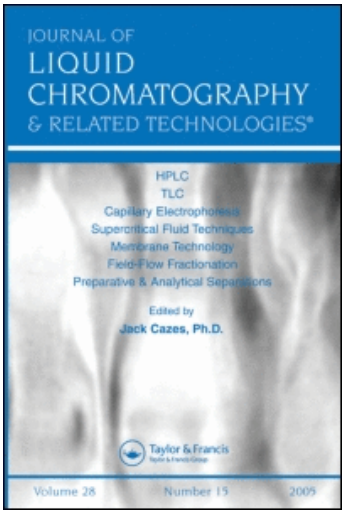

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IDENTIFICATION AND DETERMINATION OF SOME DEGRADATION PRODUCTS OF MANCOZEB BY HPLC AND MS

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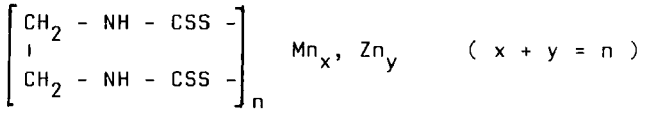
ABSTRACT

A method is described for the identification and determination of degradation products in mancozeb (manganese-zinc salt of ethylenebisdithiocarbamates). The method is based on the semi-preparative separation of ethylenebisdiizothiocyanate sulphide (EBIS) and ethylenebisthiuramdisulphide (ETD) which were prepared by the iodine oxidation of disodium salt of ethylenebisdithiocarbamate. MS spectra were applied for the identification of EBIS and ETD. Reversed- phase HPLC was used for the determination of EBIS and ETD in methanol extract of mancozeb.

INTRODUCTION

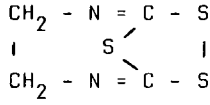
The ethylenebisdithiocarbamates (EBDTC) belong to the widely used fungicides in agriculture; for this reason it is necessary to pay attention to the research of decomposition products which are often of toxic character. Many papers deal mainly with the ethylenethiourea (ETU) determination as the main EBDTC decomposition product in biological or plant materials for its toxicity /1-3/. Review of the techniques used for ETU analysis in different materials was carried out by Bottomley et al. /4/. In agriculture the manganese-zinc EBDTC salt is used very often; it is called mancozeb. This is an insoluble

compound of polymeric character. It was published that, besides ETU, it can contain polymeric and monomeric compounds of ethylenebisdiizothiocyanate sulphide (EBIS), ethylenebisthiuram disulphide (ETD) and ethylenebisthiuram monosulphide (ETM) /5,6/.



mancozeb

ETD ETM

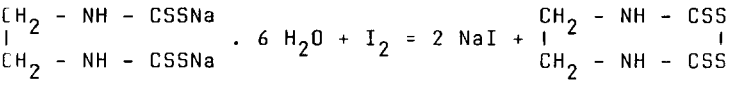


EBIS

The aim of this work was to identify and determine ETD and EBIS in mancozeb, where the possibility of the presence of monomeric and polymeric forms are to be considered.

EXPERIMENTAL

ETD and its polymer were prepared by the oxidation of disodium salt of EBDTC according to the reaction :



The ethanolic iodine solution (0.01 mole in 100 ml) was added, dropwise, to the ethanolic solution of disodium salt of EBDTC (0.01 mole in 500 ml). A yellow precipitate was gradu-

ally formed in the reaction mixture. After the addition of all iodine, the precipitate was filtered and dried. The product obtained was extracted with methanol at the laboratory temperature. The insoluble residue, after the extraction, is the polymeric ETD of yellow colour which is not soluble in methanol. The monomer of ETD was obtained after evaporation of methanol from the extract. The extract contains 15.42 % of the original amount that was determined according to a material balance of the extraction.

From the results of the elemental analysis, it can be assumed that the ETD extract is not a pure substance, because there are some differences between the calculated and the obtained results :

	C	H	N
calculated	22.84 %	2,87 %	13.32 %
obtained	23.99 %	2.99 %	12.67 %

The measurement of ETD mass spectra was made at an ionization potential of 70 eV (mass spectrometer VARIAN).

