

CHROM. 8589

## Note

### Gas chromatographic separation of dithiocarbamates of some metals

J. MASARYK, J. KRUPČÍK, J. GARAJ and M. KOŠÍK

Slovak University of Technology, Chemical Faculty Department of Analytical Chemistry, 880 37 Bratislava (Czechoslovakia)

(Received July 8th, 1975)

Dithiocarbamates are a group of compounds which possess interesting chemical and biological properties<sup>1</sup>. The extensive usage of these substances in the chemical industry in rubber, synthetic fibres and plastics and in agriculture in pesticides and herbicides has evoked an increased interest in their analysis. One of the methods used for the determination of dithiocarbamates is gas chromatography (GC) which may be based on the analysis of CS<sub>2</sub> formed on decomposition of the dithiocarbamates<sup>2</sup> or on the analysis of ethylene-N,N'-thiourea formed from the injected sample<sup>3</sup>. Hrivňák and Konečný<sup>4</sup> used gas chromatography for the analysis of propyl- and isopropyl esters of some N,N-dialkyldithiocarbamic acids. S-Alkyl N,N-dialkyldithiocarbamates have been determined by a combination of GC and mass spectrometry (MS)<sup>5</sup>. A similar technique was used for S-alkyl N-alkyldithiocarbamates<sup>6</sup>.

The analysis of chelated metal complexes by GC is a relatively new field<sup>7</sup>. No data have been reported on the application of GC to the analysis of transition-metal dithiocarbamates. The aim of this note is to indicate the possibilities and problems of GC analysis of N,N-diethyldithiocarbamates (DEDTC) of some metals.

Compounds of the type M(DEDTC)<sub>2</sub> were first studied, where M is a bivalent metal, Fe, Cu, Ni, Co, Zn, Cd or Pb. The compounds are unstable, thermal analysis showing that with increasing temperature they first melt and then decompose on further heating. The melting points of the compounds are listed in Table I; for GC analysis, a temperature below the decomposition point was used.

TABLE I

MELTING POINTS OF BIS(N,N-DIETHYLDITHIOCARBAMATES) OF SOME BIVALENT METALS

Metal	Melting point (°C)
Se	111
Cu	201
Pb	208
Zn	225
Ni	235
Cd	254
Fe	252
Co	266

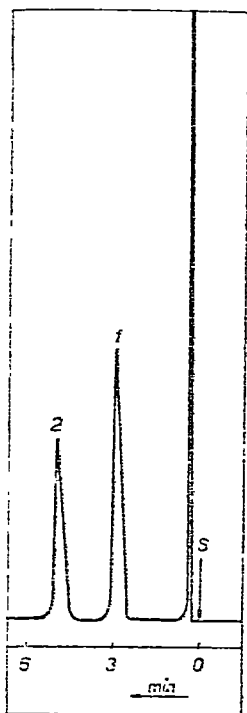


Fig. 1. GC separation of bis(N,N-diethyldithiocarbamates) of Zn and Ni. Gas chromatograph, Becker Model 419 (Packard Instruments). Glass column (2 m  $\times$  4 mm I.D.) packed with 3% SE-30 on Chromosorb W-HP (60–80 mesh, Supelco); pressure, 2 atm of nitrogen. Carrier gas (hydrogen) flow-rate, 30 ml/min; air flow-rate, 400 ml/min. Column temperature, 240° for 3 min, then programmed to 270° at 20°/min; 1 = Zn(DEDTC)<sub>2</sub>; 2 = Ni(DEDTC)<sub>2</sub>; S = start.

Some of the compounds form dimers in the solid state. While Ni(DEDTC)<sub>2</sub> exhibits a monomeric structure in the solid state<sup>8</sup>, the compound Cu(DEDTC)<sub>2</sub> shows a tendency to form dimers, [Cu(DEDTC)<sub>2</sub>]<sub>2</sub><sup>9</sup>, with two weak bridging Cu–S bonds. The compound Zn(DEDTC)<sub>2</sub>, or more correctly written [Zn(DEDTC)<sub>2</sub>]<sub>2</sub> in the solid state, has two bridging Zn–S bonds which are of the same length as the other four Zn–S bonds in the compound<sup>10</sup>. Villa *et al.*<sup>11</sup> showed by mass spectrometry that Zn(DEDTC)<sub>2</sub> also forms dimers in the vapour phase, in which Cu(DEDTC)<sub>2</sub> has a monomeric structure. This apparently shows that the weak bridging Cu–S bonds cannot maintain the dimeric structure in the vapour phase. By combining GC with MS, a monomeric structure in the vapour phase has also been confirmed<sup>12</sup> for Ni(DEDTC)<sub>2</sub>.

Fig. 1 shows the GC of Ni(DEDTC)<sub>2</sub> and Zn(DEDTC)<sub>2</sub> on the non-polar stationary phase SE-30 at 250°. The separation of N,N-diethyldithiocarbamates of other metals is currently being studied.

#### ACKNOWLEDGEMENT

The authors thank Packard Instruments, particularly Mr. J. Prüger, for the loan of a Becker Model 419 gas chromatograph.

## REFERENCES

- 1 G. D. Thorn and R. A. Ludwig, *The Dithiocarbamates and related Compounds*, Elsevier, Amsterdam, 1962.
- 2 C. Bigli, *J. Chromatogr.*, 14 (1964) 348.
- 3 W. L. Zielinski, Jr. and L. Fishbein, *J. Chromatogr.*, 23 (1966) 302.
- 4 J. Hrivňák and V. Konečný, *Collect. Czech. Chem. Commun.*, 32 (1967) 4136.
- 5 F. I. Onuska and W. R. Boos, *Anal. Chem.*, 45 (1973) 967.
- 6 F. I. Onuska and W. R. Boos, *J. Chromatogr.*, 99 (1974) 291.
- 7 J. A. Rodriguez-Vázquez, *Anal. Chim. Acta*, 73 (1974) 1.
- 8 M. Bonamico, G. Dessy, C. Mariani, A. Vaciago and L. Zambonelli, *Acta Crystallogr.*, 19 (1965) 619.
- 9 M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago and L. Zambonelli, *Acta Crystallogr.*, 19 (1965) 886.
- 10 M. Bonamico, C. Mazzone, A. Vaciago and L. Zambonelli, *Acta Crystallogr.*, 19 (1965) 898.
- 11 J. F. Villa, D. A. Chatfield, M. M. Bursley and W. E. Hatfield, *Inorg. Chim. Acta*, 11 (1972) 332.
- 12 J. Krupčík, J. Garai, Š. Holotík, D. Oktavec and M. Košík, *J. Chromatogr.*, 112 (1975) 189.