAL-EDTA COMPLEXES

No.	Composition (% by vol.) <sup>a</sup>
1	H <sub>2</sub> O-butanol-glycol monomethyl ether-conc. NH <sub>3</sub> (4.5:3.5:2.0:0.25)
2	H <sub>2</sub> O-glycol monomethyl ether-methyl ethyl ketone-acetone-butanol-conc. NH <sub>3</sub> (4.0:3.0:1.5:0.5:1.0:0.10)
3	H <sub>2</sub> O-glycol monomethyl ether-methyl ethyl ketone-acetone-conc. NH <sub>3</sub> (4:2:2:2:0.15)
4	H <sub>2</sub> O-butanol-acetone-conc. NH <sub>3</sub> (4:4:2:0.10)
5	H <sub>2</sub> O-methyl ethyl ketone-butanol-acetone-conc. NH <sub>3</sub> (4.0:2.5:1.0:2.5:0.10)
5A	(4.0:1.0:1.0:4.0:0.15)
5B	(4.0:1.0:1.0:4.0:0.15)
6	H <sub>2</sub> O-acetone-conc. NH <sub>3</sub> (1.3:8.7:0.05)
6A	(2:8:0.05)
6B	(2.5:7.5:0.05)
6C	(3:7:0.05)
6D	(3.5:6.5:0.05)
6E	(5:5:0.10)
6F	(5:5:0.10)
7	H <sub>2</sub> O-butyronitrile-methanol-HClO <sub>4</sub> (3 ml:7 ml:10 drops)

<sup>a</sup> The conc. NH<sub>3</sub> and HClO<sub>4</sub> are on a basis of 100 ml of solvent.

TABLE II

R<sub>F</sub> VALUES OF VARIOUS MIXTURES OF METAL-EDTA COMPLEXES

Solvent system No.	R <sub>F</sub> value								
	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Hg
1							0.70	0.65	0.62
2							0.68	0.58	0.55
3							0.74	0.64	0.60
4			0.46	0.54					
4	0.54		0.46						
5A	0.58			0.65					
5B			0.60	0.66	0.75				
5B	0.74		0.67	0.78					
5B			0.42	0.49		0.57	0.59	0.45	0.38
5B			0.42		0.61				
6A	0.17			0.07					
6B	0.39		0.13	0.27					
6B	0.65	0.07	0.29	0.49			0.11	0.09	0.07
6C	0.29		0.54	0.39			0.13		
6C							0.17	0.12	0.09
6D							0.59	0.46	0.26
6E							0.60	0.52	0.44
6F	0.86		0.75	0.82					
7			0.15	0.06	0.45				
7			0.22	0.09	0.42		0.58		

solubility of the metal-EDTA complexes in water and their insolubility in common organic solvents.

Comments on the specific visualization reagent and detection technique used for each EDTA complex are given below:

Cr — a violet-blue complex, self-indicating; the complex appears black under UV light and also gives a dark green color with 0.05 % (w/v) dithizone in  $\text{CCl}_4$ ;

Mn — a colorless compound which gives a yellow color with a saturated solution of 8-hydroxyquinoline in  $\text{NH}_3$ ;

Fe — a yellow-brown complex, self-indicating, which also gives a red color with 1 % (w/v) of KCNS;

Co — a violet-red complex, self indicating; the complex appears black under UV light and gives a gray-yellow color with dithizone;

Ni — a light blue complex which is yellow after spraying with dithizone;

Cu — a blue complex which gives a light green color after spraying with 8-hydroxyquinoline which appears shiny under UV light;

Zn — a colorless complex which gives a pink color after spraying with a dilute solution of  $\text{NH}_3$  and dithizone;

Cd — a colorless complex which gives a yellow color after spraying with 5 % (w/v) aqueous solution of  $\text{Na}_2\text{S}$ ; sometimes it is necessary to follow up with a dilute acid spray to develop the ion;

Hg — a colorless complex which gives a black spot after spraying with 5 %  $\text{Na}_2\text{S}$ .

For multiple spraying, the zones on the TLC plate were first marked for those reagents which were self-indicating. This was followed by spraying of the detection reagents in the order KCNS,  $\text{Na}_2\text{S}$ , dithizone and 8-hydroxyquinoline. For example, in the detection of Hg, Cd and Zn separation, the plate was sprayed with  $\text{Na}_2\text{S}$  to detect Hg and Cd. These zones were marked and the plate was sprayed with dithizone and  $\text{NH}_3$  to detect the Zn complex. The Hg and Cd spots disappeared in the presence of base.

The separations were done in the pH range of 6.5 to 7.5. Increasing the basicity or acidity of solvent system did not affect the  $R_F$  value, but it did cause tailing in the separation, which indicates decomposition of the complex. Indeed, substitution of  $\text{HClO}_4$  for  $\text{NH}_3$  in solvent systems No. 5B and No. 6B showed two bands for the EDTA separation of Fe, Cu, Co and Zn. Similar results have also been noted in the literature<sup>8</sup>.

From Table II, it is noted that the  $R_F$  value for a complex was affected by the composition of the mixture for some solvent systems. In solvent system No. 5B, addition of Cr to Fe and Co increased the  $R_F$  value of Fe and Co as compared to Ni added to a Fe and Co mixture. Similarly, a Fe-Co-Cu mixture decreased the  $R_F$  value of Fe and Co. The  $R_F$  value of the individual complex was generally higher than the same complex in a mixture, however, this difference was smaller in separations where the concentration of the complex in the mixture was identical to the concentration of the individual complex. These differences are probably due to an attraction of each complex to one another.

In solvent system No. 6 (A to F) for a Zn-Cd-Hg separation, variation in the water-acetone concentration showed a sharp influence on their respective  $R_F$  values, but the relative order of Zn-Cd-Hg remained the same. In contrast, a Cr-Fe-Co

separation for solvent system No. 6 (B and C) showed not only a difference in  $R_F$  values but also a change in the order of their detection by varying the composition of the solvent system.

Since all of the complexes studied represented a racemic mixture, attempts to separate the *d*- and *l*-isomers of  $K[Co(EDTA)]$  by TLC using optically active quartz (right-handed) incorporated into the TLC plate did not yield a satisfactory separation. The individual isomers gave different  $R_F$  values, however, a racemic mixture could not be resolved.

### Conclusions

The data obtained in this study indicate that TLC using microcrystalline cellulose as an adsorbent can be used to separate various mixtures of metal-EDTA complexes. From the solvent systems studied, the  $R_F$  values can be tailored to meet specific needs by varying the composition of the solvent mixture.

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