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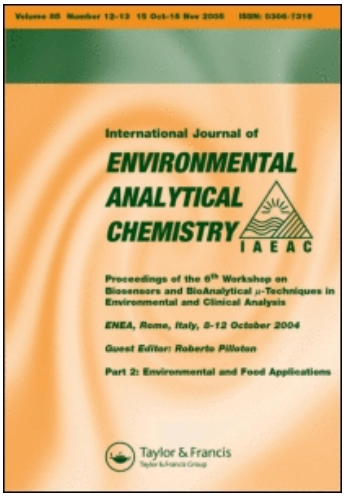

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
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To cite this Article Rathore, H. S. , Ali, I. and Kumar, A.(1989) 'Capillary Spot Test for the Detection of Trace Levels of Organophosphorus Insecticides in Water, Soil and Vegetation', International Journal of Environmental Analytical Chemistry, 35: 3, 199 — 206
To link to this Article: DOI: 10.1080/03067318908028393
URL: http://dx.doi.org/10.1080/03067318908028393

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Intern. J. Environ. Anal. Chem., Vol. 35. pp. 199–206
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CAPILLARY SPOT TEST FOR THE DETECTION OF TRACE LEVELS OF ORGANOPHOSPHORUS INSECTICIDES IN WATER, SOIL AND VEGETATION

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A simple, inexpensive and sensitive spot test has been developed for the detection of trace levels of organophosphorus insecticides such as malathion, formothion, thiometon, dichlorvos, methyl parathion, dimethoate and phosphamidon in water, soil (fertile and non-fertile) and in the leaves of "Citrus medica" (common lemon plant). Benzene solutions of p-dimethylaminobenzaldehyde and trichloroacetic acid have been used together as the detection reagent. The detection has been made at elevated temperatures and reduced pressure.

KEY WORDS: Organophosphorus insecticides, capillary spot test.

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INTRODUCTION

At present, pesticides are amongst the most useful tools available to man to get the crops properly grown and fruitfully harvested. It has been found that the use of pesticides in agriculture is a profit-induced poisoning of the environment. Organophosphorus insecticides are being used extensively because these are less persistent than organochlorine insecticides. Spot test analysis is inexpensive and readily available for the preliminary characterization of the test material. Literature survey shows that the already known spot tests which were initially developed for the detection of other basic compounds,[1] can be used with the alternative procedures for the detection of pesticide residues in different components of the environment.

Alkyl esters of phosphoric and thiophosphoric acid yield easily detectable sulphur dioxide when heated with sodium thiosulphate at 160–180 °C.[2,3] The spot test used for the detection of primary halo-alkyls[4] can be used for the detection of paraoxon, parathion, methyl parathion, chlorthion, diazinon, malathion and dipterex etc. The iodine-azide test[5] initially developed for the detection of thioketones and thiols[6] can be used for the detection of insecticides containing sulphur.[7] The insecticides containing imide group can be detected by the test through formation of pyrrole which was initially used for succinic acid and

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succinimide.[8] Some other tests have also been performed for the detection of insecticides in which spot visualization has been made with reagents such as iodine vapours,[9,10] Vaskovsky reagent[11] and p-nitrobenzene-diazonium tetrafluoroborate.[12] Besides these tests, various methods such as TLC, GLC, HPLC, colorimetry, fluorimetry and densitometry etc. have also been used for detection[13-17] and determination[18-22] of organophosphorus insecticides in different samples.

It was thought to be worthwhile to apply these tests for the detection of pesticide residues in soil, water and vegetation. Therefore, in continuation to our previous work,[23,24] now an attempt has been made to detect pesticide residues in different samples. For this purpose, a glass capillary containing a cotton plug impregnated with an equiproportional mixture of benzene solutions of p-dimethylaminobenzaldehyde and trichloroacetic acid has been used as the detector. A vacuum pump has also been used to facilitate the evaporation of the test material at low temperatures as well as a carrier of the test material to the reagent plug. The results of such a study are summarized in this paper.

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EXPERIMENTAL

Apparatus

Micro test tubes, glass capillaries (3 mm internal diameter), hot air electric drier, graduated micro pipette with vacuupet control, vacuustier pump, 17 cm and temperature controlled electric heating mantle were used.

Chemicals

Ammonium chloride (Sarabhai M. Chemicals, India), zinc dust (E. Merck, India), p-dimethylaminobenzaldehyde (BDH, India), trichloroacetic acid (BDH, India), malathion 50% EC (Cyanamid India Ltd., India), formothion 25% EC (Sandoz India Ltd., India), thiometon 25% EC (Sandoz India Ltd., India), dichlorvos 76% EC (Pesticides India, India), methyl parathion 50% EC (Pesticides India, India), dimethoate 30% EC (Rallis India Ltd., India) and phosphamidon 85% EC (Hindustan Ciba-Geigy Ltd., India) were used. All the reagents and insecticides used were of analytical grade and technical grade respectively.

