RECOVERY OF SOME CHLORINATED HYDROCARBON AND ORGANOPHOSPHOROUS PESTICIDES ON WET AND DRY ALUMINA COLUMN CHROMATOGRAPH

MOUNIR M. ALMAZ, M.M. ABU-ZAHW, I.N. NASR AND M.M. EL-TOHAMY

1 Central Agricultural Pesticides Laboratory, Agricultural Research Centre, Dokki, Egypt.

(Manuscript received 28 October 1993)

Abstract

The effect of drying and wetting of the deactivated (6% mositure) aluminium oxide column using n-hexane or benzene as eluting solvent was investigated in order to evaluate recovery rates of cetain hydrocarbon and organophosphorus pesticides.

The dry aluminium oxide column showed the best recovery values for chlorinated hydrocarbon pesticides when eluted with n-hexane or benzene.

The wet aluminium oxide column gave the best recovery values for organophosphorous pesticides when eluted with benzene. The dry aluminium oxide column also gave satisfactory recovery values for most of the tested organophosporous pesticides when benzene was used as an eluting solvent.

INTRODUCTION

Alumina was found to be the most efficient in removing lipids. It has the longest capacity per unit volume and produced better separations. The coast of the alumina may be produced better separations. The coast of the alumina may be offset by recycling (Clacy and Inman 1974).

The variations in recovery values of some chlorinated hydrocarbon and organophosphorous pesticides had been reported by many authors using alumina column (Hoskins *et al.,* 1958; Bazzi 1960; Blinn *et al.,* 1960 ; Laws and Webley 1961; Coffin and Sevary 1964; Egan et al., 1964; Boyle et al., 1965; Clacy and Inman 1974; Lane et al., 1977). Among the main factors affecting the efficiency of clean up and recovery rates are the type of the eluting solvent, the packing material of the column and its grade of activation.

The present investigation is dealing with some of these points through studying the effect of using dry or wet aluminium oxide and two elution solvents on the recovery value of certain chlorinated hydrocarbon and organophosphorous pesticides.

MATERIALS AND METHODS

Reagent

a) Chlorinated hydrocarbon and organophosphorous pesticide standards taken from BDH are tabulated in Table 1.

b) Aluminium oxide 90 active I supported by 6 % deactivated with distilled water and equilibrated for 24h before using.

c) Solvents n-hexane and benzene Pestanal grade (Riedel-dehaen) redistilled through all glass equipment.

Column Chromatography

Two types of aluminium oxide columns were prepared , one is the dry aluminium oxide column and the other is wet aluminium oxide column.

a) The dry column

A glass chromatographic column 20 mm i.d. x 40 cm was prepared by adding plug of glass wool followed by 10 g of deactivated aluminium oxide. Pesticides standard solutions directly poured onto column were eluted using 150 ml solvent. Considering the pesticide group and the type of the eluting solvent, the following columns were used:

1- Chlorinated hydrocarbon pesticides eluted using n-hexane.

2- Chlorinated hydrocarbon pesticides eluted using benzene.

3- Organophosphorous pesticides eluted using n-hexane.

Table 1. Chlorinated hydrocarocarbon and organophosphorous pesticides evaluated for recovery rates using dry or wet aluminum oxide packed columns clean-up.

Chlorinated hydrocarbon	Organophosphorous pesticides
Aldrin	Bromophos-ethyl (Nexagon)
α- BHC	Chlorfenvinphos (Gardona)
Dieldrin	Diazinon (Spectracide)
Endrin	Fenthion (Baytox)
Heptachlor	Malathion (Carbofos)
Heptachlor-epoxide	Parathion - methyl
λ - BHC (Lindane)	Phorate (Thimet)
0,p DDD	Pirimiphos methyl (Actellic)
0,p DDT	Propetamphos (Safrotin)
p,p DDD	Fenitrothion (Sumithion)
p,p DDE	
p,p DDT	

The wet column

A glass column (20 mm i.d. x 40 cm) was prepared by adding a plug of glass wool followed by 10 g of deactivated aluminium oxide. The column was pre-washed with about 20 ml solvent. The solvent was drained until its surface just coverded the top of the alumina. Pesticides standard solutions were added to the column and eluted using 150 ml of the same solvent used in prewashing the column. Considering the pesticide group and the type of the eluting solvent, the following columns were used:

1- Chlorinated hydrocarbon pesticides eluted with n-hexane.

2- Chlorinated hydrocarbon pesticides eluted with benzene.

3- Organophosphorous pesticides eluted with n-hexane.

4- Organophosphorous pesticides eluted with benzene.

