Journal of Chromatography, 137 (1977) 165–170
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CHROM. 9909

CHROMATOGRAPHY OF METAL CHELATES

VIII*. HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY OF METAL DITHIZONATES

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(Received December 28th, 1976)

SUMMARY

High-performance liquid chromatographic separations of Pb(II), Zn(II), Cd(II), Hg(II), Cu(II), Ni(II) and Co(II) dithizonates at nanogram levels by adsorption chromatography on silica gel are reported.

INTRODUCTION

In the trace analysis of elements, photometric detection of chelated metal ions is of great importance. Diphenylthiocarbazane (dithizone) (Fig. 1) forms chelates with a large number of metal ions[1] and thus has widespread use in trace metal analysis.

High-performance liquid chromatography (HPLC) appears to be a good method for the separation and determination of extracted metal chelates[2,3] and, in this paper, separations of metal dithizonates by HPLC are reported.

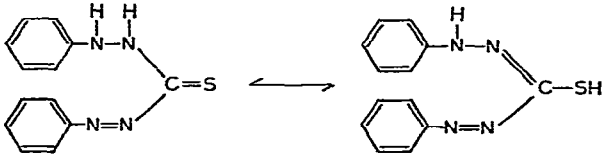


Fig. 1. Structure of dithizone.

EXPERIMENTAL AND RESULTS

Adsorbents

LiChrosorb SI 60 (30 μm) and Perisorb A (30–40 μm) silica gel were used for HPLC and DC-Alufolie Kieselgel 60 and DC-Alufolie Al_2O_3 F_{254} for thin-layer chromatography (TLC). They were all obtained from E. Merck, Darmstadt, G.F.R.

* Part VII: P. Heizmann and K. Ballschmiter, *J. Chromatogr.*, 137 (1977) 153.

TABLE I

THIN-LAYER CHROMATOGRAPHIC hR_F VALUES OF METAL DITHIZONATES

Dithizonate	*SiO_2 adsorbent*														*Al_2O_3 adsorbent*		
	Benzene		*Tetrahydrofuran in benzene (%, v/v)*					*Toluene*		*CH_3CN in CCl_4 (%, v/v)*					*Toluene*	*Benzene*	*$CHCl_3$*
	*A**	*B***	*1*	*2*	*3*	*4*	*5*	*A**	*B***	*1*	*2*	*3*	*4*	*5*			
Hg(II)	41	76	52	57	58	62	63	34	74	29	49	53	58	62	39	50	87
Cu(II)	31	61	46	52	55	59	61	25	55	19	43	47	55	58	0	0	20
Zn(II)	29	69	45	52	54	60	61	22	70	16	42	46	49	57	0	0	30
Ni(II)	29	38	42	51	54	59	61	20	35	14	38	44	50	53	3	5	83
Co(II)	23	48	31	41	45	54	56	11	38	6	27	33	42	47	14	28	85
Pb(II)	16	43	25	34	38	47	51	12	37	10	35	39	44	46	0	0	28
Cd(II)	5	20	—	—	—	—	—	3	18	2	6	11	18	20	0	0	41
Dithizone	12	—	—	—	—	—	—	10	—	—	—	—	—	—	0	0	22

* Our results.

** Results from the literature[4].

Liquid chromatograph

The liquid chromatograph consisted of the following: Labotron LDP 13 A pumps (1.5–80 ml/h) (Kontron Technik, Eching/München, G.F.R.); PTFE capillary tubing, 0.7 mm I.D. (Kontron Technik); glass columns, 2 and 3 mm I.D., 6 mm O.D. (according to Fig. 2 in ref. 3); PTFE injector (Fig. 2 in ref. 3); and a Zeiss PM 2 D detector with a micro-flow attachment and a 2-mV recorder.

Chemicals

The solvents used were benzene, carbon tetrachloride, tetrahydrofuran, acetonitrile, toluene, and chloroform (all p.a. quality from E. Merck).

Dithizone was dissolved in carbon tetrachloride and then cleaned up according to Iwantscheff[1].