Analysis of Soils

The soil samples were taken from AMU agricultural farm and non-fertile land from a depth of 0–30 cm. The detailed composition of the two types of soil has been found as below:

	Fertile soil	Non-fertile soil
Sand (%)	32.68	50.00
Silt (%)	57.00	27.60
Clay (%)	10.06	22.40
CEL (mg/100 g)	16.00	17.30
Organic matter (%)	0.61	0.19
pH	7.75	8.33

Preparation of Solutions

Solutions of p-dimethylaminobenzaldehyde (10%) and trichloroacetic acid (20%) were prepared in benzene. Solutions of insecticides and other water insoluble compounds were prepared in ethanol. Solution of ammonium chloride (0.5%) was prepared in distilled water.

Preparation of Capillary Detector

A cotton plug was loaded in a capillary with the help of an iron wire and was then impregnated with the colouring reagent. The solvent was removed by hot air drying.

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Procedure

For the detection of compounds having different functional groups, the test material was placed in a micro test tube along with 0.25 ml of 0.5% distilled water solution of ammonium chloride and 5–10 mg of zinc dust. An empty capillary was fixed in the tube with the help of a rubber stopper. The second end of the capillary was then connected to the vacuustier pump with the help of a rubber tubing. The excess solvent was removed by heating under reduced pressure. The empty capillary was then replaced by the capillary detector and the contents were heated vigorously at elevated temperatures. The colour developed on the plug was recorded.

For the detection of the insecticides in water, the standard formulations were once diluted a hundred-fold with tap water. The suspensions obtained were again diluted ten-fold, hundred-fold and thousand-fold with tap water to obtain the suspensions of different concentrations. These were then left for 24 hours at room temperature (29 °C). A known volume was then taken and colour was developed as above.

In the case of lemon leaves, the standard formulations were twice diluted a hundred-fold with ethanol and a known volume (10 ml) of the final dilution was sprayed on a known weight of leaves. The system was closed in a petri dish and left for 24 hours at room temperature (26 ± 0.5 °C). A portion of the leaves was then taken and colour was developed as above.

For the detection of the insecticides in soils, the standard formulations were

once diluted a hundred-fold with ethanol and a known volume (1 ml) was loaded on 5 g of the soil in a petri dish. The system was placed at the room temperature (23 ± 0.5 °C) for 24 hours. A known portion of the soil was then taken and colour was developed as above.

RESULTS

Several compounds of different functional groups were tested. The results obtained are summarized below.

The following compounds were tested. Their colour and lower limit of detection in μg are given in parentheses 1 and 2 respectively:

Acids:	benzoic (NC), Citric (LP) (5), malic (LO) (5), malonic (LO) (30) and salicyclic (LP) (15).
Carbonyls:	benzaldehyde (NC) and paraldehyde (LP) (10).
Carbohydrates:	dextrose (YBr) (20) and glucose (LO) (10).
Alcohols:	iso-propyl (NC), glycerol (NC) and tert-butyl (NC).
Amines:	dimethyl aniline (LO) (20), o-toluidine (LR) (30) and trimethyl amine (NC).
Amides:	acetamide (LO) (15) and benzamide (NC).
Phenols:	p-chlorophenol (LO) (100), o-nitrophenol (NC) and pyrogallol (LR) (50).
Hydrocarbons:	cyclohexane (NC), cyclopropane (NC) and toluene (NC).
Esters:	ethylacetate (NC).
Inorganics:	calcium sulphate (NC) and potassium permanganate (NC).
Miscellaneous:	carbon tetrachloride (NC) and urea (NC).
Abbreviations	used: NC—No Colour, L—Light, P—Pink, O—Orange, D—Dark, R—Red, Y—Yellow, Br—Brown, and B—Blood.

The data of the detection of various insecticides in water, lemon leaves and soils are summarized in Tables 1, 2, and 3 respectively.

DISCUSSION

Our previous work on the detection of malathion and nitrogen containing water pollutants[23,24] shows that the spot tests are important for the preliminary characterization of the test material specially at the places where either costly and sophisticated instruments are not available or they have not been installed so far.

When alkyl esters are heated with zinc dust and ammonium chloride,[1] they give pyrrole which can be detected at the mouth of the test tube with filter paper disc impregnated with p-dimethylaminobenzaldehyde and trichloroacetic acid. This test seems to be useful for detecting the presence of ester containing pesticides in soil, water, flora and fauna.

Although, many compounds with different functional groups could be detected

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Table 1 Detection of insecticides in water

Insecticides	*Concentration applied (%)*	*Volume taken for detection (ml)*	*Colour developed*	*Lower limit of detection (μg)*
Malathion	0.05	0.1	DP	
	0.005	0.1	LP	
	0.0005	0.1	NC	2
		0.4	VLP	
Formothion	0.025	0.1	DO	
	0.0025	0.1	NC	5
		0.2	VLO	
	0.00025	0.1	NC	
Thiometon	0.025	0.1	DR	
	0.0025	0.1	NC	10
		0.4	VLR	
	0.00025	0.1	NC	
Dichlorvos	0.076	0.1	DYR	
	0.0076	0.1	YR	
	0.00076	0.1	NC	4
		0.5	LYR	
Me-Parathion	0.05	0.1	DBR	
	0.005	0.1	BR	
	0.0005	0.1	NC	4
		0.8	LBR	
Dimethoate	0.03	0.1	DO	
	0.003	0.1	NC	6
		0.2	VLO	
	0.0003	0.1	NC	
Phosphamidon	0.085	0.1	DR	
	0.0085	0.1	LR	
	0.00085	0.1	NC	8
		0.9	VLR	

Abbreviations used are described in results section.

by the procedure initially developed,[24] the compounds such as malonic acid, maleic acid, malic acid and o-nitrophenol could only be detected by this procedure.

