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## A NEW DETECTION OF SOME ORGANOPHOSPHOROUS PESTICIDES SEPARATED BY TLC

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### ABSTRACT

The paper describes a new sensitive and selective thin layer chromatographic method for the detection of some organophosphorous pesticides. Fifteen organophosphorous pesticides have been separated on thin layer using different stationary phases prepared at the "Raluca Ripan" Institute of Chemistry Cluj-Napoca, Roumania (silica gel R, amino bonded silica gel R) and some mixtures with different polarities as mobile phase (petroleum ether + chloroform + ethyl acetate 65:30:5, v/v).

The detection was performed by spraying the TLC plates with a 9-methylacridine solution (0.05%) in ethanol and their examination under UV light at 366 nm. The spots present different colors and intensities. Detection limit is between 0.1 - 10 µg/spot.

## INTRODUCTION

Organophosphorous pesticides are used in agriculture and public health to control insects, weeds, animals, and vector of diseases. These compounds are likely to continue to be the most used insecticides in developing countries and it has been estimated that demand for these compounds will more than double in the next ten years.<sup>1</sup> Thin layer chromatography (TLC) is often used in separation of organophosphorous pesticides because of its simplicity, efficiency, rapidity, and low material cost. Systematic separation of the above mentioned pesticides by TLC have been described by many authors. These compounds were separated on chromatographic plates coated with alumina,<sup>2</sup> silica gel, kieselguhr-silica gel (1:1), kieselguhr-alumina (1:1),<sup>3</sup> silica gel G,<sup>4</sup> Florisil,<sup>5</sup> and hydrophilic modified silica gel (amino, cyano, diol).<sup>6</sup> The most used mobile phases were the following mixtures: hexane + acetone 9:2, v/v,<sup>3</sup> cyclohexane + benzene + methanol 6:3:1, v/v,<sup>4</sup> petroleum ether + ethyl acetate + benzene 65:5:30, v/v,<sup>7</sup> petroleum ether + benzene + chloroform + ethyl acetate 60:30:5:5, v/v.<sup>8</sup> The visualization of organophosphorous compounds was carried out by UV irradiation and by spraying with different reagents solutions as bromophenol blue,<sup>9</sup> palladium chloride,<sup>3</sup> potassium iodate - starch or 4-aminoantipyrene and potassium ferricyanide,<sup>4</sup> thioacridone,<sup>7</sup> or 2-methylthioacridone<sup>9</sup> and detection in UV light at 366 nm.

This paper describes a new sensitive and selective mode for the separation and identification of fifteen organophosphorous pesticides on silica gel R and amino silica gel R plates, using a new visualization reagent, namely 9-methylacridine.

## EXPERIMENTAL

### Reagents and Chemicals

All the pesticides were purchased from EPA-Research, Triangle Park, N. C. Both silica gel R and amino bonded silica gel R were prepared at the "Raluca Ripan" Institute of Chemistry Cluj, Roumania. The reagents used

were made in Roumania - CHIMOPAR Bucharest (petroleum ether, chloroform, ethyl acetate) Faculty of Chemistry, Department of Organic Chemistry, "Babes-Bolyai" University Cluj (9-methylacridine prepared after Tsuge method<sup>10</sup>) or foreign made - FARMITALIA Carlo-Erba (tetrahydrofuran). All the reagents were of analytical grade.

### Sample Preparation

Standard solutions of fifteen organophosphorous pesticides presented in table 1 were prepared in diethyl ether at 0.1% concentration.

### Chromatographic Separation

The chromatographic separation was performed on 20x20 cm plates coated with silica gel R and amino bonded silica gel R.<sup>11</sup> 1-10  $\mu$ L/spot volumes of fifteen organophosphorous pesticides have been applied on the chromatographic plates by means of Brand micropipettes. The development of spotted plates was carried out in an unsaturated normal chamber at room temperature by ascending technique.

The chromatograms on silica gel R were developed with the following mobile phases: petroleum ether + chloroform + ethyl acetate 65:30:5, v/v mixture up to 15 cm height or petroleum ether + tetrahydrofuran 90:10, v/v mixture up to 10 cm height. Organophosphorous pesticides spotted on amino bonded silica gel R plates were separated with petroleum ether + tetrahydrofuran 95:5, v/v mixture as mobile phase up to 10 cm height.

### Detection

The detection of pesticides was carried out by direct spraying of the plate with a 0.05% ethanolic solution of 9-methylacridine. The plates have been examined with CAMAG UV lamp at 366 nm. The color and the intensity of organophosphorous pesticide spots after UV examination are presented in Table 1.

