

## COMMUNICATION (I)

# The Thermogravimetric Behaviour of Metal Diethyldithiocarbamates at reduced pressure

### RINGKASAN

*Pengajian termogravimetri terhadap lapan dietilditiokarbamat dari Cu(II), Ni(II), Zn(II), Pb(II), Cd(II), Cr(III), Fe(III) dan Co(III) pada tekanan yang rendah (0.2 torr) menunjukkan keruapan yang lengkap bagi semua sebatian kelat ini pada suhu yang kurang dari 250° C.*

*Di samping itu, kelat-kelat dari logam duavalen adalah lebih meruap berbanding dengan kelat-kelat dari logam tigavalen.*

*Sebaliknya, pada tekanan udara biasa dan disekitar gas nitrogen yang dinamik, hanya dietilditiokarbamat dari Ni(II), Zn(II) dan Co(III) mepejalwap dengan sempurna manakala lain-lain kelat mepejalwap dengan tidak lengkap serta mengalami penguraian yang jelas.*

### INTRODUCTION

Diethyldithiocarbamic acid (DDC) readily forms chelates with monovalent, divalent and trivalent metal ions having the general formula  $M(DDC)_n$  where  $n$  is the positive charge of the metal ion. D'Ascenzo and Wendlandt (1969) have reported the preparation and thermal properties of hydrated forms of various metal chelates of DDC. They concluded that most of these chelates were highly volatile and therefore suggested their separation via the gas chromatographic technique. However, Flaherty and Mc Cutcheon (1971) have attempted to reproduce the preparation and thermal characteristics of these chelates but found no evidence of hydrate formation. According to their observation these chelates were not significantly volatile below their melting points and extensive thermal decomposition occurred after fusion.

Later Cardwell, Desarro and Uden (1976) reexamined the thermal and gas chromatographic properties of various metal diethyldithiocarbamates and showed that only those of Ni(II), Zn(II), Co(III) and Fe(III) were completely volatile whilst the others of Cu(II), Pd(II), Cd(II), Hg(II) and Pt(II) were somewhat less volatile and decomposed upon heating, though all these chelates were in general thermally stable.

A recent development in the area of trace metal analysis has been the application of organic mass spectrometry to the analysis of volatile metal chelates (Majer (1972)). Such analyses require that

the chelates utilized be relatively involatile at ambient temperatures and vacuum ranging down to  $10^{-7}$  torr. At the same time, they must be readily vaporized without decomposition at temperatures within the range 100-350° C.

In the majority of the thermal studies of metal diethyldithiocarbamates, the behaviour of these chelates was examined at ordinary atmospheric pressure, usually in a dynamic atmosphere of nitrogen or argon. The purpose of the present study was to examine the thermal behaviour of a series of diethyldithiocarbamates of Cu(II), Ni(II), Zn(II), Pb(II), Cd(II), Cr(III), Co(III) and Fe(III) at reduced pressure (0.2 torr). The results of such study would be useful in providing information for future application of mass spectrometry to the analysis of this particular class of metal chelates.

### EXPERIMENTAL

For convenience, the diethyldithiocarbamic acid and the metal diethyldithiocarbamates have been symbolised DDC and  $M(DDC)_n$ , respectively, where no distinction is made between the ligand and its anion;  $M$  denotes the metal ion and  $n$  the positive charge of the metal ion.

#### *Apparatus and Procedure*

The thermogravimetric data reported were obtained using a DuPont Model 951 Thermogravimetric Analyzer. The heating rate was 5° C/min and platinum pans were used. The sample size was maintained as nearly constant as possible (approx.

5 mg) in order to facilitate the comparison of thermograms amongst chelates and also to minimise differences arising from variations of sample weight. Evacuation of the system was effected by an Edward direct-drive pump (Model EM2) whilst measurement of pressure was aided by an Edward vacustat 2. For studies at ordinary atmospheric pressure, the system was purged with oxygen-free-nitrogen at 50 ml/min.

