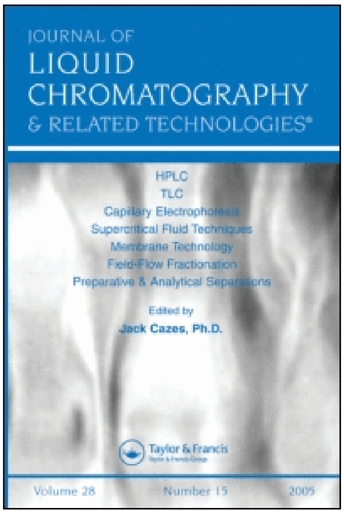

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

TLC Resolution Studies of Some Metal-Piperidinedithiocarbamate Complexes on Various Surfactant Impregnated Silica Gel-G Plates

Arati Asolkar[a]; Ashok Kumar[a]; Pratibha Pandey[a]; R. Bhardwaj[b]
[a] Department of Chemistry, D. A. University of Indore, Indore, India [b] Department of Biochemistry, D. A. University of Indore, Indore, India

To cite this Article Asolkar, Arati , Kumar, Ashok , Pandey, Pratibha and Bhardwaj, R.(1992) 'TLC Resolution Studies of Some Metal-Piperidinedithiocarbamate Complexes on Various Surfactant Impregnated Silica Gel-G Plates', Journal of Liquid Chromatography & Related Technologies, 15: 10, 1689 — 1701

To link to this Article: DOI: 10.1080/10826079208018320

URL: http://dx.doi.org/10.1080/10826079208018320

JOURNAL OF LIQUID CHROMATOGRAPHY, 15(10), 1689-1701 (1992)

TLC RESOLUTION STUDIES OF SOME METAL-PIPERIDINEDITHIOCARBAMATE COMPLEXES ON VARIOUS SURFACTANT IMPREGNATED SILICA GEL-G PLATES

ARATI ASOLKAR[1], ASHOK KUMAR[1],
PRATIBHA PANDEY[1], AND R. BHARDWAJ[2]
[1] Department of Chemistry
[2] Department of Biochemistry
D. A. University of Indore
Indore - 452 001, India

The main interest focussed over the years on the dithiocarbamates and their complexes is significantly due to their diversified applications as fungicides, pesticides, antioxidants, inhibitors in research on enzymes [1], possible protection against the lethal effects of X-rays, and in the treatment of chronic alcoholism [2], sarcoma cells [3] and acute and chronic cadmium poisoning [4]. The dithiocarbamate complexes were first experimented medicinally on the control of various dermatophytes. Some complexes of vanadium have been found to act as potential antimicrobial, insect-sterilising and ovicidal agets [5]. Certain dithiocarbamate complexes of copper have found use as fungicides, phytocides [6], and as accelerators [7] in the vulcanisation of rubber.

A literature survey suggested that the TLC analysis of metal-dithiocarbamates [8-15] has been reported, but, attempts to achieve their resolution on various surfactants impregnated silica gel-G plates and quantitative isolation are surprisingly scarce. Keeping in view the immense importance of the o62 dithiocarbamates in the vast spectral area of medicinal and analytical chemistry, it was considered worthwhile to resolve yet another class of dithiocarbamate complexes. In the present communication, piperidinedithiocarbamate(Pipdtc) complexes of Pb(II), Cd(II), Cu(II) and Fe(III) (under investigation for heir antimicrobial activity) have been resolved using various pure solvents and binary solvent mixtures, on silica gel-G plates and so also on different surfactants impregnated silica gel-G plates. Exhaustive quantitative and qualitative analysis of synthetic mixtures and alloys have been conducted, and the R_f values of metal complexes compared.

EXPERIMENTAL

All the solvents used were freshly dried and distilled. A 1% solution of ligand (sodium salt of piperidinedithiocarbamate: prepared by the method given by Macrotrigiano et al. [16]) was prepared in doubly distilled water. Standard lead, copper, cadmium and iron solutions (1000 ppm) were also prepared in doubly distilled water from their analytical reagent grade samples and standardized [17]. Alloy solution was prepared by dissolving 0.2 gms of the standard alloy in 15 ml of HCl(1+1) by heating on a water bath and then adding 1-2 ml of concentrated HNO_3. The excess of the acid was evaporated by gently heating on a boiling water bath and then the volume made upto 100 ml in a standard volumetric flask.

