

# A Feasibility Study of Miniature Florisil Columns for the Separation of Some Chlorinated Pesticides

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The official methods currently used by the FOOD AND DRUG ADMINISTRATION (1970) for multipesticide residue analysis employ chromatographic columns 22 mm i.d. x 300 mm containing about 4 inches or 25 g of Florisil as adsorbent. LAW and GOERLITZ (1970) used 5 mm i.d. x 14 cm microcolumns containing 3.0 cm of Florisil for the analysis of pesticides in water.

The purpose of this investigation was to evaluate the feasibility of miniature Florisil columns for separation of a representative variety of chlorinated pesticides. Standard materials were eluted through miniature columns and official columns simultaneously and recovery data were obtained for both. Pesticides evaluated included lindane, heptachlor, aldrin, heptachlor epoxide, dieldrin, endrin, p,p'-DDE, p,p'-TDE, p,p'-DDT, and endosulfan sulfate. The use of miniature columns, if found acceptable for routine analysis, would reduce analytical time and reagent costs, and would be ecologically advantageous in waste disposal.

## Experimental

### Reagents

(a) Florisil.--60-100 mesh PR grade commercially activated at 650°C (Floridin Co., New York, N.Y. 10022) and stored at 130°C in glass-stoppered flasks before use. The lauric acid value was calculated as specified by MILLS (1968).

(b) Sodium sulfate.--Anhydrous granular.

(c) Solvents.--Petroleum ether, ethyl ether containing 2% ethanol preservative, and hexane suitable for use in pesticide residue analysis. Commercial solvents distilled in glass may be used.

(d) Pesticide standards.--Lindane, heptachlor, aldrin, heptachlor epoxide, dieldrin, endrin, p,p'-DDE, p,p'-TDE, p,p'-DDT, and endosulfan sulfate supplied by the Environmental Protection Agency.

(e) Eluting mixtures.--94/6, 85/15, 50/50 (v/v) petroleum ether/ethyl ether.

## Apparatus

(a) Chromatographic columns.--10 mm i.d. x 300 mm with 24/40 joint at the top of the column and a coarse fritted disc and Teflon stopcock at the bottom (Kontes Glass Co., K-422450 or equivalent).

(b) Kuderna-Danish concentrators.--125 ml (Kontes Glass Co., K-570000) were used. Larger Kuderna-Danish concentrators may be used.

(c) GLC equipment.--The instrument used was a Packard Series 7800 Gas Chromatograph equipped with an electron capture detector and a 6 ft. x 4 mm i.d. column containing 10% DC-200 on 80/100 mesh Chromosorb WHP. Equipment and parameters used in this study for the GLC determinations were equivalent to those specified in the Official Method (1970). A detector sensitivity producing 1/2 full scale deflection for 1 ng of heptachlor epoxide was established.

## Column Preparation and Elution Procedures

The weight of Florisil used was determined by dividing 110 by the lauric acid value and multiplying by 4. This reduced weight (1/5 of the amount used in the official method) is based on the cross section area of the proposed column compared with the cross section area of the official column. The Florisil was added to the column and covered with a 2 cm layer of anhydrous sodium sulfate. The stopcock was turned wide open to allow a flow rate of 2-3 ml per min.

After the column was prewashed with 15 ml of petroleum ether, the sample was added in no more than 3 ml of petroleum ether. As soon as the sample solution reached a mark 1 cm above the sodium sulfate, the column was rinsed with 1 ml of petroleum ether. When the rinse reached the 1 cm mark, 35 ml of 94/6 solvent, 35 ml of 85/15 solvent, and 40 ml of 50/50 solvent were added sequentially, and each portion was allowed to reach the 1 cm mark before the next was added. Each fraction was collected in a Kuderna-Danish concentrator and evaporated to a volume suitable for GLC determination.

Since difficulties have been encountered in reproducing injections when petroleum ether is the final solvent, all fractions were concentrated to volumes allowing a major dilution with hexane before GLC injection.

## Results and Discussion

Table 1 and Table 2 give the range of recoveries, average recovery, and elution fraction for each tested pesticide using the miniature and the official Florisil column, respectively. The reported data are based on 6 determinations using the same lot of Florisil. A second lot of Florisil was checked and found to give results similar to those reported.

TABLE 1

% Recoveries of Chlorinated Pesticides Using Miniature Florisil Columns<sup>a</sup>

Pesticides	µg	94/6		85/15		50/50	
		Fraction Range	Av.	Fraction Range	Av.	Fraction Range	Av.
Lindane	5	98-102	100	-	-	-	-
Heptachlor	5	95-100	98	-	-	-	-
Aldrin	10	99-101	100	-	-	-	-
Heptachlor epoxide	10	97-99	98	Trace	-	-	-
Dieldrin	15	-	-	88-98	95	Trace	-
Endrin	15	-	-	91-99	97	Trace	-
p,p'-DDE	4	97-102	100	-	-	-	-
p,p'-TDE	4	97-100	99	-	-	-	-
p,p'-DDT	4	93-101	98	-	-	-	-
Endosulfan sulfate	5	-	-	-	-	86-100	94

<sup>a</sup>Trace: Less than 5% on one or more trials.

The results show that the miniature Florisil column will separate the tested chlorinated pesticides in the same manner as the official Florisil column. Recoveries obtained from miniature columns ranged from 86 to 102% of theoretical value. Recoveries obtained from official Florisil columns under simultaneous conditions ranged from 83 to 107% of theoretical values. The amounts of reagents used for the miniature column are approximately 20% of the amounts necessary for the official method. The elution time for 94/6, 85/15, and 50/50 (v/v) of petroleum ether/ethyl ether fractions is approximately 1 hr for the miniature Florisil column and approximately 3 hr for the official Florisil column. The study presented is limited to standards only at this time and should not be construed as an alternative method for official methodology. The author is investigating the use of miniature Florisil columns in the isolation of pesticide residues from various food commodities.

TABLE 2

% Recoveries of Chlorinated Pesticides Using Official Method  
Florisil Columns<sup>a</sup>

Pesticides	µg	94/6		85/15		50/50	
		Fraction Range	Av.	Fraction Range	Av.	Fraction Range	Av.
Lindane	5	92-100	95	-	-	-	-
Heptachlor	5	85-99	92	-	-	-	-
Aldrin	10	91-100	97	-	-	-	-
Heptachlor epoxide	10	93-107	100	-	-	-	-
Dieldrin	15	-	-	94-103	98	Trace	-
Endrin	15	-	-	94-103	99	Trace	-
p,p'-DDE	4	83-103	95	-	-	-	-
p,p'-TDE	4	90-106	96	-	-	-	-
p,p'-DDT	4	92-101	96	-	-	-	-
Endosulfan sulfate	5	-	-	-	-	93-103	95

<sup>a</sup>Trace: Less than 5% on one or more trials.

#### References

- LAW, L.M., and GOERLITZ, D.F.: J. Ass. Offic. Anal. Chem. 53, 1276-1285 (1970).
- MILLS, P.A.: J. Ass. Offic. Anal. Chem. 51, 29-32 (1968).
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