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Residue Studies of *O,S*-Dimethyl Phosphoroamidothioate on Tomatoes

Residues of *O,S*-dimethyl phosphoroamidothioate were determined in mature tomatoes. Residue values were obtained as a function of the insecticide doses and the time elapsed between final treatment and harvesting time. Plants treated with multiple doses of 0.5 kg of active ingredients/ha and 1.0 kg of active ingredients/ha yielded residues of 0.19 and 0.84 ppm, respectively, when harvested 18 days after the final treatment. Plants receiving one single treatment of 0.5 kg of active ingredient/ha yielded residues between 0.072–0.013 ppm.

The compound *O,S*-dimethyl phosphoroamidothioate (Tamarón, Bayer; Monitor, Chevron Chemical Co.) is an insecticide-acaricide of systemic activity which also is effective by contact action in controlling a variety of insects in several crops such as cotton, tomatoes, barley, corn, and apples. This organophosphorus compound is extensively sold in Central and South America and Africa. No published data exist as to the residue levels of this insecticide in plants. Thus, it was the purpose of this work to find the residue levels in tomato fruits by varying the dose of the applied material and the time interval between the last treatment and harvesting time. At present, there are no established residue levels for this organophosphorus insecticide.

EXPERIMENTAL SECTION

Plant Treatments. Plants of the V. F. *Napoli* variety were grown in seedbeds at El Cortijo, Villa de Cura, and after 25 days they were transplanted in an experimental field at the Shell Foundation Experimental Station located in Cagua, Estado Aragua. On December 17, 1971, plants were transplanted at 0.5-m intervals in rows spaced at 1.5 m. The field was divided into two sections. One section received one single treatment of 0.50 kg of active ingredient/ha 2, 4, 6, and 8 weeks prior to harvesting. Plots consisted of 3 rows, each 3 m long, having an area of 4.5 m^2. Each plot was separated from the next one by a single untreated row. The plants in the second section were subdivided into two groups which received four doses of 0.50 and 1.0 kg of active ingredient/ha, respectively, at weekly intervals. Each plot consisted of 5 rows, 5 m long, having an area of 37.5 m^2. Multiple treatments were applied on the 4, 11, 18, and 28 of February 1972. Insecticide was applied with a mist blower calibrated to deliver 420 l./ha. The total number of plants used was 519, which were planted in an area of 925 m^2. A control plot similar to those previously described, in a neighboring area, was planted and those plants did not receive insecticide treatment. Plants were given all the conventional agronomical practices such as irrigation, fertilization, deweeding, etc. During the experiment 26.4 mm of rain were collected on January 29, 1972. The tomato plants which received one single treatment were harvested on March 17, 1972. The plants which received multiple treatments were harvested at 1, 3, 7, 10, 14, and 18 days after the last insecticide treatment.

Analytical Procedure. Samples of about 1–2 kg were collected for each analysis and duplicate runs were made. About 8–10 unwashed tomatoes were quartered and opposite quarters were blended. An aliquot of about 100 g was weighed and placed in a blender. Subsequently, 0.5 g of sodium carbonate and 150 ml of acetone were added and the entire mixture was blended for 3 min. The mixture was filtered and the filtrate was transferred into a separatory funnel. The extract was partitioned with 100 ml of *n*-hexane and the acetone layer was removed. The acetone layer was saturated with 20 g of NaCl and the solution was stirred for about 40 min. The saturated acetone layer was transferred to a separatory funnel, where the insecticide was extracted with 200 ml of chloroform and with two additional 100-ml portions of a mixed solution of chloroform and acetone (9:1, v/v). The three solutions were combined and dried with 50 g of anhydrous sodium sulfate. The combined solvents were then evaporated to an oily residue in a rotary vacuum evaporator at a water bath temperature of 55°. The extract was diluted to a known volume with 2-methoxyethanol. To obtain the recovery yields for this procedure, tomatoes of the control plot were used and *O,S*-dimethyl phosphoroamidothioate of 99.7% purity was added to a 100-g aliquot of macerated tomatoes. The entire analytical procedure as previously described was applied on this mixture as well as on untreated tomatoes to check for possible interferences.