The samples of mancozeb (1 gram) were extracted with 50 ml of methanol (20 minutes). The extract was filtered and injected into the liquid chromatograph. For the determination of ETD and EBIS, the column SEPARON SIX C18 (particle size 5 μm, column lenght 15 cm, column diameter 0.32 cm) was used. Methanol (50 % in water) was used as the mobile phase at a flow-rate of 0.5 ml/min. A KNAUER UV detector (Model 87.00) was used at 254 nm.

The semi-preparative separation was carried out using a semi-preparative column of 10 x 1.2 cm. I.D. which was hand-packed with a slurry of 25 - 40 μm SILASORB SPH C18 (Lachema Brno - CSFR) in methanol. Mobile phase was 50 % methanol in water.

RESULTS AND DISCUSSION

Preparation of standards was the main problem of ETD and EBIS determinations.The results of elemental analysis have confirmed that the ETD standard which was prepared according to

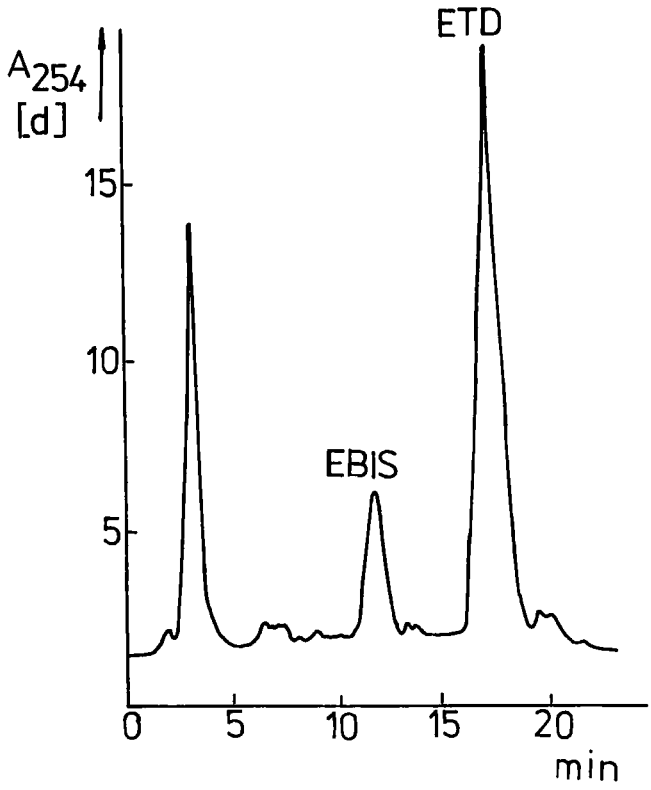


Fig 1 Chromatogram of the methanol extract of the reaction product.

Column Separon SIX C18; mobile phase : methanol - water 1:1; flow rate 0.3 ml/min.

the reaction was not a pure substance. This is confirmed in Fig 1, where 2 higher peaks appeared. Mass spectrometry was chosen for the identification of ETD which, on the basis of molecular ions and fragments of molecules, may explain the composition of the reaction product. From the mass spectrum (Fig 2), it is obvious that, under the given ionization conditions, ETD does not give the molecular ion and so it is necessary to analyse its fragments. Since, in the literature, there are not

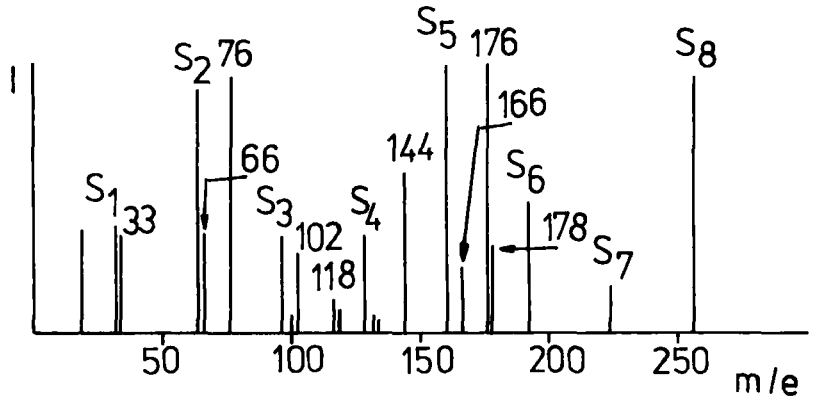


Fig 2. Mass spectrum of the methanol extract of the reaction product. (Ionization at 70 eV).

published any data from this field and we had to proceed with the analysis of mass spectrum according to the general rules of mass spectrometry.

