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The detection, separation and quantitative recovery of thirteen organophosphorus pesticides on Silica Gel GF_{254} thin-layer chromatograms

Fluorescent silica gels have been used on thin-layer chromatograms to separate and identify various pesticides[1-3]. Recently Silica Gel GF_{254} has been used in conjunction with sweep co-distillation cleanup of plant extracts for residue analysis of parathion, malathion and diazinon[4]. However, there has been no assessment of the general applicability of these gels for the separation, detection or quantitative recovery of organophosphorus pesticides. This paper reports the detection limits, separation properties, and quantitative elution of thirteen organophosphorus pesticides from Silica Gel GF_{254}.

Experimental

The standard technique of ascending thin-layer chromatography was employed. Silica Gel GF_{254}® (Merck) was layered on 20 × 20 cm glass plates at two thicknesses (250 and 500 μ) and activated at 120° for 1 h. The pesticide stock solutions were prepared in redistilled acetone and various sub-dilutions were made from these. The pesticides used in this study, along with their chemical names, percent purity and source of supply are listed in Table I. The pesticides were divided into three groups according to their R_F values for easy identification after TLC.

Ten-microliter aliquots of the acetone solutions of the compounds were spotted and the plates were developed in 15 % acetone–hexane. The plates were then removed, air-dried, and placed under UV light in order to visualize the compounds. The areas on the plate where the pesticides were detected were scraped off and the pesticides were extracted from the silica gel with either acetone, hexane or ethanol and made to an appropriate dilution for GLC. GLC was carried out using a Varian Aerograph Model 600D chromatograph equipped with a 250-mCi tritium electron-capture detector. A glass column, 4 ft. long, was packed with 4 % QF-1–6 % SE-30 on Chromosorb W (acid-washed, 80–100 mesh). The column temperature was maintained at 195° with a nitrogen gas flow of 100 ml/min. The injection port temperature was 230° and the detector temperature was maintained at 190°. The retention times for the compounds used based on R_{aldrin}* are as follows: Dursban® 1.24, diazinon 0.58, disulfoton 0.68, Sumithion® 1.74, mevinphos 0.08, malathion 1.66, carbophenothion 3.82, Methyl Trithion® 2.97, phorate 0.49, parathion 1.63, methyl parathion 2.18, ethion 3.92, azinphosmethyl 11.31.

Results and discussion

Fig. 1 shows a typical plate that has been spotted with different amounts of the five organophosphorus pesticides in group III. All the pesticides used show up as dark spots on a fluorescent green background.

The sensitivity of detection of pesticides in groups I, II and III are shown in Table II. The amounts spotted varied from 0.5 to 64 μg in each case, and all plates were run in duplicate. Parathion, methyl parathion and azinphosmethyl were detected at a level of 0.5 μg. Diazinon, Sumithion, carbophenothion and Methyl Trithion were

* R_{aldrin} = 3.1 min.

TABLE I

ORGANOPHOSPHORUS COMPOUNDS USED IN THIS STUDY

	Chemical name	*% purity*	*Source*
Group I			
Dursban®	O,O-Diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate	99.0	Dow
Diazinon	O,O-Diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate	96.1	Geigy
Disulfoton	O,O-Diethyl S-2-(ethylthio)ethyl phosphorodithioate	96.8	Chemagro
Sumithion®	O,O-Dimethyl O-(4-nitro-*m*-tolyl) phosphorothioate	98.0	Stauffer
Group II			
Mevinphos	Methyl 3-hydroxy-α-crotonate dimethyl phosphate	96.0	Shell
Malathion	Diethyl mercaptosuccinate, S-ester with O,O-dimethyl phosphorodithioate	99.6	Cyanamide
Carbophenothion	O,O-Diethyl *p*-chlorophenylmercaptomethyl dithiophosphate	94.6	Stauffer
Methyl Trithion®	S-[(*p*-Chlorophenylthio)methyl] O,O-dimethyl phosphorodithioate	85.8	Stauffer
Group III			
Phorate	O,O-Diethyl S-(ethylthio)methyl phosphorodithioate	99.0	Cyanamide
Ethion	O,O,O′,O′-tetramethyl S,S′-methylene bisphosphorodithioate	95.5	Niagara
Parathion	O,O-Diethyl O-*p*-nitrophenyl phosphorothioate	98.8	Velsicol
Methyl parathion	O,O-Dimethyl O-*p*-nitrophenyl phosphorothioate	99.0	Chemagro
Azinphosmethyl	O,O-Dimethyl S-[4-oxo-1,2,3-benzotriazine-3(4H)-yl]methyl phosphorodithioate	98.5	Chemagro