To 2.0 ml of each of the 1000 ppm solutions prepared, added 5.0 ml of 1% ligand solution. pH adjusted at 3.5 for Pb(II), 3.0 for Cd(II), 4.5 for Cu(II) and 5.5 for Fe(III) (using 1M ammonia and 1M perchloric acid solutions). To 10 ml of alloy solution added 10 ml of 1% ligand solution and pH adjusted at 4.5. Then 2.0 ml of 20% naphthalene solution in acetone added to the above solutions. The adsorbed complexes filtered, washed several times with distilled water, dried and dissolved in 10 ml of chloroform.

An ascending irrigation technique was employed using commercially available silica gel-G and chromatoplates of size 20x10 cm^2. The glass plates were prepared by coating them with silica gel-G (thickness 0.75 mm) with the help of stahl type applicator. The plates were air-dried, activated at 60 $^\circ$C for 24 hours before use. In quest for better resolution, various surfactants were also tried.

(i) Silica gel-G + 1% sodium lauryl sulphate.
(ii) Silica gel-G + 1% tetrabutyl ammonium bromide.
(iii) Silica gel-G + 1% triton X-100

0.1 ml of the solutions prepared were spotted separately at 2.0 cm from the one edge of the plate. The spots were air dried at room temperature and then placed in a chamber that was saturated with either pure solvent vapours (Table 1) or binary solvent vapours (Table 2). The plates were developed until the solvent front had travelled a distance of 16.5 cm. About 45-70 minutes were usually required. The plates were dried and the spots of lead and cadmium made visible by placing the plates in iodine chamber for 40 seconds. Cu(II) and Fe(III)-piperidinedithiocarbamates were detected by their characteristic colours

TABLE 1. TLC DATA

Solvents: A= Hexane; B= Cyclohexane; C= 1,4 Dioxan; D= Carbon tetrachloride; E= Benzene; F= Toluene; G= Xylene; H= Petroleum ether; I= Chloroform; J= Ethylacetate ; K= Acetone; L= Methanol; M= Acetonitrile

Metal-Ppidtc	D*	Identification		R_f x100 values in pure solvents												
(pH range)		I_1	I_2	A	B	C	D	E	F	G	H	I	J	K	L	M
Pb (3.0 -5.0)	1.0	colour-less	bright yellow	00	00	94	00	51	28	24	00	93	98	98	98	96
Cd (3.0 - 5.5)	1.5	colour-less	light yellow	00	00	84	00	37	20	18	00	88	T	T	96	93
Cu (1.5 - 4.5)	0.8	yellow-ish brown	greenish brown	00	00	98	00	74	57	47	00	94	98	98	99	98
Fe (3.5 - 8.0)	1.0	light grey	yellow	00	00	88	00	38	24	20	00	92	86	97	97	94

D* = Detection in μg.
I_1 = Original colour of spots after development of plates.
I_2 = Colour of spots after development in iodine chamber.

TABLE 2

R_f x100 VALUES OF METAL-Pipdtc COMPLEXES IN BINARY SOLVENTS

S.No.	Binary solvents	R_f x100 values			
		Pb	Cd	Cu	Fe
1.	Chloroform : Benzene (20:80)	62	32	74	46
2.	Chloroform : Benzene (80:20)	85	83	92	85
3.	Xylene : Benzene (20:80)	46	29	66	34
4.	Xylene : Benzene (80:20)	22	16	47	18
5.	Toluene : Benzene (20:80)	43	24	62	28
6.	Toluene : Benzene (80:20)	30	18	57	20
7.	Xylene : Chloroform (80:20)	23	13	44	18
8.	Xylene : Toluene (20:80)	40	18	74	32
9.	Xylene : Toluene (80:20)	30	22	61	24
10.	Chloroform : Toluene (20:80)	48	16	78	32
11.	Ethyl acetate : Toluene (20:80)	95	T	96	91
12.	Ethyl acetate : Benzene (20:80)	95	T	96	94
13.	Ethyl acetate : Xylene (20:80)	94	T	95	89
14.	1,4 Dioxan : Toluene (20:80)	87	82	96	85
15.	Acetonitrile : Xylene (20:80)	91	88	95	90
16.	Methanol : Xylene (20:80)	95	90	98	91