Gas Chromatograph

a) Chlorinated hydrocarbon pesticides

Residues of chlorinated hydrocarbon pesticides were dissolved in n-hexane then determined using a PYE-Unicam 304 gas chromatograph equipped with electron capture detector (NI^{63} source) attached to a PYE-Unicam PU4810 computing integrator under the following conditions : column packing, 1.5 m x 4 mm i.d. packed with 3% QF-1on chromosorb W.H.P. (100-120 mesh), temperature (^{o}C) : injection 250, column 170, detector 300 and flow gases (ml/min.): nitrogen 40,10% methan / argon 20 (Purge), using these conditions, the retention times of the pesticides under investigation are as tabulated in Table 2.

Table 2. Retention time of chlorinated hydrocarbon pesticide standards detected by ECD ^{63}Ni GLC.

Pesticides	R_t	RR_t*
α- BHC	2.89	0.63
Lindane	3.71	0.81
Heptachlor	3.91	0.86
Aldrin	4.55	1.00
Heptachlor-epoxide	8.74	1.92
p,p DDE	9.86	2.16
o,p DDD	11.97	2.63
o,p DDT	12.61	2.77
Dieldrin	13.78	3.02
Endrin	16.27	3.57
p,p DDD	17.76	3.90
p,p DDT	19.29	4.24

* Relative retention time to aldrin.

4- Organophosphorous pesticides eluted using benzene.

b) Organophosphorous pesticides

Organophosphorous pesticide residues were dissolved in n-hexane and injected in a PYE - Unicam 204 gas chromatograph equipped with Tracor flame photometric detector operated in the phosphorus mode (525 nm filter) under the following conditions : column packing, 1.5 m x 4 mm i.d. packed with 4 % SE-30 + 6% OV-210 on gas chromosorb-Q (80-100 mesh); temperature (^{o}C) : injection 250, column 200, detector 300, and flow of gases (ml/min.) : nitrogen 30, hydrogen 30, air 30. The retention times of the pesticides under investigation using these conditions are tabulated in Table 3.

Table 3. Retention time for organophosphorous pesticide standards detected by EPD- GLC.

Pesticides	R_t (min).	RR_t*
Phorate	3.72	0.41
Diazinon	4.52	0.50
Propetamphos	5.19	0.57
Pirimiphos-methyl	7.64	0.84
Fenthion	9.21	1.02
Malathion	10.62	1.17
Fenitrothion	11.69	1.29
Bromophos-ethyl	12.93	1.43
Chlorfenvinphos	14.68	1.63
Parathion - methyl	23.53	2.61

* Relative retention time to chlorpyrifos (R_t = 9.01 min).

Table 4. Eluting patterns of chlorinated hydrocarbon pesticides from deactivated aluminium oxide column.

Pesticides	Sensitivity (Pg)	% Recovery of pesticides **			
		Dry column		Wet column	
		n-hexane	Benzene	n-hexane	Benzene
Aldrin	5	86.4	104	-	-
BHC	2	68.6	72	-	-
Dieldrin	10	97.8	93	-	76
Endrin	30	100.0	88.2	3	100
Heptachlor	3.1	93	69	-	37
Heptachlorepoxide	6.5	100	97.9	-	57.7
Lindane	2.3	100	100	-	24
o,p DDD	19.3	100	95.9	-	88.7
o,p DDT	15	100	71.7	-	100
p,p DDD	12.8	96.2	106	-	101
p,p DDE	6.3	107	87.8	5	66.7
p,p DDT	18.2	62	84	2	100

* At 512 attenuation, the concentration that gives peak height equal to 10% FSD.

** Figures are the average of two duplicates.

- Signifies zero recovery.

Table 5. Eluting patterns of organophosphosphorous pesticides from deactivated aluminium oxide column.

Pesticides	Sensitivity* (Pg)	% Recovery of pesticides **			
		Dry column		Wet column	
		n-hexane	Benzene	n-hexane	Benzene
Bromophosethyl	2.4	100	90.7	12.93	85
Chlorfenvinphos	2.2	78	79.0	55.20	100
Diazinon	3.3	7	100	-	93.78
Fenthion	3.1	40	100	9.80	84.70
Malathion	2.1	9	85.02	-	100
Parathionmethyl	2.5	62.4	92.10	-	100
phorate	2.4	30	-	-	100
Pirimiphosmethly	3.3	10	100	0.70	93.20
Propetamphos	2.4	-	100	-	100
Fenitrothion	1.0	4	100	-	100

* At 8 attenuation, the concentration that gives peak height equal to 10% FSD.

** Figures are the average of two duplicates.

- Signifes zero recovery.

