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### Separation of acetylacetonate chelates by thin-layer chromatography

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Acetylacetone, whose enol form is a weak acid,  $K_a = 1.12 \times 10^{-19}$ , very easily forms metal salts. Virtually all the metals of the periodic table have been used to prepare metal acetylacetonates (metal  $\beta$ -diketonates). For these compounds, which for the most part are characterized by their unusual thermal stability, volatility and solubility in many organic solvents, many uses have been proposed. The chemical literature abounds in the evaluation of metal acetylacetones for use in a wide variety of applications. These include the extraction of metals from ores by complexation, which is based on their stability and resistance to hydrolysis<sup>1</sup>, and the most prevalent use is as a catalyst system for polymerization of olefins and dienes<sup>2,3</sup>. Considerable work has been published in the area of oligomerization, co-dimerization and dimerization<sup>4</sup>. Other areas of catalysis include epoxy curing, hydrogenation and oxidation<sup>5</sup>. A partial list of miscellaneous applications includes flame-resistant formulations, lubricants, dyes, metal film deposition and vinyl stabilizers. Many rare earth acetylacetonates are also known and their extreme stability has suggested uses such as organometallic lasers, phosphors, control devices in nuclear applications and catalysis in polymer and optical systems. In view of the increasing importance of metal acetylacetonate complexes, it is desirable to develop effective methods for their separation and identification. The physical and chemical properties of this type of metal complex suggest that multistage fractionation procedures such as thin-layer (TLC), paper (PC), gel, gas-liquid (GLC) and liquid chromatographic techniques can be employed for separation of metal diketonates.

Burstall *et al.*<sup>6</sup> and Pollard *et al.*<sup>7</sup> have used solvent systems containing nitric acid and butanol with some acetylacetone in the PC separation of some inorganic ions. Since the rate of complex formation may affect this type of separation, Berg and Strassner preferred to spot the paper with the metal complexes of copper, cobalt and iron and to develop the chromatogram in a solvent system of cyclohexane, dioxane and methanol<sup>8</sup>.

The efficient resolution of multicomponent mixtures of some trifluoroacetylacetonates by GLC has been demonstrated<sup>9</sup>. Karayannis and Corwin have recently reported the chromatography of thirty-nine metal acetylacetonates by hyperpressure chromatography, but only limited separations were achieved<sup>10</sup>. GC studies on mixed ligand complexes of Fe(II), Co(II) and Ni(II) containing dimethylsulfoxide and decafluoro-3,5-heptanedione were reported<sup>11</sup>. Separations of Fe(II) and Co(II) com-

plexes from the Ni(II) complex were achieved, but no separation of the Fe(II) complex from the Co(II) complex was observed.

The TLC separation of a few transition metal acetylacetonates has been done on alumina and silica gel<sup>12</sup>. This study showed that in the solvents benzene, chloroform and diethyl ether, the divalent complexes of Co, Mn, Ni, and Cu migrated not at all or very little as compared with the trivalent complexes of Co, Mn, Cr and Fe. The acetylacetonate and benzoyl chelates of Cu, Co and Ni were also prepared from its metal ion and chromatographed on silica gel in an alkaline solvent system containing a small amount of acetylacetonate<sup>13</sup>. Atomic number *versus* chromatographic behavior has been reported for the lanthanide  $\beta$ -diketonates on alumina<sup>14</sup>.

We report here the TLC behavior of various representative and transition metal  $\beta$ -diketonates (ackacks) on a microcrystalline cellulose absorbent using complexes where the acetylacetonate acts as a mono- and bi-dentate ligand and the metal has a coordination number of either one, four, six or eight.

## EXPERIMENTAL

### Plate preparation

The microcrystalline cellulose slurry was prepared and spread on 20 × 5 cm plates at a thickness of 0.75 mm as previously reported<sup>15,16</sup>.