#### Preparation, Purification and Analysis of Metal Chelates

Analytical grades sodium diethyldithiocarbamate, metal salts and solvents were used in the synthesis and recrystallisation of metal chelates.

In general, the metal diethyldithiocarbamates were prepared by mixing warm aqueous solutions of the metal salt (sulphate, chloride or nitrate) with an alcoholic solution of sodium diethyldithiocarbamate so that a ligand/metal ratio of 4:1 was established. The precipitated chelates were filtered, washed, dried and purified by recrystallisation in chloroform. The purity of these chelates was confirmed by elemental microanalysis for carbon, nitrogen and hydrogen contents, the results of which are given in Table 1. The Hewlett-Packard C.H.N. Analyzer (Model 185-B) hooked to an integrator (H.P. 3380A) was used for the microanalyses.

## RESULTS AND DISCUSSION

Thermogravimetric measurements of the selected eight metal diethyldithiocarbamates at reduced pressure (0.2 torr) showed complete

volatilisation for all these chelates below 250°C as displayed in Fig. 1. It is interesting to observe that the chelates from the divalent metals (Zn(II), Cu(II), Pb(II), Cd(II) and Ni(II)) were more volatile than those from the trivalent metals (Co(III), Fe(III) and Cr(III)). Similar observation has also been reported by Honjo *et al.*, (1978) in their study of the fractional sublimation of various metal diethyldithiocarbamates at reduced pressure of under  $2 \times 10^{-2}$  torr. In addition, the study also indicated complete volatilisation for all the chelates involved in the present study.

For the divalent metal chelates, Zn (DDC)<sub>2</sub> was the most volatile, followed in order by Cu (DDC)<sub>2</sub>, Pb (DDC)<sub>2</sub>, Cd (DDC)<sub>2</sub> and Ni (DDC)<sub>2</sub>. In fact, the last two have more or less the same volatility. As for the trivalent metal chelates, Co (DDC)<sub>3</sub> was more volatile than Fe(DDC)<sub>3</sub> with, in turn, was more volatile than Cr (DDC)<sub>3</sub>.

In contrast, thermogravimetric measurements of the same eight chelates at ordinary atmospheric pressure and in a dynamic nitrogen atmosphere indicated complete volatilisation for only three of the chelates, viz., Zn (DDC)<sub>2</sub>, Ni (DDC)<sub>2</sub> and Co (DDC)<sub>3</sub>, whilst the others were less volatile and decomposed to various extents as shown in Fig. 2. This observation was similar to that by Cardwell *et al.* (1976) with the following differences: (a) Fe(DDC)<sub>3</sub> was completely volatile, and (b) Fe(DDC)<sub>3</sub> and Zn(DDC)<sub>3</sub> have the same volatility which, in turn, was better than that of Ni(DDC)<sub>2</sub> and Co(DDC)<sub>3</sub>, both of which also

TABLE 1  
Microanalytical data of metal diethyldithiocarbamates

Chelate	Carbon (%)		Nitrogen (%)		Hydrogen (%)	
	Found	Calc.	Found	Calc.	Found	Calc.
Cu (DDC) <sub>2</sub>	33.35	33.36	7.76	7.80	5.71	5.60
Ni (DDC) <sub>2</sub>	33.64	33.81	7.88	7.89	5.61	5.68
Zn (DDC) <sub>2</sub>	33.63	33.19	8.04	7.74	5.42	5.57
Pb (DDC) <sub>2</sub>	24.62	23.84	5.74	5.56	4.05	4.00
Cd (DDC) <sub>2</sub>	29.27	29.37	6.65	6.85	5.42	4.93
Cr (DDC) <sub>3</sub>	35.74	36.26	8.37	8.46	5.84	6.09
Fe (DDC) <sub>3</sub>	36.18	35.99	8.45	8.39	5.76	6.04
Co (DDC) <sub>3</sub>	35.26	35.77	8.54	8.34	5.61	6.00

