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Gas Chromatographic Determination of Dithiocarbamate Fungicides in Workroom Air

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Dithiocarbamate fungicides are applied extensively and worldwidely in the control of a number of plant diseases in practically all crops.

Different products such as methyl-, ethyl-, ethylenbis- and propylenbis- dithiocarbamates belong to the dithiocarbamate fungicide family, and most of them are linked to metal ions such as Na, Zn, Mn, Fe or their mixtures. The most common products are: thiram (TMTD), ziram, ferbam, nabam, zineb, maneb, mancozeb and propineb (Table 1). Etem is the oxidation product of the ethylenbisdithiocarbamates. Because of their very low solubility both in polar and apolar solvents and in water, they are generally formulated as wettable powder or dust, alone or in mixture with other fungicides. (Worthing 1983). The vapor pressure of the compounds is practically zero, therefore in the workroom air of the formulation plants as well as in storerooms, they are present only as dust. Even though the toxicity of pure products is quite low, concern over the worker's health has arisen, due to the possible content of carcinogenic and goitrogenic ETU (ethylenethiourea) as an impurity or as formation compound during processing procedures (Bottomley et al. 1985).

A provisional threshold level value (TLV) of 5 mg m^{-3} in the workroom air, based on the TLV officially stated for thiram (ACGIH 1984-85), has been fixed for all the dithiocarbamates in our Company's factories. Therefore, a rapid, sensitive and simple procedure is needed for the detection of dithiocarbamates in the workroom air, in order to achieve environmental monitoring of these compounds.

Analytical methods for dithiocarbamates in small amounts are based on the CS_2 evolution, reaction to form a coloured complex and spectrophotometric determination (Keppel 1971). These methods are time consuming and require skill in the preparation of the reagents. The head space gas chromatographic method of the evolved CS_2 described for the residue analysis (McLeod & Ritcey 1973; Anonymous 1981) was tried by us but without success, owing to difficulty in diluting the evolved CS_2 in order to remain in the linear dynamic range of the GC detector. On the basis of attempting to improve the latter method (Anonymous 1981), we developed a solvent-layer procedure which permitted a quicker analysis and processing of several samples simultaneously.

MATERIALS AND METHODS

Workroom air sampling is performed as previously described (Maini and Boni 1983) by means of a static Gelman EC-3000 apparatus, using pre-weighed microporous filtering membranes (Gelman Metricel DM-800, 0.8 um, 47 mm) with an air flow rate of about 20 L min^{-1} (Maini and Collina 1980). Personal samplers can also be used, provided that the sampling time is lengthened.

After weighing, the filtering membrane is carefully rolled up with forceps and introduced into a 15-mL screw-cap test tube. The filter is wetted slightly with 4-5 drops of distilled water, and then 5 mL of 2,2,4-trimethylpentane (isooctane) are added. A reagent containing 3% $SnCl_2$ in 37% HCl, daily and freshly prepared, is then added, filling it up to the rim. The test tube is immediately and tightly capped, and placed in an oven at 80°C for 1 h with periodical shaking every 10-15 min. After cooling to room temperature, an aliquot of the solvent layer is diluted with isooctane to a suitable concentration for the electron-capture detector linearity range. Care should be taken to avoid CS_2 volatilization from the solvent.

GC determination is performed by alternating injections of the sample solution with a freshly prepared standard containing 1 ug mL^{-1} CS_2 in 2,2,4-trimethylpentane. Detector responses should be within the linear dynamic range and should give similar peak heights. A Varian 1440 B GC instrument equipped with ^{63}Ni electron-capture detector was used. Our GC operating conditions were the following: pyrex glass column 275 x 0.3 cm, packed with 30% DC-200 on Gas-Chrom Q, 80-100 mesh. Other suitable columns can be used, such as 0.5% Carbowax 1500 on Carbopak B, 1 m long or 15% OV-17 on Gas-Chrom Q, 3.5 m long. Temperatures were: 55°C, 130°C and 225°C, respectively for the column, the injection port and the detector. Carrier gas: pure nitrogen at 40 mL min^{-1}.

The quantitative results should be given as CS_2 or as the single different dithiocarbamates, in mg m^{-3}. In this case a conversion factor should be used to transform the CS_2 into the respective product (Table 1).