### Solvent preparation and chelate application

The solvent systems were prepared from the reagent grade chemicals listed in

TABLE I

### SOLVENT SYSTEMS FOR THE SEPARATION OF METAL-ACETYLACETONATE CHELATES

Solvent system	Composition*
1	Ethyl alcohol-water (50:50)
2	Ethyl alcohol-15 M NH <sub>3</sub> -glacial acetic acid (70:30:2)
3	Ethyl alcohol-glacial acetic acid-ethyl acetate
	A. 70:30:15
	B. 70:40:5
	C. 70:30:0
	D. 65:25:10
4	Acetone-water-12 M HCl-KCl (86:8:6:4 g)
5	Acetone-methyl ethyl ketone-water-12 M HCl-KCl (42:48:5:5:4 g)
6	<i>tert.</i> -Butyl alcohol-water-6 M HCl
	A. 80:15:5
	B. 80:18:2
7	Ethyl alcohol-methyl alcohol-15 M NH <sub>3</sub> -12 M HCl (35:35:30:2)
8	Ethyl alcohol-glacial acetic acid-water-ethyl acetate-diethyl ether (80:5:15:20:5)
9	Amyl alcohol-12 M HCl-benzene
	A. 85:15:0
	B. 70:20:10
	C. 60:20:20
	D. 60:30:10
	E. 50:30:20

\* The ratios given are by volume, except where indicated otherwise.

Table I. The chromatographic tank (Desaga) containing 100 ml of solvent was allowed to equilibrate for 1 h, with a development time varying with the solvent system but averaging about 1 h for a run of 15 to 17 cm. The metal acetylacetonates were obtained from Research Organic/Inorganic Chemical Co., Sun Valley, Calif., U.S.A. They were prepared in 4–6% (w/v) ethanol, except for the beryllium, calcium, strontium and barium chelates, which were applied from a methanol solution.

The metal chelates used were of the type:  $\text{CH}_3 \cdot \text{C}(\text{OM}) = \text{CHCOCH}_3$ , where M is Ti, Li, Na and K;  $\text{M}(\text{CH}_3\text{COCHCOCH}_3)_2$ , where M is Ni, Co, Cu, Zn, Bi, Ca, Si, Ba, Cd, Pt, Pd;  $\text{M}(\text{CH}_3\text{COCHCOCH}_3)_3$ , where M is Sc, V, Cr, Mn, Fe, Co, Al, Ga, In;  $\text{M}(\text{CH}_3\text{COCHCOCH}_3)_4$ , where M is Ti, Zr, Hf.

TABLE II  
COMPOSITION OF SPRAY REAGENTS AND COLORS OF DETECTED CHELATES

	<i>Reagent</i>	<i>Composition</i>	<i>Chelate detected (color)</i>
A	(i) Alizarin (ii) 1 M NaOH	Saturated ethanolic solution	Ca (pink), Be (pink)
B	(i) Alizarin red S (ii) 6 M $\text{NH}_3$	0.1% (w/v) Aqueous solution	Ni (purple), Fe (blue) Cu (pink), Zn (violet) Zr (pink-red), Sc (purple-red) Hf (pink-red)
C	(i) Potassium rhodizonate (ii) 6 M $\text{NH}_3$	0.1 (w/v) Aqueous solution	Sr (orange-pink), Ba (red-pink)
D	(i) Dimethylglyoxime	1% (w/v) Ethanolic solution	Ni (pink)
E	(i) 8-Hydroquinoline (ii) 6 M $\text{NH}_3$	0.5 g in 60% (w/v) Ethanol-water solution	Al (yellow-green in UV) Ga (yellow), In (yellow)
F	KNCS	1% aqueous solution	Fe (red)
G	(i) KI  (ii) $\text{Na}_2\text{S}_2\text{O}_3$	10% (w/v) KI-Aqueous solution  2% (w/v) $\text{Na}_2\text{S}_2\text{O}_3$ -aqueous solution	Tl (yellow)  Pt (pink), use G(i) only
H	$\text{SnCl}_2$	5% (w/v) in 5 M HCl	Pd (blue-green)
I	Tannic acid	10% (w/v) aqueous solution	Ti (yellow), V (gray)
J	Fluorescein	0.1% Ethanolic solution	Li (yellow), K (yellow) Na (yellow in UV)
K	1-(2-Pyridylazo)-2-naphthol	0.2% (w/v) Ethanolic solution	In (red), Ga (red), Cd (orange-red) Zn (blue-red), Al (orange in UV)
L	1-Nitroso-2-naphthol-3,6-disulfonate	1% (w/v) Aqueous solution of disodium salt	$\text{Co}^{2+}$ (brown) $\text{Co}^{3+}$ (brown)
M	Self-indicating complexes		Cr (pale violet), Co (green) Fe (yellow)