TABLE II

THE SENSITIVITY OF DETECTION OF THIRTEEN ORGANOPHOSPHORUS PESTICIDES ON SILICA GEL GF_{254}

The visible detection of the pesticides is classified as follows: ○, not detectable; ⊕, faintly detectable; +, weak but easily detectable; ++, strong and easily detectable; +++, very strong and easily detectable. The amounts spotted varied from 0.5 to 64 μg in each case.

No.	*Compound*	R_F *value*	*Layer thickness 250 μ*								*Layer thickness 500 μ*							
			0.5	*1*	*2*	*4*	*8*	*16*	*32*	*64*	*0.5*	*1*	*2*	*4*	*8*	*16*	*32*	*64*
1	Dursban	0.9	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
2	Disulfoton	0.83	○	○	○	○	○	○	⊕	+	○	○	○	○	○	○	⊕	+
7	Diazinon	0.54	○	⊕	⊕	+	++	++	+++	+++	○	⊕	⊕	+	++	++	+++	+++
8	Sumithion	0.39	○	⊕	+	+	++	+++	+++	+++	○	⊕	+	+	++	++	+++	+++
10	Carbophenothion	0.91	○	⊕	+	+	++	++	+++	+++	○	⊕	+	+	++	++	+++	+++
9	Methyl Trithion	0.78	○	⊕	+	+	++	++	+++	+++	○	⊕	+	+	++	++	+++	+++
3	Malathion	0.40	○	○	○	○	○	○	⊕	+	○	○	○	○	○	○	⊕	+
6	Mevinphos	0.12	○	○	○	⊕	+	+	+	+	○	○	○	⊕	⊕	+	+	+
5	Phorate	0.74	○	○	○	○	⊕	+	+	+	○	○	○	○	○	⊕	+	+
4	Ethion	0.59	○	○	○	○	○	⊕	+	+	○	○	○	○	○	○	⊕	+
13	Parathion	0.45	⊕	+	+	++	++	+++	+++	+++	○	⊕	+	+	++	++	+++	+++
12	Methyl parathion	0.32	⊕	+	+	++	++	+++	+++	+++	○	⊕	+	+	++	++	+++	+++
11	Azinphosmethyl	0.16	⊕	+	+	++	++	+++	+++	+++	○	⊕	+	+	++	++	+++	+++

