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Residues of Dithiocarbamates on Cucumber in Central Highlands of Jordan

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ABSTRACT :

Dithiocarbamates residues on cucumber fruits and soil samples under plastic house conditions were determined using Head space Technique. This technique was based on the decomposition of dithiocarbamates by hydrochloric acid to the corresponding amines and carbon disulfide. Carbon disulfide was measured by gas liquid chromatography with electron capture detector. Residues of dithiocarbamates (zineb and maneb) fungicides on cucumber fruits were higher than the tolerance levels. Moreover, zineb and maneb were found to have waiting periods of 6 and 5 days in the first spray treatment, and 3 and 2 days in the second spray treatment, respectively. On the other hand, the half life times (LT50) of zineb and maneb in soil were found to be 5.3 and 5.5 days in the first spray treatment, and 4.2 and 5.2 days in the second spray treatment, respectively.

Key words : Residues, Dithiocarbamates, Zineb, Maneb, Cucumber, Plastic house, Jordan.

INTRODUCTION

Cucumber is one of the most important cash crops in Jordan. It is normally planted all over the year with variation of planting areas. Agricultural progress in the developing countries is closely associated with the use of pesticides which play an

important role in controlling plant pests, and providing adequate food supply. Thus, pesticides have been increasingly used all over the world for crop protection and pest control. In Jordan as well as in other developing countries, there are poor records of waiting periods and lack of knowledge concerning the use and effects of pesticides. Dithiocarbamates are the most commonly used organic fungicides in controlling fungal diseases especially ethylene bis-dithiocarbamates (EBDC) such as zineb and maneb. These fungicides are used to control downy mildews in vegetables and ornamentals (Kidd et al 1986). The objectives of this study are to determine the residues of zineb and maneb on cucumber fruits and in soil cultivated with cucumber under plastic house conditions in the Central Highlands of Jordan.

MATERIALS AND METHODS

Field experiment :

An experiment was conducted in Madaba district to determine residues of dithiocarbamates under plastic house conditions. Cucumber seedlings Cucumis sativus var. Sahara were transplanted on May 24, 1990 using complete randomized block design. This design was blocked with four replicates into 4 rows by 30 m per row. Each row was divided into 4 plots, with 50 cm between each plot. 35-40 plants were planted in each plot in both sides. There was 50 cm unplanted area between rows. Beds of 60 cm wide were covered with thin black mulch of one metre wide. Drip irrigation system was layered on beds for better water supplements.

Zineb (Perozin^{R} 80% wettable powder) and maneb (Dianeb 80% wettable powder) were applied at the rate of 50 g/20 L twice throughout the season. The first application was conducted on the 14 of July, while the second application was on 25 of September. Four replicate plots were sprayed with water and served as a control for comparison.

Fruit and soil samples were separately taken from the middle of each row at random. These samples were taken at different times after spraying. Weights of the fruit samples ranged between 2 and 3 kg. Soil samples were taken from the top 2 cm of soil by scratching the soil surface using a trowel. Weight of each sample ranged between 1 - 1.5 kg. These samples were placed in polyethylene plastic bags (Mustafa et al, 1991), then labelled and kept cool in a cooler containing ice. This cooler was transferred to the residue laboratory in Al-Baga'a for residue analysis.

Sample preparation :

Fruit samples were cut by a sharp knife into small pieces and mixed thoroughly. While soil samples were crushed and passed through 2 mm sieve to remove large particles and plant parts. Then, three 50 kg sub samples were taken randomly from each sample. Each sub sample was folded with aluminum foil, and frozen in a refrigerator at -30^{o}C until analysis. The cultivated soil had silty clay texture, pH 7.8, EC 13 mmohs/cm, percent of moisture 3.59% and percent of organic matter 1.2%.

Analytical procedures :

Dithiocarbamates were analyzed using Head Space technique (Al-Shuriaqi, 1987). This technique was based on decomposition of dithiocarbamates by hot hydrochloric acid to corresponding amines and carbon disulfide (CS_2). The produced carbon disulfide was measured using gas chromatography with electron capture detector (ECD).