#### Detection

The spots were revealed by the spraying technique and the color was observed in daylight or under UV light. Table II lists the visual reagents used and the color of the detected chelate. For multiple detection the reagents given in Table III are listed in the order of detection. The  $R_F$  values (Table III) are averages of four to five runs.

TABLE III

$R_F$  DATA ON THE SEPARATION OF VARIOUS MIXTURES OF METAL ACETYL-ACETONATES

Mixture	Solvent system (Table I)	Reagent (Table II)	$R_F$	Mixture	Solvent system (Table I)	Reagent (Table II)	$R_F$
Fe	1	F	1.00	Al	6A	E	0.45
Ni		D	0.00	In		K	0.34
Co	2	M	1.00	Ga		K	0.12
Ni		B	0.64	Tl		G	0.00
Fe		B	0.01	Ga	9E	E	0.86
Co	2	M	1.00	In		E	0.28
Cu		B	0.49	Al		E	0.01
Fe		B	0.01	Tl		G	0.00
Cu	2	B	0.53	Zn	6B	K	0.76
Zn		B	0.50	Cd		K	0.60
Ni	2	B	0.61	Al		K	0.31
Cu		B	0.52	Cd	7	K	0.66
Zn		B	0.46	Zn		K	0.50
Al				Al		K	0.04
Ca	3A	A	0.56	Ti	9B	I	0.22
Sr		C	0.19	V		I	0.12
Ba		C	0.09	Sc		B	0.04
Ca	3B	A	0.51	Ti	9C	I	0.25
Sr		C	0.15	V		I	0.11
Ba		C	0.10	Sc		B	0.04
Co	4	M	1.00	Ti	9D	I	0.70
Fe		M	0.73	Sc		B	0.14
Ni		D	0.10	Zr		B	0.05
Co	5	M	1.00	Ti	9D	I	0.70
Fe		M	0.64	V		I	0.13
Ni		D	0.20	Hf		B	0.05
Cr	4	M	1.00	Ti	9D	I	0.67
Zn		B	0.80	Sc		B	0.13
Cu		B	0.60	Hf		B	0.05
Mn		B	0.17	Li	8	J	0.61
Cr	5	M	1.00	Na		J	0.40
Zn		B	0.57	K		J	0.29
Cu		B	0.51	Pt	9A	G	0.94
Mn		B	0.08	Pd		H	0.62
Cr	4	M	1.00	Be	3C	A	0.93
Mn		B	0.15	Sr		C	0.19
Ni		D	0.05	Ba		C	0.09

TABLE III (continued)

Mixture	Solvent system (Table I)	Reagent (Table II)	$R_F$	Mixture	Solvent system (Table I)	Reagent (Table II)	$R_F$
Co	4	M	1.00	Be	3D	A	0.95
Mn		B	0.16	Ca		A	0.64
Ni		D	0.07	Sr		C	0.28
Co(II)	4	L	1.00	Ba		C	0.10
Co(III)		L	0.20				
Co(II)	5	L	1.00	Ti	9D	I	0.67
Co(III)		L	0.12	V		I	0.15
				Zr		B	0.05