RESULTS AND DISCUSSION

Data shown in Tables 4 and 5 demonstrate the effect of using dry and wet deactivated aluminium oxide column and two elution solvents on the rate of recovery of certain chlorinated hydrocarbon and organophospours pesticides, respectively. Relative retention times for the tested pesticides were calculated using aldrin for chlorinated hydrocarbon group and chlorpyrifos for organophosphorous group as tabulated in Tables 2 and 3.

The dry alumina column showed better recovery values of chlorinated hydrocarbon pesticides when eluted with n-hexane or bonzene (Table 4). These findinges are in agreement with those obtained by Wells and Johnstone (1977). The wet alumina column showed good recovery values for five of the twelve tested pesticides when benzene was used as the elution solvent, while five pesticides were poorly recovered, and two disappeared. Zero recovery values were almost obtained from the wet alumina-column using n-hexane as the elution solvent. It could be concluded that the wet aluminium oxide column is not the suitable clean up method for chlorinated hydrocarbon pesticides especially when using n-hexane as an elution solvent.

The best recovery values of organophosphorous pesticides were obtained when the wet aluminum oxide and benzene elution were used. The dry alumina column column also showed good recoveries when eluted with benzene except with phorate which did not show up after clean up (Table 5). The results indicated that using n-hexane for elution of organophosphorous pesticides from either wet or dry alumina columns had rsulted in poor recovery rates.

REFERENCES

1. Bazzi, B. 1960. Determination of residues of 0, 0-dimethyl- S-methylcarbmoylmethyl phosphorothioate (Rogor) in olives and various vegetable materials. Pulb. Soc. Gen. Ind. Min. Chem., Milan; through Chem. Abstr., 58, 6125 d (1963).

2 . Blinn, R.C., F.A. Gunther and M.S. Mulla. 1960. Infrared determination of aldrin and dieldrin in aldrin-treated soil. J. Econ. Entomol., 53,1129.

3 . Boyle, W.H., R.H. Burttschell and A.A. Rosen. 1965. Infrared identification of chlorinated insecticides in the tissues of poisoned fish. 150 th Meeting Amer. Chem. Soc., Sept. 12-17.

4 . Clacy, R.R. and R.D. Inman. 1974. Adsorption chromatographic separation of chlorinated hydrocarbons from lipids. J.A.O.A.C., 57 : 399-404.

5 . Coffin, D.E. and G.Savary . 1964. Procedure for extraction and clean-up of plant material prior to determination of organophosphate residues. J.A.O.A.C., 47 : 875.

6 . Egan, H., E.W. Hammond and J. Thomson. 1964. The analysis of organophosphorus pesticide residues by gas chromatography. Analyst, 89:175.

7 . Hoskins, W.M., W.R. Erwin and R. Miskus. 1958. A polyethylene-alumina column for purification of tissue extracts before analysis. J. Agric. Food Chem., 6 : 914.

8 . Lane, L.G., T.C. Gray and J.P. Minyard. 1977. Aluminium oxide clean-up of feed grade fats for residues. J.A.O.A.C., 60: 682-684.

9 . Laws, E.Q. and D.J. Webley. 1961. The determination of organophosphorus insecticides in vegetables. Analyst, 86:249.

10 . Wells, D.E. and S.J. Johnstone. 1977. Method for the separation of organochlorine residues before gas-liquid chromatographic analysis. J. Chromatog., 140:17-28.

معدل استرجاع بعض المبيدات الكلورينية العضوية والفوسفورية العضوية على عمود الالومينا الجاف والرطب

منير محمد الماظ ، مصطفى أبو زهو ، إسلام نعمان نصر
محمود التهامى

المعمل المركزى للمبيدات – مركز البحوث الزراعية – الدقى .

درس تأثير تجفيف وترطيب أكسيد الالومنيوم عند استخدامه فى العمود الكروماتوجرا فى مع استخدام الهكسان العادى أو البنزين كمذيبات لازاحة المركبات من العمود على معدل استرجاع بعض المبيدات الكلورينية والفوسفورية العضوية.

ثبت أن العمود الجاف لأكسيد الالومنيوم يعطى أفضل قيم لمعدلات الاسترجاع للمبيدات الكلورينية العضوية عندما تمت الازاحة بالهكسان العادى أو البنزين .

ولقد أعطى العمود الرطب لأكسيد الألومنيوم (٦٪ رطوبة) أفضل القيم لمعدلات استرجاع المبيدات الفوسفورية العضوية عندما تمت الإزاحة بالبنزين . كما أعطى العمود الجاف قيما جيدة لمعدلات استرجاع المبيدات الفوسفورية العضوية المختبرة عندما استعمل البنزين فى الازاحة.