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Note

Gas chromatography of metal diethyldithiocarbamates with electron-capture detection

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The ease of formation of thermally stable chelates of the divalent ions Zn(II), Cd(II), Ni(II), Hg(II) and Pb(II) with diethyldithiocarbamate (DEDTC) in aqueous solution and their subsequent gas chromatographic separation and flame-ionization detection have been reported[1–3]. Successful separations were achieved on glass and metal columns at 210–270°, both isothermally and with temperature programming. No evidence of on-column decomposition has been reported, although thermal analysis[4] studies have shown some decomposition near or above the melting points of chelates. Dimeric structures have also been reported for $(DEDTC)_2Zn(II)$ and $(DEDTC)_2Cu(II)$ chelates. Mass spectrometric[5] studies have confirmed the existence of dimeric zinc chelates even in the vapour phase, whereas the copper chelate was dimeric only in the solid state. The complexing ability of DEDTC has been utilized for the determination of trace levels of arsenic in water and biological media using electron-capture detection (ECD)[6].

In this study, we have investigated the gas chromatography of volatile chelates of nickel, zinc, cadmium, mercury and lead with DEDTC.

EXPERIMENTAL

Gas chromatography

A Varian Model 1740 GC unit equipped with a nickel-63 ECD (d.c. mode) was used. The glass column (120 cm × 2 mm I.D.) was packed with 3% SE-30 coated on 100–200 mesh Varaport-30. The carrier gas (nitrogen) flow-rate was 70 $ml \cdot min^{-1}$ in all experiments.

Preparation of chelate solutions

Benzene or toluene was employed as the solvent for the metal chelates. The metal chelates were prepared by addition of AnalaR-grade metal salt solutions (chlorides or nitrates) to stoichiometric amounts of NaDEDTC solutions. The chelates formed were filtered off, washed with hot water and recrystallized from hot benzene solutions. The crystals were dried in hot air and were kept in a desiccator in the dark. A 50-ppm stock solution in terms of the metal of each chelate was prepared

and standardized by atomic-absorption spectrophotometry. Further dilutions were made with benzene to obtain the required solutions for injection into the gas chromatograph.

RESULTS AND DISCUSSION

Volatile diethyldithiocarbamates of Zn(II), Cd(II), Hg(II), Ni(II) and Pb(II) were thermally stable under the conditions used.

The column was deactivated by making several injections of a 5% solution of dimethylchlorosilane in toluene, which invariably reduced the retention times and gave symmetrical peaks over a period of 48 h. The retention data in Table I were obtained after exhaustive silanization; the silanization of the column was carried out once a week in order to ensure peak performance.

TABLE I

RETENTION TIMES OF METAL CHELATES

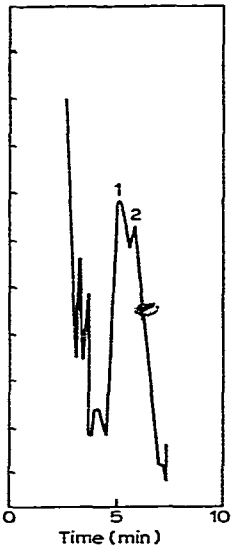
Injector, 250°; detector, 260°; solution injected, 5 μl of a 2-ppm solution of each chelate.

Oven temperature (°C)	*Retention time of chelate (min)*				
	Pb	*Zn*	*Ni*	*Hg*	*Cd*
220	No elution	16.50	26.15	22.33	No elution
230	No elution	11.00	20.00	18.50	16.10
240	10.50	7.50	15.00	10.50	11.00
250	6.85	4.25	5.75	5.50	4.75
260	5.00	3.50	4.60	4.65	3.90
270	4.00	2.25	3.25	3.00	3.85

From the retention times (Table I), it can be seen that Pb(II) and Cd(II) chelates are not eluted below 240°; this could be due to strong adsorption on active sites in the column. The separation of Zn(II) and Ni(II) chelates was good in the range 220–240° but for the separation of all of the metals temperature programming up to 270° is essential. Isothermal operation at temperatures above 250° impairs the resolution of various peaks to the extent that no reliable separation is achieved.

