

Gas chromatography of metallic derivatives of ethylenebis(dithiocarbamic acids)

The dithiocarbamates are well-recognized fungicides. The general method of analysis of these compounds is based upon the liberation of carbon disulfide¹⁻⁵. Gas chromatographic analysis has been used to measure carbon disulfide and hydrogen sulfide collected from decomposition of thiocarbamic compounds⁶⁻⁸. They have been measured as well by ultraviolet⁹ and infrared¹⁰ spectrophotometric techniques, and by paper chromatography¹¹. Recent work has described the thin-layer chromatography of Zineb and Maneb¹².

The instability of these derivatives is quite well known, undergoing degradation to ethylenethiuram monosulfide (ETM) and its polymer, and ethylenethiourea (ETU) with the evolution of carbon disulfide.

This communication reports the feasibility of gas chromatographic analysis of the metallic ethylenebis(dithiocarbamates) Zineb, Maneb and Nabam, based on the thermal release of ETU on sample injection.

Experimental

The zinc, manganese and disodium ethylenebis(dithiocarbamates) (Zineb, Maneb and Nabam, respectively) were obtained from Dr. D. E. ROSEN, E.I. du Pont de Nemours and Co., Wilmington, Dela. The ETM sample was received from Dr. I.A.M. FORD, Robinson Bros., West Bromwich, Staffs., England. The ETU standard was purchased from Eastman-Kodak, Rochester, N.Y. The fungicides evidenced decomposition prior to melting. The melting points of ETM and ETU were 116° and 199.5°, respectively.

Gas chromatography was carried out utilizing an F & M Model 1609 flame ionization instrument containing a modified flow system (Applied Science Labs., Inc., State College, Pa.) incorporating a 6 ft. by 0.25 in. glass coil column packed with 4% QF-1 fluorosilicone on 80-100 mesh HMDS-pretreated Chromosorb W. The analytical operating conditions are given in Table I.

TABLE I
GAS CHROMATOGRAPHY OF ZINEB, MANEB AND NABAM

Compound	Corrected elution ^a (min)		<i>t_R</i> ^o
Zineb	0.2	0.6	3.75 ^d
Maneb		0.6	3.75 ^d
Nabam	0.2	0.45 ^c 0.6 ^c	3.75 ^d
ETM		0.6	
ETU			3.75
Ethylenediamine	0 ^b		

^a Column; see Experimental. Conditions: column temperature 180°; detector temperature 225°; injector 70 V; nitrogen carrier 86 ml/min; hydrogen 72 ml/min; air 300 ml/min; range 1000; hydrogen flame detector.

^b Eluted at solvent front.

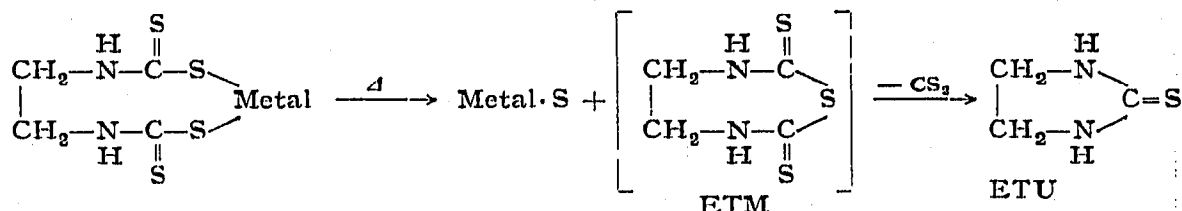
^c Trace.

^d Major peak.

Results and discussion

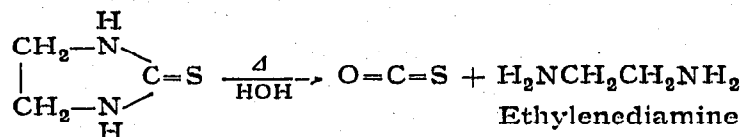
It is interesting to note that chromatography was carried out below the melting point of ETU. Lability of the fungicides was indicated by the predominant appearance of ETU and minor amounts of ETM and several other components as reported in Table I.

The thermal breakdown to ETU is suggested as follows:



It is felt that thermal cleavage of the metallic ethylenebis(dithiocarbamates) to ETU is hastened through the ETM stage owing to the observation that ETM itself may be chromatographed with little or no conversion to ETU. The solution medium for the analysis of ETM and ETU was dimethylsulfoxide. An aqueous medium was provided for Zineb and Nabam, having the form of an emulsion, and a clear solution, respectively. It should be pointed out that attempts to chromatograph ETM in pyridine resulted in a considerable loss in ETM with the production of two minor peaks (one being ETU) and two major peaks, the largest of which had elution of 3.93 relative to ETM.

The gaseous decomposition products of dithiocarbamate fungicides have been investigated by several workers¹³⁻¹⁶. COX, SISLER AND SPURR¹³ concluded that carbon disulfide and ethylenediamine may be liberated from Nabam solutions, while MOJE, MUNNECKE AND RICHARDSON¹⁷ described carbonyl sulphide as a volatile fungitoxicant from Nabam in soil. The acid hydrolysis suggested by the latter investigators indicated the concomitant formation of ethylenediamine. The appearance of this compound by gas chromatographic analysis might be expected to occur as follows:



Chromatography of ethylenediamine, however, resulted in its elution at the solvent front and not coincidental to any of the sample peaks.

In order to appreciate the quantitative relationships of ETU formation, a standard curve for Nabam degradation is given in Fig. 1. While the sensitivity units are in hundreds of micrograms of Nabam, the corresponding high attenuation ($\times 1000$) of the signal should be denoted.

A general extension of this preliminary investigation to the analysis of the dithiocarbamate class by gas chromatography via *in situ* degradation during sample injection is presently under study.

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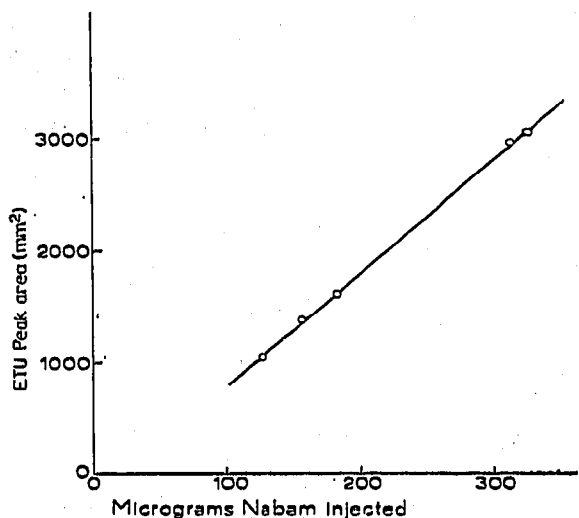


Fig. 1. Standard curve for Nabam based on ETU liberation. Attenuation: $\times 1000$.

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