The test can be used successfully for selective and sensitive detection of phosphorus insecticides in water, lemon leaves and soils (Tables 1, 2 and 3). It is obvious from the results that the limit of detection is lowest in water and highest in soils. For example, lower limit of detection of malathion in water, leaves and soils is 2 μg, 16 μg and 20 μg respectively. The change in lower limit of detection may be due to stronger adsorption of the insecticides on soils than on leaves. For

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Table 2 Detection of insecticides in lemon leaves

Insecticide applied (10 ml)	*Weight of leaves taken for spray (mg)*	*Concentration of insecticide applied (%)*	*Weight taken for detection*		*Colour developed*
			Leaves (mg)	*Insecticides (μg)*	
Malathion	780	0.0050	25	16	LP
Formothion	662	0.0025	15	6	LBR
Thiometon	647	0.0025	20	8	LO
Dichlorvos	765	0.0076	30	30	YR
Me-Parathion	1,525	0.0050	20	7	RO
Dimethoate	1,320	0.0030	30	7	YO
Phosphamidon	555	0.0085	25	38	RBR

Abbreviations used already described under Table 1.

Table 3 Detection of insecticides in soils

Type of soil taken	*Insecticide applied (1 ml)*	*Concentration of insecticide applied (%)*	*Weight taken for detection*		*Colour developed*
			Soil (mg)	*Insecticides (μg)*	
FERTILE	Malathion	0.5	20	20	LO
	Formothion	0.25	30	15	LR
	Thiometon	0.25	25	13	LRO
	Dichlorvos	0.76	15	23	LP
	Me-Parathion	0.5	15	15	LBrR
	Dimethoate	0.3	25	15	LYR
	Phosphamidon	0.85	15	26	LR
NON-FERTILE	Malathion	0.5	20	20	LO
	Formothion	0.25	50	25	LBR
	Thiometon	0.25	30	15	LR
	Dichlorvos	0.76	25	38	LR
	Me-Parathion	0.5	20	20	LRO
	Dimethoate	0.3	30	18	LR
	Phosphamidon	0.85	20	34	LYR

Abbreviations used already described under Table 1.

accurate detection of the insecticides in complex matrices such as leaves and soils, a comparison with the standard is necessary.

The following tentative reaction scheme may be postulated for the production of pink colour with malathion. The reaction mechanism of colour production needs further study and it is in progress.

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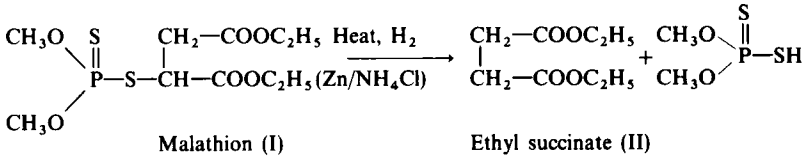
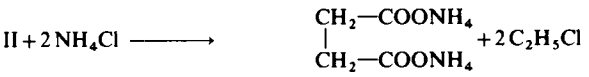
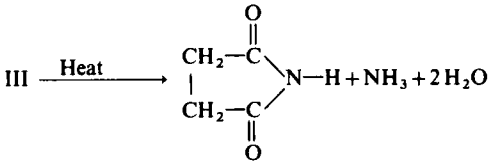
TENTATIVE REACTION SCHEME WITH MALATHION



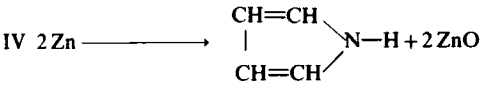
Malathion (I) Ethyl succinate (II)



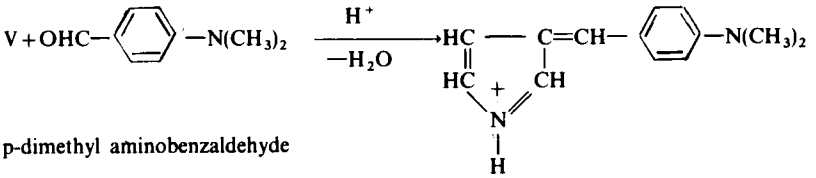
Ammonium succinate III



Succinimide IV

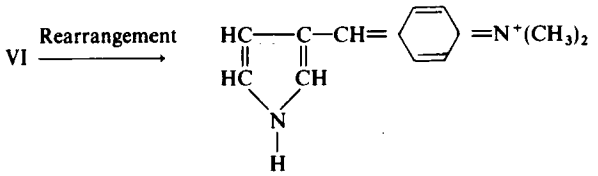


Pyrrole V



p-dimethyl aminobenzaldehyde

VI



Quinonoidal compound
(Pink colour)

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