In the temperature range studied, Zn(II) and Cd(II) chelates showed both monomeric and dimeric structures in the vapour phase (see Figs. 1–3), whereas the other metal chelates showed monomeric structures only. Liquid phases such as SE-30 generally effect separations on the basis of molecular weight. Therefore, it has been assumed that the first peak represents the monomer and the second peak the dimer. By measuring the areas of unresolved peaks of Zn(II) and Cd(II) chelates at different temperatures, an estimate of the proportions of the monomeric and dimeric forms in the vapour phase was obtained (Table II).

From Table II, it can be seen that the proportions of the monomeric and dimeric forms of Zn(II) chelate vary in the range 230–250° but remain constant at higher temperatures. On the other hand, the monomeric–dimeric composition of the Cd(II) chelate remains nearly constant in the temperature range 230–260°.



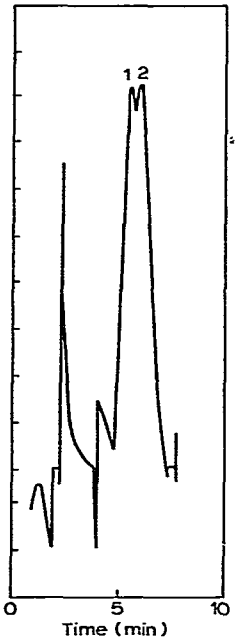


Fig. 1. Unresolved peaks of monomeric and dimeric forms of Zn(II) chelate. Column temperature, 250°; sample volume, 5 μl of 2-ppm solution. 1, Monomeric form; 2, dimeric form.

Fig. 2. Unresolved peaks of monomeric and dimeric forms of Cd(II) chelate. Column temperature, 250°; sample volume, 5 μl of 2-ppm solution. 1, Monomeric form; 2, dimeric form.

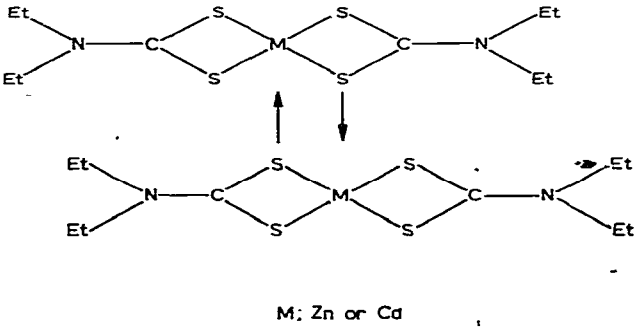


Fig. 3. Vapour-phase structure of dimeric zinc(II) and cadmium(II) diethyldithiocarbamates.

Detection limits

Detection limits are reported in Table III.

From the results, it seems practical to use gas chromatography for trace level measurements of lead, zinc, nickel, mercury and cadmium in various media with DEDTC as chelating agent. A concentration factor of 100 can be achieved with respect to the original sample and with respect to the benzene extract of the chelate. Hence a detection limit of 10^{-11} g of these metals could be reached, and investigations are now in progress in our laboratory.

TABLE II

VAPOUR PHASE COMPOSITION OF Zn(II) AND Cd(II) CHELATES

Chromatographic conditions as in Table I.

Temperature (°C)	*Composition of chelates (%)* *			
	Zn		*Cd*	
	Monomer	*Dimer*	*Monomer*	*Dimer*
230	55	45	70	30
240	64	36	70	30
250	75	25	75	25
260	75	25	70	30
270	75	25	90	10

* Estimated error ±15%.

TABLE III

DETECTION LIMITS OF METALS AS DEDTC CHELATES

Injector, 260°; detector, 270°; column, 250°; sample, 10 μl; solvent, toluene.

Metal	*Detection limit (ng)*	*Practical measurement range (ng)*
Pb	6	8–10
Zn	3	5–10
Ni	2	3–8
Hg	3	4–8
Cd	4	6–8

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