Table 1. Common names, registry number and conversion factors (F) from CS_2 for the most common dithiocarbamate fungicides.

Common Name	Chemical	Reg. No.		F
Thiram	Tetramethylthiuramdisulfide	137-26-8		0.634
Ziram	Zinc dimethyldithiocarbamate	137-30-4		0.50
Ferbam	Ferric dimethyldithiocarbamate	14484-64-1		0.55
Nabam	Disodium ethylenebisdithiocarbamate	142-59-6		0.596
Maneb	Manganese ethylenebisdithiocarbamate	12427-38-2		0.575
Zineb	Zinc ethylenebisdithiocarbamate	12122-67-7		0.555
Mancozeb	Complex of zinc salt and maneb	8018-01-7	abt.	0.57[a]
Propineb	Zinc propylenebisdithiocarbamate	9016-72-2		0.533
Etem	5,6-dihydroimidazo(2,1-C)-1,2,4-dithiazole-3-thione	33813-20-6		0.197

[a] Molecular structure not well known.

Preliminary recovery tests were performed by using both pure zineb and ziram in talc mixtures and testing several commercial formulations based on zineb, maneb, ziram, thiram, mancozeb and etem, alone or in mixture with other fungicides.

RESULTS AND DISCUSSIONS

The linear dynamic range of carbon disulfide in 2,2,4-trimethylpentane, using the GC conditions specified above is quite small, ranging from 0-25 ng injected. Therefore, suitable dilutions should be done. Preliminary recovery tests performed with zineb or ziram/talc mixtures revealed the necessity to change the published conditions for the head space GC method (McLeod & Ritcey 1973; Anonymous 1981) initially adopted by us. Therefore, the final method uses stronger conditions (Table 2).

The method was also tested for eventual interferences from the Metricel membrane filter as well as from the coformulants of the dithiocarbamate fungicides or from other active ingredients commonly formulated in mixture with dithiocarbamates, such as sulphur, copper oxychloride, cymoxanil, carboxin and carbendazim.

Results showed that no analytical artifacts or interferences arose from the procedure (Table 3). The method is very good and valid for these kinds of sample which contain low amounts of dithiocarbamates, ranging between the high level of the formulations and the trace level of the residues.

Table 2. Comparison between preliminary recovery tests on dithiocarbamate/talc mixtures with different reaction conditions.

		% Recovery	
Dithiocarbamate	% in talc	4 N HCl/hexane–60°C 30 min	37% HCl/isooctane–80°C 1 h
Ziram	7.9	56.2	86.0
"		44.2	82.5
Zineb	13.0	28.2	91.5
"		33.5	84.7

The recoveries were generally good with % recovery values of 89.6 ± 6.8, 93.5 ± 9.8, 84.5 ± 10, 84.2 ± 7, 86.5 ± 21.6 for formulations of zineb, ziram, thiram, mancozeb and maneb, respectively. The overall mean recovery was 88.3 ± 11.1% out of 36 determinations (Table 3).

Extensive monitoring in factory workrooms showed that dithiocarmate levels in the workroom air are generally below our fixed TLV. Moreover, the dithiocarbamate content in the total dust was generally in agreement with the theoretical contents of the formulations, with variations following the sampling site (Table 4).

We presume that this procedure, with small adaptations in the sampling method, could also be used to monitor the farmers' exposure to dithiocarbamates during applications.

REFERENCES

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Table 3. Recovery tests using different formulations containing dithiocarbamate.