The chelates were extracted from 10^{-5} *M* aqueous solutions of the elements. The pH of the aqueous layer was chosen to give only the primary chelates $M(II)Dz_2$ (M = Metal, Dz = dithizone). The pH values used for extraction were as follows: Hg(II), Cu(II) and Cd(II) dithizonates, 2; Co(II), Ni(II) and Pb(II) dithizonates, 7; and Zn(II) dithizonate, 8. TLC was used as a control.

Thin-layer chromatography of metal dithizonates

TLC was used to establish the optimal conditions for the separation in HPLC. Using single-component eluents or binary mixtures of solvents with small polarity differences, transposition of the TLC results to HPLC is possible. Table I summarizes the results of TLC separations on silica gel and alumina. Some of the results are not in accordance with those reported in the literature[4–6]; the reasons for this are not known.

The chelates were eluted in the sequence Hg(II) > Cu(II) > Zn(II) > Ni(II) > Co(II) > Pb(II) > Cd(II). On silica the chelates of Cu(II), Zn(II) and Ni(II) were eluted with small differences in their R_F values and their separation by HPLC would be difficult. The chelate of Cd(II) was strongly adsorbed. Separations of the components Hg(II)/Cu(II)/Zn(II)[Ni(II)]/Co(II)/Pb(II) by HPLC should be possible.

HPLC of metal dithizonates

The columns used were dry filled according to the Kirkland method[7]. When carefully applied, this method results in columns with good separation characteristics. All separations were carried out on silica gel at medium solvent flow-rates (10–40 ml/h) and medium pressures (20–50 bar), and benzene was used as the eluent. The dithizonates were detected at 525 nm.

When 20 μl of chelate solution were injected, the standard deviation of the peak areas was 1.5% for septumless injections and 4% for septum injections. For a given signal to noise ratio of 5:1, 10^{-8} g of Hg(II) and Cu(II) could be determined. By enriching the chelate in the organic layer, determinations of the elements in aqueous solutions at picogram levels should be possible.

The results of the metal-chelate separations are shown in Tables II–IV.

On short columns (Table II), separations between the components of Hg(II)/Ni(II)/Co(II) or Hg(II)/Zn(II)/Co(II) are possible (Figs. 2 and 3), whereas the separations of Hg(II)/Cu(II) and Cu(II)/Ni(II) are difficult.

The separation of Hg(II)/Cu(II) is improved when a longer column with a larger internal diameter is used (Table III). Here, also, the separation of Cu(II)/Ni(II)

TABLE II

HPLC OF METAL DITHIZONATES

Column, 300 × 2 mm LiChrosorb SI 60 (30 μm); eluent, benzene (10 ml/h); detection, 525 nm. t_A = analysis time. Elution sequence and retention times (min) at 10 ml/h: Hg(II) (6.8) > Cu(II) (7.8) > Ni(II) (9.7) > Zn(II) (10.0) > Co(II) (18.4).

Parameter	*Hg(II)/ Cu(II)*	*Hg(II)/ Ni(II)*	*Hg(II)/ Zn(II)*	*Hg(II)/ Co(II)*	*Cu(II)/ Ni(II)*	*Cu(II)/ Zn(II)*	*Cu(II)/ Co(II)*	*Ni(II)/ Co(II)*	*Zn(II)/ Co(II)*
Resolution, R_s	0.5	1.6	1.0	3.7	0.8	0.5	2.9	2.6	1.6
t_A (min)	12	13	15	20	13	15	20	20	20

TABLE III

HPLC OF METAL DITHIZONATES

Column, 600 × 3 mm LiChrosorb SI 60 (30 μm); eluent, benzene; detection, 525 nm. t_A = analysis time. Elution sequence and retention times (min) at 40 ml/h: Hg(II) (7.6) > Cu(II) (9.4) > Ni(II) (11.5) > Co(II) (16.3).