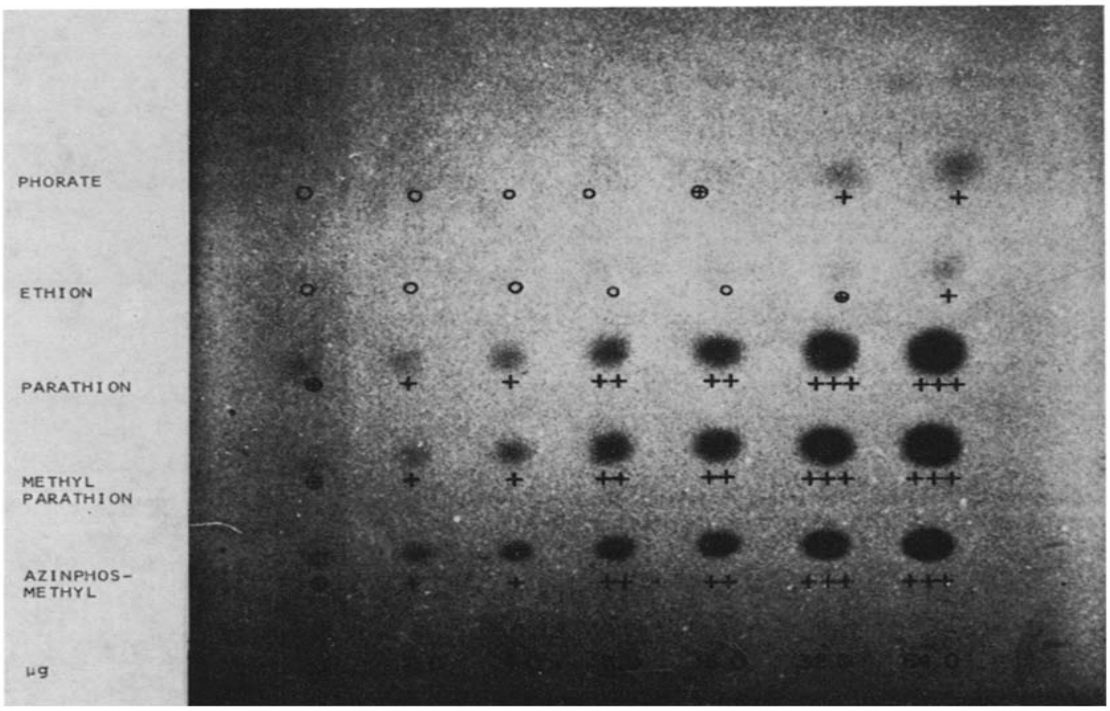

Fig. 1. A thin-layer chromatogram of five organophosphorus pesticides on Silica Gel GF_{254}.

visible at the 1-μg level. Mevinphos, phorate and ethion were visible at the 4-, 8- and 16-μg levels, respectively. Malathion and disulfoton were detected at 32 μg and Dursban was not visible even at 64 μg.

The recovery of the thirteen pesticides as measured by gas chromatography is shown in Table III. In general, the effectiveness of the solvent used for extraction of the pesticide from the gel increased with increasing polarity. Hexane gave very poor recoveries of all pesticides and, except for Dursban (47 %), all recoveries were less than 10 %. Improved recoveries were obtained when acetone was used to elute

TABLE III

THE RECOVERY OF THIRTEEN ORGANOPHOSPHORUS PESTICIDES FROM SILICA GEL GF_{254}

Pesticide	*% recovery ± S.D.*	
	Acetone	*Ethanol*
Diazinon	79.8 ± 1.8	90.3 ± 5.8
Disulfoton	67.8 ± 1.6	83.5 ± 6.7
Dursban	71.3 ± 3.9	87.3 ± 4.5
Sumithion	80.4 ± 5.6	87.4 ± 5.3
Mevinphos	94.8 ± 3.3	91.7 ± 4.3
Malathion	52.1 ± 4.4	80.3 ± 2.4
Carbophenothion	29.7 ± 0.9	34.0 ± 1.1
Methyl Trithion	22.0 ± 1.6	39.2 ± 1.6
Phorate	83.7 ± 4.1	91.6 ± 6.0
Parathion	92.7 ± 0.7	93.9 ± 2.6
Methyl parathion	91.6 ± 2.4	94.7 ± 6.6
Ethion	92.0 ± 2.1	95.0 ± 4.4
Azinphosmethyl	90.8 ± 11.1	95.9 ± 14.0

the pesticides from the silica gel. Mevinphos, parathion, ethion, methyl parathion, and azinphosmethyl recoveries were above 90 %. All other recoveries were above 80 % except carbophenothion and Methyl Trithion. Ethanol proved to be the most efficient solvent and generally gave recoveries of 80–90 %.

The data presented here indicate that Silica Gel GF_{254} can be used for the separation, detection and quantitative recovery of many organophosphorus compounds. The limit of detection for some compounds is as little as 0.5 μg. Ethanol was the best solvent for the extraction of the pesticides from the gel and for the most part gave recoveries in excess of 80 %.

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Department of National Health and Welfare,
Food and Drug Directorate, Tunney's Pasture,
Ottawa 3, Ont. (Canada)

D. C. VILLENEUVE
A. G. BUTTERFIELD
D. L. GRANT
K. A. MCCULLY

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