For determination of dithiocarbamates as CS_2 residues in fruit samples, 100 ml distilled water was placed in 250 ml glass bottle, 1.0 g of tin chloride was added, followed by 50 g of fruit sample (Al-Shariaqi, 1987). Then 40 ml of 4N HCL was added and the bottle was closed quickly with screw caps containing silicon-rubber septum. The bottle was placed in the water bath at 90°C for 2 hours. During the 2 hours, the bottles were shaken vigorously by hand for 2 minutes. Shaking was repeated every 1/2 hour until injection.

A 250 ul gas were taken from the glass bottle by a gas tight syringe and injected immediately into the gas liquid chromatography. Each sample was injected 3 times. After each injection, the syringe was placed in the dry oven at 40°C for 2-3 minutes to remove any gas that might remain inside the syringe from the previous injection.

In the analysis of dithiocarbamate residues of soil samples, 25 g were taken for each sample (Rhodes, 1977). This sample was placed in 125 ml distilled water. In addition, 1.0 g of tin chloride. A 40 ml of 4N HCl were added to the 250 ml glass bottle.

Then the same procedure was followed as previously described in fruit samples.

Recovery tests were carried out to measure the efficiency of this method in determination of dithiocarbamate residues in these samples. In addition, blanks were prepared to check for any contamination in the solvents and equipment with any residues of dithiocarbamates.

Carbon disulfide was determined by gas liquid chromatography using electron capture detector (Dani, model 13865). Glass column of 5 m x 2 mm were filled with 10% DC and 15% QF on gas chromosorb A (80-100 mesh). Used temperature (°C) were 60 for the oven, 102 for the detector and 80 for the injection port. Gases flow were 20-25 ml N2/minute for the carrier gas and 45-50 ml/minute for the auxiliary gas.

Peak area of each injection was recorded. Concentration of carbon disulfide residues was calculated according to the following formula :

$$CS2\ (mg/kg) = \frac{As.\ Wst.\ F}{Ast.\ Ws}$$

where

CS2 : Concentration of residues in sample represented as mg/kg.

50 x 10-3 : Weight of analyzed sample in kg = Ws

Wst : Absolute amount of CS2 in the standard bottle in mg.

As : Peak area obtained from sample

Ast : Peak area obtained from standard

F : Recovery factor calculated from $\frac{100}{\%\ \text{recovery}}$

RESULTS AND DISCUSSION

In the first spray treatment, mean residues of zineb as CS_2 on cucumber fruits ranged between 0.930 and 0.341 ppm after 1 hour and 8 days after spray treatment, respectively, with significant differences ($P < 0.05$) (Fig. 1a). However, mean residues of maneb on cucumber fruits ranged between 0.783 and 0.282 ppm after 1 hour and 8 days, respectively without significant differences (Fig. 1a). In the second spray treatment, mean residues in cucumber fruits decreased significantly ($p < 0.05$) from 0.845 to 0.375 ppm for zineb, from 0.699 to 0.400 ppm for maneb after 1 hour to 8 days, respectively (Fig. 1b).

Mean residues of zineb in soil increased from 12.33 after 1 hr to 13.41 ppm after 1 day of first spray treatment, without significant differences ($p < 0.05$) and then decreased significantly ($p < 0.05$) to 2.458 ppm after 2 weeks of the first spray treatment (Fig. 2a). Mean residues of maneb increased from 10.53 to 12.346 ppm from 1 hr to 1 day after treatments respectively, without significant differences, then decreased significantly ($p < 0.05$) to 2.314 ppm after 2 weeks of the spray treatment, with significant differences (Fig. 2a).