The main fragments of ETD were assumed : m/e = 166 - CS loss; m/e = 134 - CS_2 loss; m/e = 177 - SH loss; m/e = 178 - S loss and low probable m/e = 176 - H_2S loss; m/e = 144 - H_2S_2 loss. The mass spectrum shows evidence of the existence of all these fragments though these are of different intensities (Fig 2).

In the ETD standard, the ETM presence was also assumed. From the literature, it is known that ETM, in the monomeric form, occurs in the solution only as EBIS /6/. Thus, we also assumed the presence of EBIS fragments. EBIS can also be the decomposition product of ETD (H_2S loss), which is not probable from theoretical point of view. In the interpretation of spectra, it is necessary to consider also the intensities of the individual fragments and to assume certain probabilities of their origin. In the case of EBIS, the presence of molecular ion m/e = 176 and that of further fragments was assumed : m/e = = 132 - CS loss; m/e = 118 - NCS loss; m/e = 100 - CS_2 loss. Besides the fragment m/e = 132 (only on the background level)

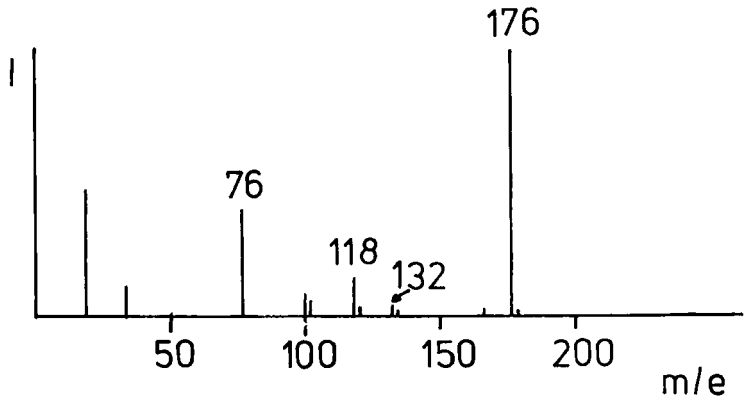


Fig 3. Mass spectrum of the first fraction after semi-preparative separation (Ionization at 70 eV).

the presented ions were found in the spectrum with much higher intensity than their origin could be assumed from the ETD molecules. The fragment m/e = 176 was very intense in the mass spectrum, which indicates that it is the molecular ion of EBIS.

We may suppose that ETD and EBIS are present in the reaction product that was prepared according to the procedure presented in the Experimental. From the chromatogram (Fig 1) two main peaks are to be seen which obviously belong to EBIS and ETD. For the purification of reaction product we used the semi-preparative column. Two main fractions were collected; they probably contained only ETD and EBIS. After vacuum evaporation of mobile phase, MS analysis of the residues was done (Figs 3 and 4).

According to the mass spectrum of the first fraction, only the presence of EBIS can be assumed because all fragments and molecular ion of EBIS are occured (Fig 3). Some ETD fragments can be also seen, but only at the background level. This demonstrates very low concentration of ETD in the EBIS fraction. The mass spectrum of the second fraction is shown in Fig 4. The EBIS molecular ion is significantly smaller and the other fragments of ETD are confirmed.

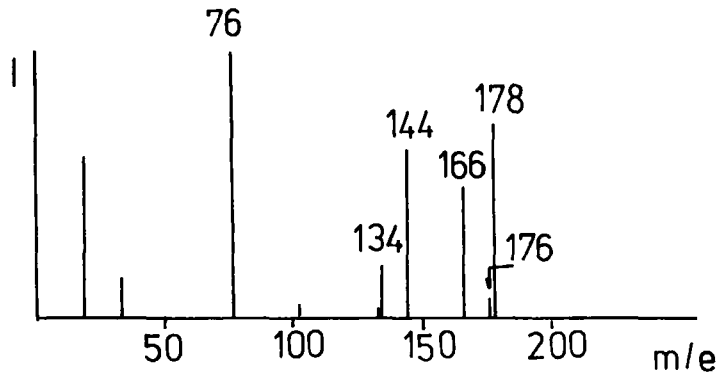


Fig 4. Mass spectrum of the second fraction after semi-preparative separation (Ionization at 70 eV).