(Table 1). For each system five runs were carried out and the R_f values obtained were found reproducible in different identical runs. For quantitative determination, the respective spots were scraped off carefully and the silica gel-G with the respective complex dissolved in 10 ml of chloroform. Since the solutions of lead and cadmium complexes in chloroform are colourless, the lead and cadmium ions are quantitatively replaced by cupric ions by the addition of 10^{-3} M solution of cupric nitrate to their respective solutions. The solutions are shaken vigorously in a separating funnel in order to get a stable yellow colour in the chloroform layer. The transmittance and absorbance of the clear chloroform solution then noted. With reference to the calibration graph plotted for the respective metal-

TABLE 3

R_f x100 VALUES OF METAL-Pipdtc COMPLEXES IN FIVE BINARY SOLVENT SYSTEMS USING DIFFERENT SURFACTANTS

Adsorbents	Benzene-Chloroform 80 : 20				Benzene-Xylene 80 : 20				Benzene-Toluene 80 : 20				Chloroform-Toluene 20 : 80				Xylene-Toluene 20 : 80			
	Pb	Cd	Cu	Fe	Pb	Cd	Cu	Fe	Pb	Cd	Cu	Fe	Pb	Cd	Cu	Fe	Pb	Cd	Cu	Fe
Silica gel-G	62	32	74	46	46	29	66	34	43	24	62	28	48	16	78	32	40	18	74	32
Silica gel-G +1% sod. lauryl sulphate	70	48	78	52	48	34	66	36	42	26	68	28	48	32	68	39	30	20	52	20
Silica gel-G +1% Tetra butyl ammonium bromide	66	47	79	58	52	35	66	48	44	21	61	31	45	21	56	31	29	17	47	22
Silica gel-G +1% Triton X-100	64	36	75	44	48	28	66	36	42	23	62	30	46	20	72	34	38	20	70	28

TABLE 4

QUALITATIVE AND QUANTITATIVE DETERMINATION OF COPPER AND IRON IN SYNTHETIC SAMPLE

Amount of metal ions present (μg) in synthetic mixture	Amount taken (μg)	Amount found by the present method* (μg)	Relative standard deviation (%)	R_f x100 value
Cu: 2000 Fe: 2000	Cu: 20.0	19.59	1.02	73
Pb: 2000 Cd: 2000	Fe: 20.0	18.88	1.27	45

Solvent: Chloroform : Benzene (20:80);
Conditions: 1.0% reagent solution = 5 ml; 20% naphthalene solution in acetone = 2 ml;
pH = 4.5; Wavelength: λ_{max} for copper = 435 nm and λ_{max} for iron = 505 nm.

* : Average of five replicate determinations.

TABLE 5

QUALITATIVE ANALYSIS OF ALLOYS: IDENTIFICATION OF LEAD, COPPER AND IRON IN ALLOYS WITH REFERENCE TO THEIR R_f VALUES

Binary Solvents	ALloys	R_f x100 values (using different surfactants)				Identification of Pb, Cu, Fe in Alloys
		Silica gel-G	Silica gel-G + 1% Sodium lauryl sulphate	Silica gel-G + 1% Tetrabutyl ammonium bromide	Silica gel-G + 1% Triton-X-100	
Benzene:	A	74	76	78	74	Cu
Chloroform	B	62, 72, 46	69, 78, 50	66, 76, 58	63, 75, 42	Pb, Cu, Fe
(80:20)	C	60, 74, 45	69, 76, 52	66, 80, 60	60, 76, 40	Pb, Cu, Fe
Benzene:	A	65	66	67	66	Cu
Xylene	B	46, 66, 33	48, 68, 37	-*, 66, 48	48, 64, 34	Pb, Cu, Fe
(80:20)	C	45, 64, 32	48, 64, 36	-*, 64, 48	46, 67, 36	Pb, Cu, Fe