Components	*Flow-rate 40 ml/h*		*Flow-rate 20 ml/h*	
	Resolution, R_s	*t_A (min)*	*Resolution, R_s*	*t_A (min)*
Hg(II)/Cu(II)	0.7	12	1.1	24
Hg(II)/Ni(II)	1.7	14	2.1	28
Hg(II)/Co(II)	3.0	20	3.2	40
Cu(II)/Ni(II)	0.6	14	0.8	28
Cu(II)/Co(II)	1.7	20	2.0	40
Ni(II)/Co(II)	1.4	20	1.6	40

TABLE IV

HPLC OF METAL DITHIZONATES

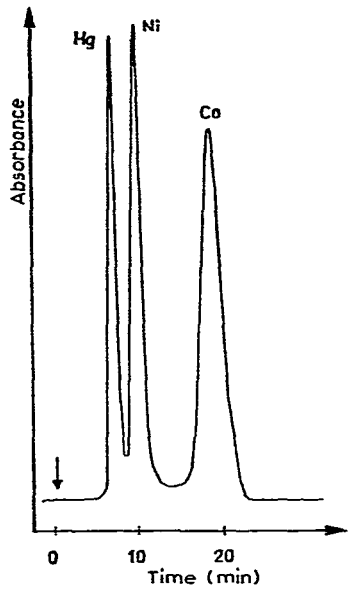
Column, 500 × 2 mm LiChrosorb SI 60 (30 μm); eluent, benzene (20 ml/h); detection, 525 nm. t_A = analysis time. Elution sequence and retention times (min) at 20 ml/h: Hg(II) (3.9) > Cu(II) (4.5) > Ni(II) (5.8) > Zn(II) (7.0) > Co(II) (9.4) > Pb(II) (14.2).

Parameter	*Hg(II)/ Zn(II)*	*Hg(II)/ Pb(II)*	*Cu(II)/ Zn(II)*	*Cu(II)/ Pb(II)*	*Ni(II)/ Zn(II)*	*Zn(II)/ Co(II)*	*Zn(II)/ Pb(II)*	*Co(II)/ Pb(II)*
Resolution, R_s	1.0	2.2	0.6	1.8	0.3	0.5	1.0	0.9
t_A (min)	15	24	15	24	15	13	24	24

is poor. Separations of the other elements are possible, even at high eluent flow-rates (40 ml/h or greater). Fig. 4 illustrates the separation of the Hg(II)/Cu(II)/Ni(II)/Co(II) dithizonates.

The chelates of Zn(II) and Pb(II) show tailing and poor resolutions, R_s (Table IV). Fig. 5 shows the separation of the Hg(II)/Zn(II)/Pb(II) chelates, while Fig. 6 shows the separation of the chelates of Hg(II), Ni(II), Co(II) and Pb(II).

The chelate of Cd(II) is strongly adsorbed. Its separation from the other



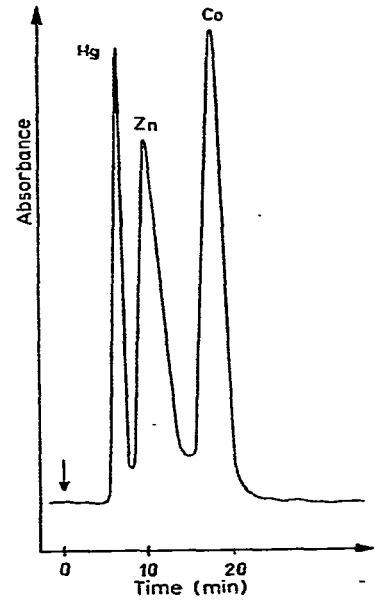


Fig. 2. HPLC separation of metal dithizonates. Packing, LiChrosorb SI 60 (30 μm); glass column, 300 × 2 mm; solvent, benzene; flow-rate, 10 ml/h.

Fig. 3. HPLC separation of metal dithizonates. Packing, LiChrosorb SI 60 (30 μm); glass column, 300 × 2 mm; solvent, benzene; flow-rate, 10 ml/h.