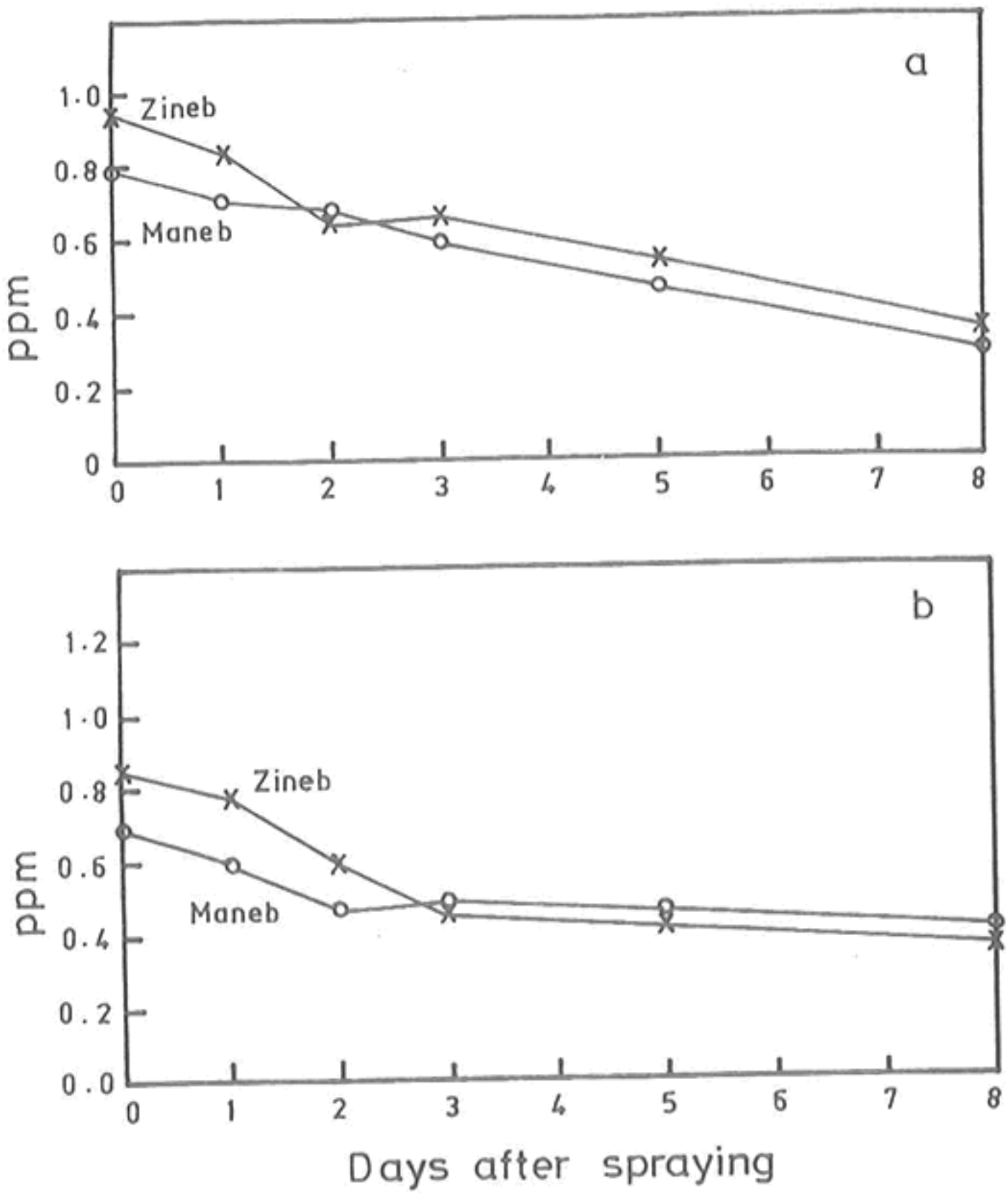

Fig. 1 (a-b) : Residues of zineb and maneb determined on cucumber fruits after the first spray treatment (a) and the second spray treatment (b).

Mean residues of zineb in soil increased from 12.49 to 13.33 ppm after 1 hour and 1 day of the second spray treatment, respectively, without significant differences ($p<0.5$), then decreased significantly ($p<0.05$) to 2.272 ppm after 2 weeks (Fig. 2b). Mean residues of maneb increased from 12.4 to 13.1 ppm after 1 hour and 1 day of the second spray treatment, respectively, then decreased to 2.704 ppm after 2 weeks of the spray treatment with significant differences (Fig. 2b). Mean residues of maneb increased from 12.4 to 13.1 ppm after 1 hr and 1 day of the second spraying, respectively, then decreased to 2.704 ppm after 2 weeks of the spray treatment, with significant differences (Fig. 2b).