Benzene:	A	61	68	60	60	Cu
Toluene	B	42, 60, 28	42, 66, 28	43, 60, 30	40, 60, 30	Pb, Cu, Fe
(80:20)	C	43, 60, 26	40, 68, 27	44, 60, 30	41, 65, 31	Pb, Cu, Fe
Chloroform:	A	78	68	58	74	Cu
Toluene	B	47, 77, 30	48, 68, 40	44, 56, 30	49, 74, 36	Pb, Cu, Fe
(20:80)	C	46, 80, 32	49, 67, 40	48, 58, 33	48, 70, 34	Pb, Cu, Fe
Xylene	A	78	52	49	70	Cu
Toluene	B	40, 76, 30	30, 54, 20	30, 48, 21	38, 69, 29	Pb, Cu, Fe
(20:80)	C	42, 78, 30	32, 53, 21	30, 47, 22	39, 74, 30	Pb, Cu, Fe

Certified Composition (in per cent): For Alloys A, B and C

(A) = JSS 505-4;
C: 0.20; S: 0.0086;
Cu: 0.10; Si: 0.30;
Mn: 0.64; Cr: 0.50;
Ni: 1.82; Al: 0.026;
P: 0.02; Mo: 0.22;
N: 0.006.

(B) = NKK No.916;
Cu: 0.27; Mn: 0.11;
Si: 0.41; Fe: 0.54;
Mg: 0.10; Cr: 0.05;
Ni: 0.06; Zn: 0.30;
Ti: 0.10; Sn: 0.05;
Pb: 0.04; V: 0.02;
Zr: 0.05; Bi: 0.03;
Ca: 0.03; Co: 0.03;
Sb: 0.01; C:0.03;
B: 0.0066.

(C) = NKK No. 1021;
S: 15.56; Fe: 0.99;
Cu: 2.72; Mn: 0.20;
Hg: 0.29; Cr: 0.03;
Ni: 0.14; Zn: 1.76;
Ti: 0.04; Sn: 0.10;
Pb: 0.18; V: 0.007;
Zr: 0.01; Bi: 0.01;
Sb: 0.01; Ca: 0.004.

* = Lead spot masked by iron spot.

piperidinedithiocarbamates, the concentration in ug of the metal ions found out (Tables 4 and 6).

RESULTS AND DISCUSSION

The Pb(II), Cu(II), Cd(II) and Fe(III) complexes are quantitatively formed in the pH ranges 3.0-5.0, 1.5-4.5, 3.0-5.5 and 3.5-8.0 respectively. The spectra measured for the reaction at various pH values show that only one type of complex is formed in each case. Their TLC resolution datas are exhibited in Tables 1 - 6. All the pure and binary solvent systems used (Tables 1 & 2, respectively) gave satisfactory separation of the complexes except acetone and ethylacetate, in which tailing was observed in the case of Cd(II) complex. Tailing persisted even when ethylacetate was taken in combination with benzene, xylene and toluene. Table 3 presents the R_f x100 values of the metal-piperidinedithiocarbamates in the five best combinations of binary solvents, using different surfactants. Results depict that more satisfactory resolution was obtained in the case of 1% tetrabutyl ammonium bromide as an adsorbent. The results also show an interesting trend in the R_f values. It is observed that the R_f value is maximum for Cu(II) complex followed by Pb(II), Fe(III) and Cd(II) complex in all the solvent systems. From this it can be concluded that the nature of the metal exerts the main influence on the difference in the chromatographic properties of the metal-piperidinedithiocarbamates. Pure solvents such as hexane, cyclohexane, carbon tetrachloride and petroleum ether did not help in the development of spots. Another noteworthy observation was that the metal-piperidinedithiocarbamates usually gave comparatively high R_f values with solvents of considerably higher dielectric constants.