DITHIOCARBAMATE FUNGICIDE	TRADE NAME FORMULATION	ACTIVE INGREDIENTS (% CONTENTS)	WEIGHED AMOUNT (mg)	% RECOVERY
Zineb	Crittox	Zineb (76)	2.10	96.7
"	"	"	5.70	98.9
"	DueZeta S	Zineb/Sulphur (4/40)	0.3	91.9
"	"	"	0.2	92.9
"	Vitex Azzurro	Zineb/Sulphur (52/20)	11.2	85.6
"	"	"	7.4	85.8
"	"	"	3.8	84.9
"	"	"	1.9	84.5
"	Super Ramedit	Zineb/Copper oxy-chloride (13/30 Cu)	1.3	81.0
"	"	" "	1.4	85.4
"	"	" "	1.0	85.5
"	"	" "	0.5	84.6
Zineb/Etem	Siaprit	Zineb/Etem/Sulphur (45/5/20)	1.6	92.1
"	"	" "	2.8	104.6
TOTAL ($\bar{X}$ ± SD)				**89.6 ± 6.8**
Ziram	Ramedit	Ziram/Copper oxy-chloride (57/12.5 Cu)	2.1	111.9
"	"	" "	1.5	86.9
"	Crittam 80	Ziram (76)	4.1	87.0
"	"	"	4.0	86.7
"	"	"	1.6	95.6
"	"	"	1.3	92.7
TOTAL ($\bar{X}$ ± SD)				**93.5 ± 9.8**
Thiram	Blekritt	Thiram/Carboxin (30/30)	0.9	89.1
"	"	"	0.6	95.8
"	"	"	1.3	73.2
"	"	"	3.2	71.9
TOTAL ($\bar{X}$ ± SD)				**84.5 ± 10**
Maneb	Critteb 80	Maneb (80)	1.7	85.8
"	"	"	1.9	72.1
"	"	"	5.7	65.7
"	"	"	6.9	69.7
"	Policritt M	Maneb/Carbendazim (50/6)	1.4	110.0
"	"	" "	1.1	115.7
TOTAL ($\bar{X}$ ± SD)				**86.5 ± 21.6**
Mancozeb	Acarie M	Mancozeb (60)	2.2	94.8
"	"	"	3.2	89.9
"	Vitex 4/40 Combi	Mancozeb/Cymoxanil (40/4)	3.2	77.5
"	"	" "	3.2	81.6
"	"	" "	1.2	77.4
"	"	" "	2.0	84.2
TOTAL ($\bar{X}$ ± SD)				**84.2 ± 7**
OVERALL MEAN OF 36 ANALYSES				**88.3 ± 11.1**

Table 4. Results from actual samples collected in the SIAPA - Galliera factory during monitoring of workroom air in 1984.

DATE	TRADE NAME FORMULATION	DITHIOCARBAMATE FUNGICIDE	CONTENT %	WORK SECTION	AIR SAMPLED, m^3	RESULTS		
						TOTAL DUST $mg\ m^{-3}$	DITHIOCARBAMATE $mg\ m^{-3}$	% IN DUST
20th March	Vitex Azzurro	Zineb	52	Packing	1.08	2.92	1.18	40.4
"	" "	"	52	"	1.00	3.47	1.61	46.4
"	" "	"	52	"	1.07	7.76	3.43	44.2
"	" "	"	52	"	1.32	9.16	3.48	38.0
21st March	" "	"	52	"	0.84	3.15	1.31	41.6
"	" "	"	52	"	1.00	1.03	0.61	59.2
6th July	Super Ramedit	"	13	"	1.15	1.31	0.14	10.7
"	" "	"	13	"	1.05	0.62	0.062	10.0
18th July	" "	"	13	Mixing	1.83	0.08	0.003	3.7
"	" "	"	13	"	1.08	0.23	0.016	6.9
1st October	Blekritt	Thiram	30	"	0.70	1.30	0.042	3.2
4th October	Acarie M	Mancozeb	60	"	1.38	0.36	0.042	11.7
18th October	"	"	60	Packing	1.54	4.35	1.78	40.9
"	"	"	60	"	0.89	3.40	1.25	36.7
10th December	Vitex Azzurro	Zineb	52	Mixing	1.18	0.14	0.031	22.1
"	" "	"	52	"	1.13	0.48	0.096	20.0
1st October	Blekritt	Thiram	30	Packing	0.15	2.16	0.057	2.6
18th October	Acarie M	Mancozeb	60	"	0.12	3.45	0.45	13.0
"	"	"	60	"	0.19	2.35	0.58	24.7
12th December	Vitex Azzurro	Zineb	52	Mixing	0.95	0.33	0.044	13.3
"	" "	"	52	"	1.0	0.34	0.137	40.3
"	" "	"	52	"	0.72	0.37	0.116	31.3
"	" "	"	52	"	0.22	1.00	0.422	42.2

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