Residues of dithiocarbamates i.e. zineb and maneb on cucumber fruits were found to be higher than the tolerance level of 0.05 ppm (Al-Shuraiqi et al, 1985) after the spray treatment (Fig. 1 a-b). Pease and Halt (1977) found 1.5 ppm of maneb residues on treated cucumbers 1 day after treatment. In the first spray treatment, residues of zineb and maneb were decreased to reach the tolerance level of 0.05 ppm after 5.7 and 4.5 days of spray treatment, respectively (Fig. 1a). This leads to the conclusion that zineb and maneb under the used experimental conditions should have the waiting periods of 5.7 and 4.5 days after the first spray treatment, respectively. Al-Shuraiqi et al., (1985) suggested that dithiocarbamates, particularly zineb and maneb must have a waiting period of 7 days after spray treatment on cucumber fruits in Jordan. Moreover, the results of the present study have shown that residues of zineb

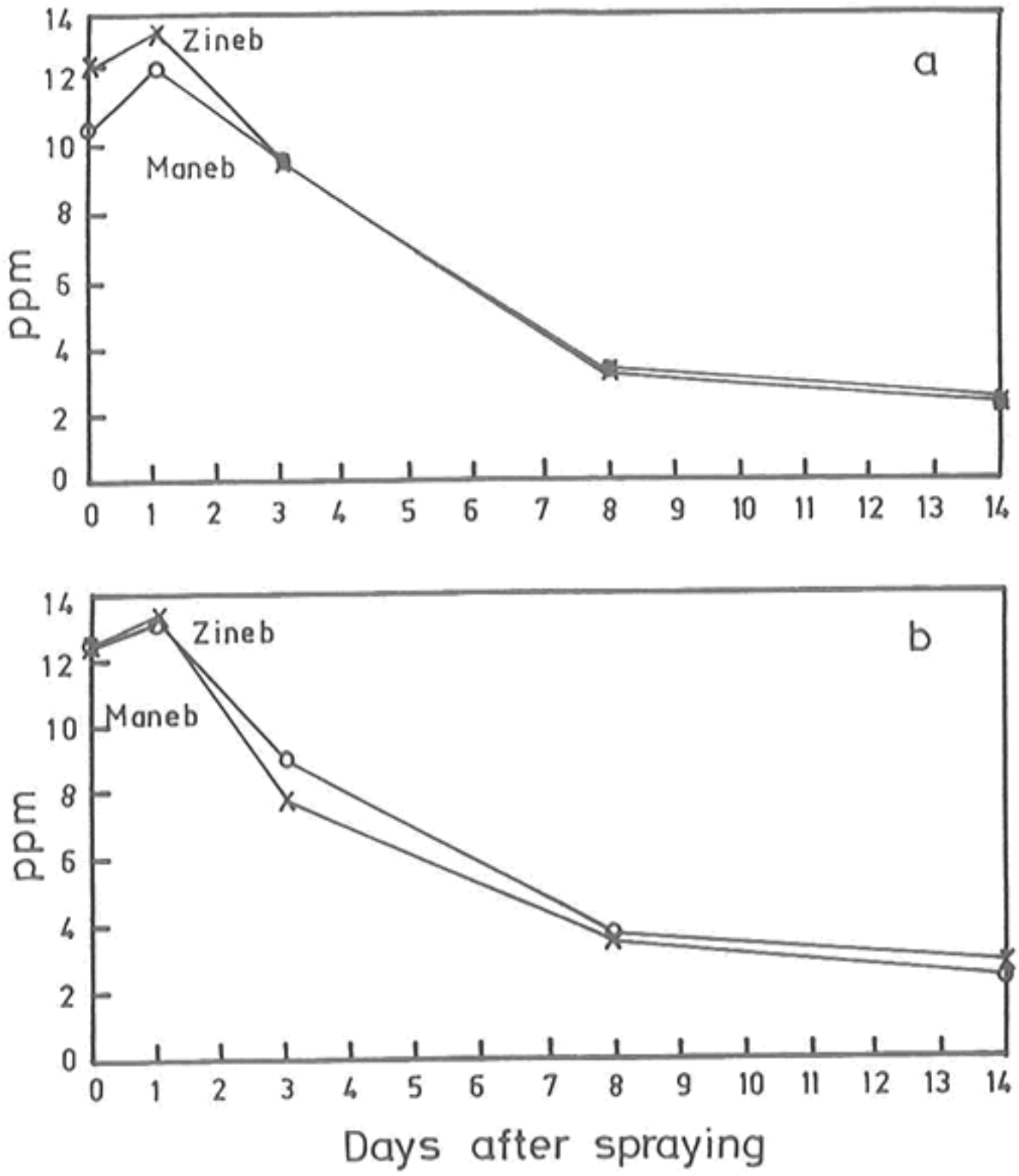

Fig. 2 (a-b) : Residues of zineb and maneb determined in soil after the first spray treatment (a) and the second spray treatment (b).

and maneb were less than 0.35 ppm after 7 days from spraying.

In the second spray treatment, residues of zineb and maneb noticeably decreased and reached the tolerance level of 0.05 ppm after 2.8 and 1.8 days of spray application, respectively (Fig. 1b). Furthermore, these residues were less than 0.4 ppm when recorded after 8 days after the second spraying.

Environmental factors, particularly temperature and relative humidity might affect the degradation of dithiocarbamates (Bontoyan and Looker, 1973). In this study, the waiting periods for zineb and maneb in cucumber fruits under plastic house conditions were 5.7 and 4.5 days in the first spraying, and 2.8 and 1.8 days in the second one, respectively as mentioned previously. This variations might be attributed to the higher in temperature during the second spraying as compared with that in the first application. The increase in average temperature was about 13-15°C. Bontoyan and Loker (1973) reported that concentration of ethylenethiourea (ETU) increased under temperature of 49°C and 80% relative humidity. ETU disappeared rapidly by conversion to other metabolites. This indicates that high temperature degrades zineb and maneb to ETU and other metabolites.