Gas Chromatographic Analysis. The gas-liquid chromatographic analyses were performed on a Varian Model 2100 chromatograph equipped with a flame photometric detector (FPD). The FPD detector was operated in conjunction with a bypass valve, which was installed at the column exit so as to prevent the extinguishing of the flame due

Table I. Recovery of *O,S*-Dimethyl Phosphoroamidothioate Added to Tomatoes

Added, ppm	Found, ppm[a]			% recovery
0.038	0.031	0.025	(0.028)	73
0.19	0.16	0.12	(0.14)	73
0.48	0.39	0.33	(0.36)	75
1.00	0.75	0.69	(0.72)	72
			Average	73.2

[a]Values in parentheses indicate the average of replicate samples.

Table II. *O,S*-Dimethyl Phosphoroamidothioate Residues on Tomatoes

Single treatments[a]					Multiple treatments					
No. of weeks prior to harvesting	Residue, ppm[b]			No. of days after final treatment	Residue, ppm[b]					
					0.5 kg active ingredient/ha			1.0 kg active ingredient/ha		
2	0.079	0.065	(0.072)	1	0.46	0.54	(0.50)	1.14	1.18	(1.16)
4	0.062	0.074	(0.068)	3	0.30	0.26	(0.28)	1.27	1.33	(1.30)
6	0.009	0.017	(0.013)	7	0.18	0.26	(0.22)	1.11	1.15	(1.13)
8			N.D.[c]	10	0.21	0.25	(0.23)		*d*	
				14	0.17	0.23	(0.20)	0.87	0.93	(0.90)
				18	0.16	0.22	(0.19)	0.80	0.88	(0.84)

[a]Single treatment of 0.5 kg of active ingredient/ha. [b]Value in parentheses is the average of the two values. [c]None detected. [d]Samples lost.

to the passage of the solvent through the detector. In its open mode the valve vents the column exit while the detector receives carrier gas directly from the carrier gas supply tank at a flow rate equal to that of the column. After a judicious selection of a time period in which the solvent is vented, the valve is returned so as to deliver the column effluents to the detector. The entire procedure is performed within 40 sec after the injection.

A gas chromatographic column 6 ft × ¼ in. o.d., 2 mm i.d. packed with 3% Versamid 900 on Chromosorb W, AW-DMCS 80–100 mesh, was used. Critical temperatures were: column oven, 193°; injector, 225°; and detector, 200°. Detector flow rates used were: hydrogen, 150 ml per min; air, 25 ml per min; and oxygen, 20 ml per min. Nitrogen was used as carrier gas at a flow rate of 80 ml per min. One nanogram of the insecticide yielded a 1.0-cm peak height at an electrometer attenuation of 64×10^{-9} A full scale. The minimum detectable concentration was about 0.010 ppm at a signal-to-noise ratio of 2.

Peak heights were used for quantitation; standards yielding a slightly lower and a slightly higher peak height than that of the sample were injected prior to and after the injection of the sample. The retention time of the *O,S*-dimethyl phosphoroamidothioate was 2.3 min.

RESULTS AND DISCUSSION

Table I shows the results obtained from the recovery studies. The insecticide is water soluble so that the recovery yields can be expected to be low, especially when extracting from a crop which has a high water content. The results indicate that the % recovery is constant over the range of 0.038–1.00 ppm. The average value of 73.2% was used to correct the results obtained in the residue studies.

Table II shows the results obtained in the residue studies for both the single treatment and multiple treatment studies. The single treatment studies were performed so as to obtain a knowledge of the persistence of the insecticide. The results show that one single treatment of 0.5 kg of active ingredient/ha, 2 and 4 weeks prior to harvesting, leaves a residue of 0.072 and 0.068 ppm, while at 6 weeks a residue of 0.013 ppm can be found. No residue can be detected when harvesting 8 weeks after the single treatment.

The multiple treatments of 0.5 kg of active ingredient/ha reveal that harvesting after 1 day from the final treatment yields a residue of 0.50 ppm. Samples collected on the third day after the last treatment show that the residue concentration drops sharply to 0.28 ppm. The samples collected after the third day show that the residue concentration remains constant over the time period studied or decrease at a negligible rate. The 0.5 kg of active ingredient/ha treatment is the recommended dose. However, the treatment of 1.0 kg of active ingredient/ha reveals a different behavior. The residue values obtained for the samples harvested on the third day after the final treatment are higher than the values obtained for the samples harvested 1 day after the final treatment. This effect may be explained by the fact that it is difficult to obtain reliable samples during this time period due to the unavoidable handling involved (Gunther, 1969), with consequent alteration of the freshly deposited insecticide. However, after the third day, the residue concentrations decrease exponentially. After 18 days, a value of 0.84 ppm is obtained. The interval of 18 days was selected on the basis that it is the minimum recommended time to be elapsed between the final treatment and harvesting.

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