Table 1. The determination of ETD and EBIS in mancozeb

sample	ETD (%)	EBIS (%)
1	0.017	1.39
2	0.024	0.85
3	0.017	0.89
4	0.015	0.98
5	0.020	2.19
6	0.022	1.63

Relative standard deviations were 10.2 % for ETD and 3.4 % for EBIS for 3 measurements.

The ETD and EBIS standards prepared in this way were used for the determination of these substances in methanolic extracts of *mancozeb* samples. The results were evaluated by linear least - squares fitting of the curves of amount of ETD or EBIS injected against peak area. The concentrations of the standard solutions were 3 - 20/ug of ETD or 80 - 400/ug of EBIS in 1 ml of methanol and the calibration graphs were linear. The results

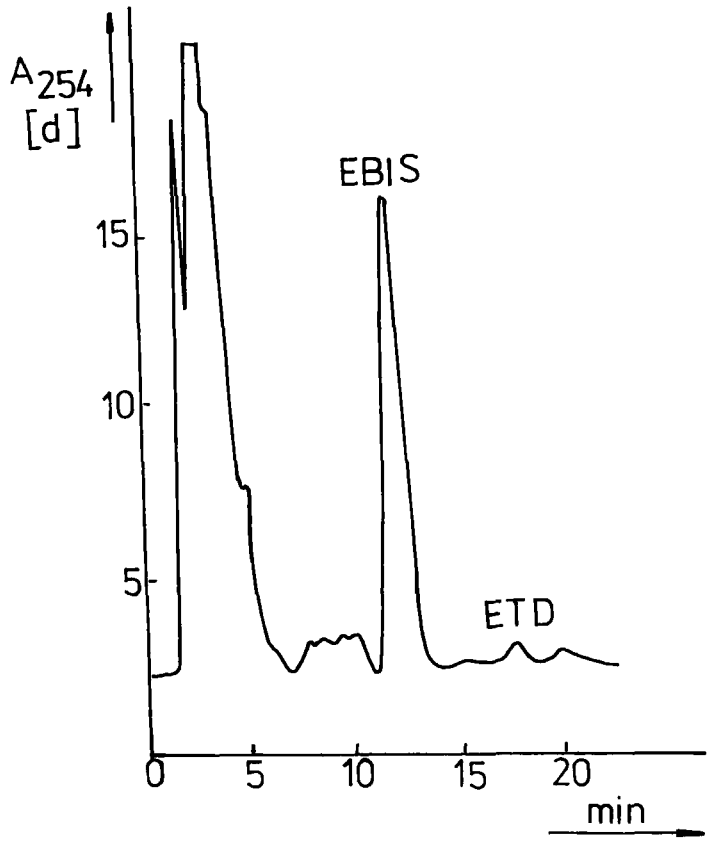


Fig 5. Chromatogram of the methanol extract of mancozeb (sample 1).

Column Separon SIX C18; mobile phase : methanol - water 1:1; flow rate 0.3 ml/min.

of the determinations of ETD and EBIS are given in Table 1. The chromatogram of the methanolic extract of the sample of mancozeb is shown in Fig 5.

From the comparison of the chromatograms (Fig 1 and Fig 5), it is obvious that the EBIS content is higher in mancozeb, which is obviously caused by the fact that EBIS is the ETD decomposition products.

The stability of ETD and EBIS in the methanol extract was also checked. EBIS and ETD were stable during two hours. After two hours, the level of ETD slowly dropped and the level of EBIS slowly increased. This indicates that the sample should be worked-up rapidly after the extraction and EBIS is the decomposition product of ETD.

From Table 1, it is obvious that the ETD content in mancozeb is about 0.02 % of total amount of the sample. Certain variation of ETD and EBIS contents may be cause by the problems connected with the technology of mancozeb preparation. The presented method of ETD and EBIS determinations in mancozeb may be used for the quality control of mancozeb samples.

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