TABLE 6

QUANTITATIVE DETERMINATION OF COPPER AND IRON IN ALLOY NKK No. 1021.

Alloy	Certified Composition (%)	Amount taken (µg)	Amount found by present method* (µg)	Relative standard deviation(%)	R_f x100 value
NKK No. 1021 (Al-Si-Cu-Zn alloy)	S: 15.56; Fe: 0.99; Cu: 2.72; Mn: 0.20; Hg: 0.29; Cr: 0.03; Ni: 0.14; Zn: 1.76; Ti: 0.04; Sn: 0.10; Pb: 0.18; V: 0.007; Zr: 0.01; Bi: 0.01; Sb: 0.01; Ca: 0.004	Cu: 5.44	5.42	1.20	74
		Fe: 1.98	1.97	1.98	45

Solvent: Chloroform : Benzene (20:80);
Conditions. pH-4.5; Wavelength: λ_{max} for copper = 435 nm and λ_{max} for iron = 505 nm.

*: Average of five replicate determinations.

Qualitative and quantitative analysis of alloys (Tables 5 and 6, respectively) and synthetic mixture (Table 4) also present satisfactory results. Identification of lead, copper and iron in alloys is confirmed by comparing the R_f values of the various distinct spots obtained during the analysis of alloys, with the R_f values obtained for the individual metal complexes, in that specific solvent mixture. In the quantitative analysis of alloys by TLC, an amount of 5.44 µg of copper and 1.98 µg of iron in 10 ml of chloroform gave a mean absorbance of 0.15 and 0.09 with a relative standard deviation of 1.20% and 1.98%, respectively. After the qualitative analysis of the synthetic mixture (containing 20.0 µg each of copper, lead, iron and cadmium), the quantitative estimation of the desired spots of copper and iron in 10 ml of chloroform gave mean absorbance of 0.40 and 0.37 with a relative standard deviation of 1.02% and 1.27%, respectively.

REFERENCES

1. Thorn, G.D., Ludwig, R.A., "The Dithiocarbamates and Related Compounds", Elsevier, Amsterdam (1962).

2. Vidulich, G.A., Evans, D.F., Kay, R.L.: J. Phys. Chem., 71, 656 (1967)

3. Vidulich, G.A., Kay, R.L.: Rev. Sci. Instrum. 37, 1662 (1966).

4. Jones, N.M., Jones, S.G.: Inorg. Chim. Acta. 79, 288 (1983).

5. Graziosi, G., Preti, C., Tosi, G.: Transition. Met. Chem. 7, 267 (1982).

6. Coldworth, M.C., Green, F.L., Swith, M.A.: J. Agr. Research. 66, 277 (1943); Chem. Abstr. 37, 5544 (1943).

7. Galemberti, L.: Chem. Zentri. 289 (1941); Chem. Abstr. 36, 7361 (1942).

8. Fishbein, L., Fawkes, J.: J. Chromatog. 19, 364 (1965).

9. Snef, H.J.: ibid. 21, 363 (1966).

10. Rai, J., Kukreja, V.P.: Chromatographia. 3, 499 (1970).

11. Ballschmoiter, K.: Z. Anal. Chem. 254, 348 (1971).

12. Rao, A.L.J., Singh, S.: ibid. 267, 46 (1973).

13. Singh, N., Kumar, R., Kansal, B.D.: Chromatographia. 11, 408 (1978).

14. Singh, N., Rastogi, K., Kumar, R., Srivastava, T.N.: Analyst. 106, 599 (1981).

15. Timberbaev, A.R., Petrukhin, O.M., Zolotov, Yu. A.: Zh. Analit. Khim. 37, 1360 (1982).

16. Macrotrigiano, G., Pellacani, G.C., Preti, C.: J. Inorganic Nucl. Chem. 36, 3709 (1974).

17. Vogel, A.I.: "A Text Book Of Quantitative Inorganic Analysis" Longmann Publ., 3rd Edn., (1973).