## THERMOGRAVIMETRIC BEHAVIOUR OF METAL DIETHYLDITHIOCARBAMATES

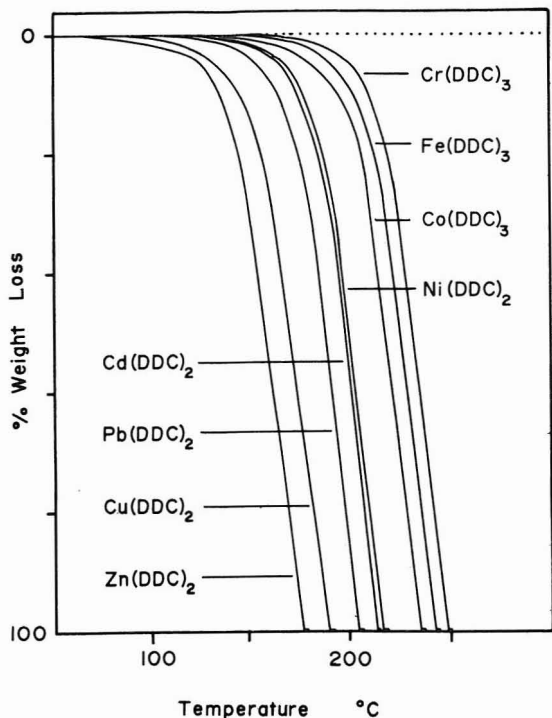


Fig. 1. Thermogravimetric Curves of Metal Diethyldithiocarbamates at Reduced Pressure (0.2 torr).

displayed the same volatility. On the other hand, in the present study  $\text{Fe}(\text{DDC})_3$  was not completely volatile and  $\text{Zn}(\text{DDC})_2$  was very much more volatile than  $\text{Ni}(\text{DDC})_2$  which, in turn, was more volatile than  $\text{Co}(\text{DDC})_3$ . Furthermore, both  $\text{Cd}(\text{DDC})_2$  and  $\text{Pb}(\text{DDC})_2$  have extremely poor volatilities as indicated by the rather extensive decomposition and the absence of sublimate exhibited by both these chelates.

### ACKNOWLEDGEMENT

The author wishes to thank the Department of Chemistry, Universiti Pertanian Malaysia for providing the facilities required for the present study and Mr. Nazari Ahmad for assisting in the thermogravimetric measurements. A special word of thanks goes to Dr. S. Dilli, Department of Analytical Chemistry, University of New South Wales, Sydney, Australia, for valuable advice and encouragement.

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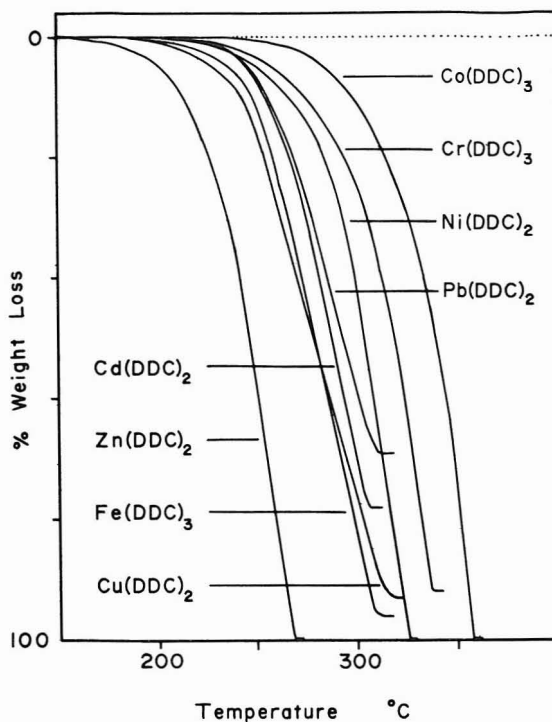


Fig. 2. Thermogravimetric Curves of Metal Diethyldithiocarbamates at 1 atmosphere.

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(Received 3 April 1981)