## RESULTS AND DISCUSSION

In this study thirty mixtures prepared from twenty-seven metal acetylacetonates were separated in seventeen different solvent systems. Most of the solvent systems from which successful separations were performed contained some amount of alcohol and/or acid. The varying solubilities of the acetylacetonates in the alcohol coupled with the competition that the solvent and these solute molecules have for the many active sites (hydroxyl groups) on the microcrystalline cellulose would indicate that the metal ion is most important in determining their chromatographic behavior. While there may be some interaction between the metal chelates in a mixture, our study shows that this effect is not large enough to greatly influence a change in the  $R_F$  value in a mixture *versus* that of the individual complex. For example, in solvent No. 5 Cr, Zn, Cu and Mn gave respective  $R_F$  values of 1.00, 0.60, 0.55 and 0.08 when chromatographed individually *versus* respective  $R_F$  values of 1.00, 0.57, 0.51 and 0.08 when chromatographed in a mixture. The solubility of the chelates of Co, Ni and Cu as well as the polarization of these metal ions has also been used to explain their paper chromatographic behavior<sup>8</sup>. Furthermore, it was also observed that the  $R_F$  value of the metal chelate did not change from one mixture to another in any given solvent system.

Solvent system No. 2 was reported by Swain and Sudmeier to separate some kinetically inert anionic and cationic metal chelates<sup>17</sup>. As shown in Table III, efficient separations of mixtures of Fe, Co, Ni, Cu and Zn acetylacetonate complexes could be accomplished by this solvent system. A change in the alcohol from ethanol to butanol or propanol caused much tailing of the complexes. On increasing the amount of ethyl acetate and decreasing the amount of acetic acid (solvent system No. 3), the alkaline earth complexes of Ca, Sr, and Ba all showed an increase in their  $R_F$  value. Complete removal of the ethyl acetate from these systems results in a poor separation.

To verify that the metal chelates were being chromatographed and not the ions, a plate was spotted with the metal ion and chromatographed identical to the procedure used with the metal acetylacetonates. In all cases either no migration of the ions was observed or the ion was spread throughout much of the plate or the  $R_F$  value of the individual ion did not correspond to that reported in Table III for the chelate. For example, in solvent system No. 6A no migration of the Al, In, Ga or

Tl ions was observed. Spreading occurred for the ions Cr, Mn (No. 4), Zn (No. 5), Al (No. 7) and Li (No. 8). Fe(III) in solvent system No. 1 had an  $R_F$  value of 0.75 (1.00 for complex), Zr(IV) in solvent system No. 9D had an  $R_F$  value of 1.0 (0.05 for complex), Fe(III) in solvent system No. 2 had an  $R_F$  value of 0.44 (0.01 for complex), and Na(I) in solvent system No. 8 had an  $R_F$  value of 0.18 (0.40 for complex). It was further observed that the addition of a small amount of acetylacetone (1.0 ml) in each solvent system did not affect the  $R_F$  value of any of the complexes reported in Table III<sup>18</sup>.

It is difficult to come to any general conclusion regarding a separation based on the oxidation number of the metal. Al(III), In(III) and Ga(III) have a higher  $R_F$  value in solvent system No. 9E as compared with Tl(I), yet Cd(II) and Zn(II) migrated farther than Al(III) in systems No. 6B and 7. The alkali metal complexes (No. 8) and the alkaline earth metal complexes (No. 3D) did separate on the basis of size, with the larger metal ion migrating less than the smaller metal ion. As previously indicated, the size of the metal ion (polarization) and solubility of the complex in the solvent system must then both be considered with respect to the fact if the complex will migrate in a particular solvent system<sup>8</sup>.

The first-row transition metal acetylacetonates were separated in solvent systems which contain some potassium chloride (Nos. 4 and 5). The data show excellent separation for these complexes, even up to the separation of the Co(II) and Co(III) acetylacetonates. Removal of the potassium chloride from the solvent gave considerable spreading to one or more of the bands. It would appear that potassium chloride is sufficient to increase the ionic strength of the solvent to overcome the small differences between these solutes.

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