## RESULTS AND DISCUSSION

By following the described separation method, it is possible to achieve complete separation of all fifteen organophosphorous pesticides, as well as the

Table 1

**R<sub>f</sub> x100 Values of Standard Organophosphorous Pesticides Separated on Silica Gel R and Amino Silica Gel R Thin Layers**

No.	Pesticide	Chemical Name Of Pesticide	Silica Gel R	R <sub>f</sub> x 100			Color in UV light at 360 nm <sup>a</sup>
				Amino Silica Gel R			
			Mobile Phase				
			A	B	C		
(1)	(2)	(3)	(4)	(5)	(6)	(7)	
1	Fenthion	O,O-dimethyl-O-4-methyl-m-tolyl-phosphorothioate	90	76	75	dark brown ****	
2	Fenitrothion	O,O-dimethyl-O-4-nitro-m-tolyl-phosphorothioate	84	68	59	dark brown ****	
3	Parathion-methyl	O,O-dimethyl-O-4-nitrophenyl-phosphorothioate	82	64	51	dark brown ****	
4	Parathion-ethyl	O,O,-diethyl-O-4-nitrophenyl-phosphorothioate	88	72	77	dark brown ****	
5	Azinphos-methyl	S-(3,4-dihydro-4-p-oxobenzo[d][1,2,3]-triazin-3-ylmethyl)-O,O-dimethyl-phosphorodithioate	60	18	12	dark brown ***	
6	Phosmet	O,O-dimethyl-S-phthalimidomethyl-phosphorodithioate	67	23	16	dark brown ***	
7	Phosalone	S-6-chloro-2,3-dihydro-2-oxobenzoxazol-3-yl-methyl-O,O-dimethyl-phosphorodithioate	81	41	36	brown→ violet-grey ***	

Table 1 (continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)
8	Methidathion	S-2,3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-ylmethyl-O,O-dimethylphosphorodithioate	76	35	32	brown→ violet-grey ***
9	Dimethoate	O,O-dimethyl-S-methylcarbamoylmethylphosphorodithioate	20	6	4	violet→ violet-brownish **
10	Malathion	Diethyl-(dimethoxythiophosphorylthio)succinate	78	53	47	brown→ violet-grey ***
11	Disulfoton	O,O-diethyl-S-2 ethylthioethylphosphorodithioate	95	85	92	fluorescent violet→ brown***
12	Bensulfide	S-2-benzene-sulphonamidoethyl-O,O-disopropylphosphorodithioate	42	19	9	violet→ brown ***
13	Ethion	O,O,O',O'-tetraethyl-S,S'-methylene-bis-(phosphorodithioate)	90	96	98	brown-greenish →brown-grey**
14	Chlorfenvinphos	2-chloro-1-(2,4-dichlorophenyl)vinyl-diethylphosphate	62	58	18	brown-grey ***
15	Ethephon	2-chloroethylphosphonic acid	0	0	0	fluorescent yellow-greenish ****

A - petroleum ether + chloroform + ethyl acetate 65:30:5, v/v

B - petroleum ether + tetrahydrofuran 90:10, v/v

C - petroleum ether + tetrahydrofuran 95:5, v/v

<sup>a</sup> Light blue color on fluorescent background of chromatographic plate;

\* Spot intensity

separation of single members in the class. The pesticide spots present different colors and intensities on a light fluorescent background. These intensities and colors vary from dark brown to fluorescent greenish yellow and are shown in the table.

Best separations were obtained on silica gel R layers with petroleum ether + chloroform + ethyl acetate 65:30:5, v/v and with petroleum ether + tetrahydrofuran 90:10, v/v mixtures as mobile phase and on amino bonded silica gel R layers with petroleum ether + tetrahydrofuran 95:5, v/v mobile phase. This procedure separates a mixture of at least ten pesticides, with the condition that it does not contain compounds with closed  $R_f$  values (Fenthion, Parathion-methyl, Phosalone, Azinphos-methyl, Chlorfenvinphos).

### CONCLUSION

A new method for the detection of fifteen organophosphorous pesticides on silica gel R and amino silica gel R thin layers has been discovered and described to assist in identification and separation of these compounds.

The visualisation of these pesticides was performed at room temperature by direct spraying with 9-methylacridine and examination under UV light at 366 nm. The detection limit was between 0.1 - 10  $\mu\text{g}/\text{spot}$ .

The best separations were obtained on silica gel R layers with petroleum ether + tetrahydrofuran 90:10, v/v mobile phase and on amino silica gel R layers with the petroleum ether + tetrahydrofuran 95:5, v/v mobile phase.

The elaborated method can be applied at the separation and identification of some organophosphorous pesticides from water, soil or fruit.

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