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PERSISTENCE OF DIMETHOATE IN VEGETABLES

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Dimethoate in treated pumpkin is separated by thin layer chromatography using silica coated chromatoplate from coextracted materials. Spot area measurement and comparison of colour are used to give a semiquantitative determination of the amount of pesticide which persisted on the crop. The method is sensitive to detect upto 0.1 µg of dimethoate. The need for a preliminary cleanup procedure is eliminated. Residues of dimethoate in crop declined after 14 days.

Key words: Dimethoate, Vegetables, Residues, Harvest.

Introduction

Crop losses due to attacks of pests are controlled by the use of pesticides in agricultural fields. Dimethoate [0.0-dimethyl s-(N-methyl carbamoyl-methyl) phosphorodithioate], due to its systemic properties, high insecticidal activity and relatively low toxicity to mammals, has found an increasing used for the control of several species of phytophagous insects and mites injurious to a great number of cultivated plants. Its spectrum of activity and properties are consistently documented by a wide literature.

Since its discovery, many researches on its residues have been undertaken, even so much work is still needed to be done. The studies which have been carried out have started to investigate the main aspects of the problem of dimethoate residues namely (a) quantitative determination of the pesticide and of its degradation products, (b) quantitative research on the chemical composition of its metabolites originating in the vegetal tissues (c) the pattern of distribution of the insecticide and of its metabolites, in the vegetal organs (d) the toxicological effects of its residues upon the health of human beings, domestic animals and wildlife. This paper gives a comprehensive picture of dimethoate residues restricted to vegetal food products and the information is reported for harvest residues in vegetables.

Considerable interest has been shown in the thin layer chromatographic separation of standards of organophosphorus pesticides [1-3]. However, little use of these procedures has been reported for the determination of residues on crop samples. A molybdenum blue colorimetric method has been described for the determination of dimethoate [4,5] and its oxygen analogue after they have been separated on slica-gel chromatoplate. This chromatographic technique gives a degree of identification that is lacking in most other colorimetric methods [6-8], but the operations required are cumbersome and time consuming. Kovacs and others [9,10] have illustrated the use of thin-layer chromatography as a semi-quantitative process applied to extracts of kale, lettuce, strawberries, apples etc., co-extractives causing little interference with those organophosphorus pesticides studied [11-14]. Hence, to have a picture of the persistence of dimethoate, a semi-quantitative thin-layer chromatographic technique has been used in the present studies. It is an inexpensive rapid and accurate identification technique.

Experimental

Reagents

n-Hexane	–	redistilled
Acetonitrile	–	redistilled
Dichloromethane	–	redistilled
Sodium sulphate	–	grannular anhydrous material
Sodium chloride	–	5% w/v aqueous solution
Silica-gel G	–	for thin-layer chromatography
Spray reagent	–	(i) Para nitro benzyl pyridine 2% in acetone. (ii) Pentamine: 10% in acetone.

Treatment. Seed were grown in earthern pots in the laboratory premises. They were treated after 2 weeks with dimethoate 40 EC, calculated for pots area @ 0.5 lb a.i./acre by ordinary hand sprayer and ensured that the whole plant has been covered by the spray.

Sample preparation. One hundred grams pumpkin was added to 200 ml acetonitrile, blended at high speed for 1-2 mins and filtered through glass wool. The extract was transferred to 1 litre separatory funnel to which was added 100 ml n-hexane. This was shaken vigorously for several minutes, and 10 ml sodium chloride solution and 500 ml distilled water were added. This was mixed thoroughly and the aqueous layer discarded. The solvent layer was washed with two 100 ml portions of distilled water and dried over anhydrous sodium sulphate. Following drying, the solvent was decanted into a 500 ml roundbottom flask. The drying agent was washed with two 25 ml portions of n-hexane and added to flask. The

samples was evaporated to dryness on a rotatory evaporator and the residue was dissolved in 10 ml of methylene chloride.

Thin layer chromatography. Thin layer chromatographic plates (20 x 20 cm) were coated with silica gel (applied with Desagas TLC applicator). Samples to contain 0.1 µg, were spotted with Drummond microlitre pipette at 2 cm intervals. The chromatograms were developed using n-hexane-acetone (2:1) for dimethoate. The plates were air dried and then sprayed.

Recovery studies. Studies were carried out on the recovery of dimethoate from fortified pumpkin extracts which had not been subjected to column clean up; 10 ml of the final extract was spiked with dimethoate to give concentrations of 0.5 - 10 ppm. 80-100% recovery was found (Table 1).

Development and visualisation of chromatoplate. Plates were developed by ascending chromatography with hexane acetone. The developed plate was sprayed with (a) 2% para nitrobenzyl pyridine, heated at 110° for 30 mins, and sprayed with 10% pentamine. Dimethoate spots showed as blue spots. Minimum of 0.1 µg of dimethoate could thus be detected.

The well defined spots were circumscribed carefully and each area measured and compared visually for color development with standard solution of dimethoate.

Results and Discussion

The column cleanup procedure proved unnecessary for dimethoate, which could be readily separated from the pigments in the extract using the n-hexane-acetone (2:1) solvent system for chromatography on silica gel thin layers.

The recoveries of dimethoate shown in the Table 1 are generally acceptable and are typical of those obtained for TLC.

The elimination of column clean up is an important feature of the method, as it reduces a possible source of error, enables the handling of more samples and results in considerable time saving. This might be improved by a further concentration of the sample prior to chromatography or by spotting a larger aliquot of the sample solution. However, this could result in overloading from co-extratives and a preliminary clean up step might then become necessary. Dimethoate was detected quantitatively at 0.5 ppm by spotting a larger aliquot. The method offers a viable alternative to gas chromatography as it is simple, selective and does not require particularly sophisticated facilities.

Conclusion

Residues of dimethoate declined below 1 ppm after 14 days of treatment (Table 2). The crop is safe to harvest after this period under the conditions.

TABLE 1. RECOVERY OF DIMETHOATE ADDED.

Wt. of sample (gm)	Dimethoate added (mg)	Dimethoate added (ppm)	Vol. of extract (ml)	Vol of extract spotted (µl)	% recovery
50	0.5	10	10	2	100
50	0.25	5	10	4	100
50	0.1	2	10	12	83.3
50	0.050	1	10	25	80
50	0.025	0.5	10	50	80

TABLE 2. RESIDUES OF DIMETHOATE FOUND AFTER TREATMENT.

S. No.	Day after treatment	Wt. of sample (gm)	Final vol. of extract/ ml	Vol. spotted on TLC (µl)	ppm
1.	0	100	10	1	10
2.	1	100	10	2	5
3.	2	100	10	3	3.33
4.	3	100	10	4	2.5
5.	7	100	10	5	2
6.	14	100	10	10	1
7.	28	100	10	25	N.D.

N.D. = Not detectable.

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