Application of the Rapid Micromethod of Sample Cleanup for Gas Chromatographic Analysis of Common Organic Pesticides in Ground Water, Soil, Plant and Animal Extracts[1]

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A rapid micromethod of sample cleanup for the analysis of aldrin, heptachlor, heptachlor epoxide, dieldrin, endrin, parathion, diazinon, and malathion has been reported recently (3). The cleanup procedure, using high purity grade silica gel, has been extended to include several additional pesticides.

Materials and Methods

Reagents and Equipment. Unless otherwise indicated, materials and equipment were the same as previously mentioned

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(3). The pesticides used were analytical grades of DDT isomers (o,p'; p,p'), DDD, DDE, methoxychlor, thimet, methyl parathion, ronnel, BHC isomers (Alpha, Beta, Delta), lindane, thiodan, telodrin, toxaphene, chlordane, ovex, perthane, Kelthane and Sevin, kindly furnished by various pesticide manufacturers. Those pesticides were added to extracts of ground water, soil, animal and plant tissues at 0.01 or 0.1 ppm level depending on sensitivity of the gas chromatographic detector for the pesticide. Eluting solvents were 7%, 20%, 30%, 40%, 60%, 80% (v/v) solutions of benzene in hexane, and benzene. All solvents were nanograde (Mallinckrodt Chemical, St. Louis, Mo.).

Procedure. The method used was identical with that previously published (3) except for the different eluting solvents, indicated in Table I. Total volumes of 4, 6, and 8 ml were collected separately and analyzed for pesticide residue content by gas liquid chromatography. Pesticide residue recoveries were determined by comparing of retention time and peak area of each pesticide with that of a known quantity of pesticide in hexane added to the precleaned extract.

Results and Discussion

The study was undertaken to show that the rapid micromethod of sample cleanup using activated silica gel, high purity grade 950, with some modifications, can be used for residue cleanups of pesticides listed in Table I. Total recovery of pesticide residues was obtained in the 8 ml elution for all pesticides used except methyl parathion and Kelthane (Table I) where a 12 ml elution mixture was needed to achieve 100% recovery. Thiodan was eluted from the chromatographic microcolumn as two isomers at different rates. Almost total recoveries for both isomers were obtained using 8 ml of 80% (v/v) benzene in hexane.

TABLE I

Selective elution of insecticides from microcolumns packed with 1 gm silica gel

Pesticide	Solvent system	Distribution in eluate, % recovery estimated from GLC		
		4 ml	6 ml	8 ml
DDE	7% (v/v) benzene in hexane	(a) 88 ± 4	100 ± 0	100 ± 0
o,p' DDT	7% (v/v) benzene in hexane	60 ± 7	100 ± 0	100 ± 0
p,p' DDT	7% (v/v) benzene in hexane	39 ± 2	100 ± 0	100 ± 0
DDD	20% (v/v) benzene in hexane	42 ± 4	91 ± 1	98 ± 1
Methoxychlor	100% (v/v) benzene	35 ± 4	78 ± 3	100 ± 0
Thimet	100% (v/v) benzene	52 ± 4	95 ± 2	100 ± 0
Methyl parathion	100% (v/v) benzene	3 ± 1	47 ± 4	88 ± 3
Ronnel	60% (v/v) benzene in hexane	70 ± 5	97 ± 1	100 ± 0
BHC Alpha	30% (v/v) benzene in hexane	78 ± 7	100 ± 0	100 ± 0

TABLE I (concl.)

Pesticide	Solvent system	Distribution in eluate, % recovery estimated from GLC		
		4 ml	6 ml	8 ml
BHC Beta	40% (v/v) benzene in hexane	91 ± 6	100 ± 0	100 ± 0
BHC Delta	40% (v/v) benzene in hexane	64 ± 6	99 ± 1	100 ± 0
Lindane	40% (v/v) benzene in hexane	71 ± 7	100 ± 0	100 ± 0
Thiodan (low m.p. isomer)	80% (v/v) benzene in hexane	87 ± 7	95 ± 4	98 ± 1
Thiodan (high m.p. isomer)	80% (v/v) benzene in hexane	16 ± 5	85 ± 7	100 ± 0
Trithion	60% (v/v) benzene in hexane	32 ± 2	88 ± 1	100 ± 0
Telodrin	30% (v/v) benzene in hexane	90 ± 4	98 ± 1	99 ± 0
Chlordane	20% (v/v) benzene in hexane	97 ± 2	100 ± 0	100 ± 0
Ovex	80% (v/v) benzene in hexane	89 ± 3	100 ± 0	100 ± 0
Perthane	40% (v/v) benzene in hexane	95 ± 2	100 ± 0	100 ± 0
Kelthane	80% (v/v) benzene in hexane	87 ± 3	89 ± 1	93 ± 3

(a) Recovery is the average of 4 replicates to nearest percent.

The broad peaks of toxaphene, which could not be resolved into soluble peaks, were obtained; therefore, determining percentage recovery was impossible. However, the broad peaks were eluted from the silica gel microcolumns using 30% benzene in n-hexane solvent mixture. Although the peaks of chlordane were broad, recovery data could be determined. Low solubility of Sevin residue in n-hexane made it impossible to subject Sevin to the procedure.

During experimental testing, only traces of plant pigments were present in the eluate of the pesticides tested and the pigments did not interfere with the gas chromatography. The low polarity plant pigments could be eliminated by eluting the microcolumns with 2% benzene in hexane prior to the eluting of all pesticides studied except DDE, o,p' DDT, p,p' DDT.

In order to isolate pesticides from large amounts of fats and waxes, partitioning between solvents as advocated by Jones and Riddick (2) and Burchfield and Storrs (1) may be used prior to column chromatography. All tested pesticides have successfully been separated and detected quantitatively at 0.01 ppm level in soil, plant and animal tissues and at 0.01 ppb level in water extracts

The principal advantages of this method lie in (a) its simplicity which permits many samples to be handled routinely; (b) the high purity silica gel grade 950 microcolumns are effective and economical; and (c) interfering nonvolatile substances like waxes and fat residue are removed, thus extending gas chromatographic column life and also improving chromatographic results. It is hoped that the procedure will also be found advantageous for cleaning up other pesticides prior to paper, thin layer, and gas chromatographic analyses.

References

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