On the other hand, the decrease in concentration of dithiocarbamates in cucumber fruits was also due to dilution factor i.e. growth of fruits after spraying. This agreed with Mustafa et al., (1989) who concluded that the decline in residues of some insecticides in pepper was attributed to the increase in fruit growth.

Residues of zineb and maneb in soil were degraded with the time to reach the half life time (LT 50) after 5.3 and 5.5 days, respectively in the first spraying. In the second spray the half life time (LT 50) was 4.2 and 5.2 days for zineb and maneb, respectively. Rhodes (1977) found that [C14] maneb had half life between 4 and 8 weeks in treated soil under open field conditions. The difference between the present result and that obtained by Rhodes (1977) might be attributed to the high temperature and relative humidity under plastic house conditions. On the other hand, the type of soil and soil found might have an effect on degradation of dithiocarbamates fungicides in soil which is interested for further work.

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ملخص :

قدرت متبقيات مبيدات الدايثيوكاربمبت (الزينب والمانيب) على ثمار الخيار والتربة تحت ظروف البيوت البلاستيكية باستخدام طريقة Head Sapce Technique . تعتمد هذه الطريقة على تحطيم مركبات الدايثيوكاربمبت وتحرير ثاني كبريتيد الكربون باستخدام حامض الهيدروكلوريك ، ثم قدرت كمية ثاني كبريتيد الكربون باستعمال جهاز الكروماتوغرافيا السائل الغازي مع كشاف ملتقط الإلكترونات ECD .

أظهرت نتائج تحليل متبقيات مبيدات الدايثيوكاربمبت (الزينب والمانيب) على الخيار كميات أعلى من الحدود المسموح بها وهي ٥ر٠ جزء بالمليون . ووجد أن فترة الأمان للزينب والمانيب كانت ستة وخمسة أيام في معاملة الرش الأولى ، بينما كانت ثلاثة أيام ويومين في معاملة الرش الثانية على التوالي . أما نتائج تحليل متبقيات المبيدات في عينات التربة فقد أظهرت أن فترة نصف العمل للزينب والمانيب كانت ٣ر٥ و ٥ر٥ يوم في معاملة الرش الأولى و ٢ر٤ و ٢ر٥ يوم في معاملة الرش الثانية على التوالي .

كلمات مفتاحية : متبقيات ، دايثيوكاربمبت ، زينب ، مانيب ، خيار ، بيوت بلاستيكية ، الأردن.