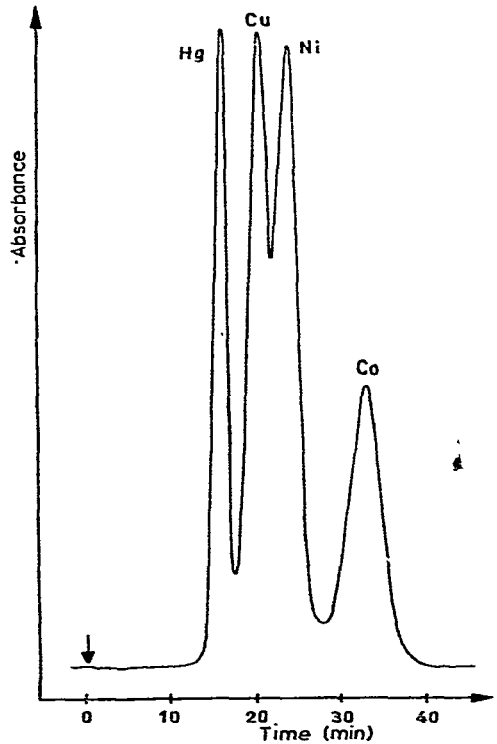
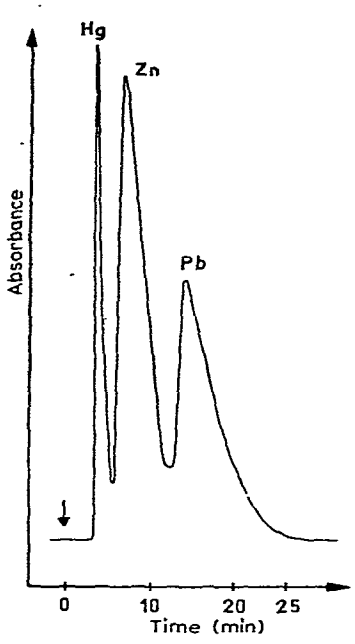
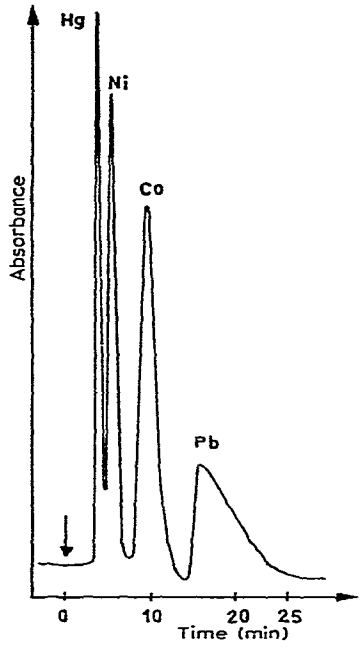


Fig. 4. HPLC separation of metal dithizonates. Packing, LiChrosorb SI 60 (30 μm); glass column, 600 × 2 mm; solvent, benzene; flow-rate, 20 ml/h.





Figs. 5 and 6. HPLC separation of metal dithizonates. Packing, LiChrosorb SI 60 (30 μm); glass column, 500 × 2 mm; solvent, benzene; flow-rate, 20 ml/h.

components can be accomplished by using a more polar eluent or a less polar adsorbent. On Perisorb A, the separation of the Cd(II) chelate from the other chelates is possible, but even here the Cd(II) chelate shows strong tailing.

CONCLUSION

HPLC on silica gel (LiChrosorb SI 60) with benzene as eluent permits the separation and determination of the dithizonates of Hg(II)/Ni(II)/Co(II)/Pb(II)/[Cd(II)], Hg(II)/Cu(II)/Co(II) and Hg(II)/Zn(II)/Pb(II). The separation of Cu(II)/Ni(II)/Zn(II) is difficult, but as the TLC results show, this separation can be improved by using alumina as adsorbent. Glass columns packed with 5-μm material are commercially available and can be used at head pressures up to 3000 p.s.i. Better resolutions and shorter analysis times than those reported here can be obtained.

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