Ex. 7

# Behavior of Chlorinated Naphthalenes in Analytical Methods for Organochlorine Pesticides and Polychlorinated Biphenyls

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**Chlorinated naphthalenes are industrial chemicals with properties similar to those of polychlorinated biphenyls (PCB); they are recovered from foods by analytical methods for multiple residues of organochlorine pesticides. The chlorinated naphthalenes may interfere with the gas chromatographic determination of several organochlorine pesticides. A silicic acid column chromatographic method previously developed to separate PCB from organochlorine pesticide residues, particulary DDT and its analogs, also separates chlorinated naphthalenes from the pesticides and permits GLC determination without interference.**

Chlorinated naphthalenes are industrial chemicals with a variety of suggested uses related to their electrical, flame retardant, and fungus-resistant properties, stability, and compatibility with other materials (1). Many of their physical properties and suggested uses are similar to those of polychlorinated biphenyls (PCB) (2). Residues of PCB have been found in various wildlife samples, particularly fish and fish-eating birds (3). PCB are recovered by multipesticide residue methods and may interfere in the gas chromatographic determination of organochlorine pesticides. To eliminate this possible interference, a method to separate PCB from pesticides was developed and reported (4). Gas chromatography of chlorinated naphthalenes also results in multicomponent chromatograms with the similar possibility of interference in analysis of organochlorine pesticides.

Work was done to determine the behavior of chlorinated naphthalenes in the Food and Drug Administration's multipesticide residue methods (5) and to establish that these chemicals can be separated from organochlorine pesticides by silicic acid column chromatography (4).

## Results and Discussion

Three Halowaxes® (chlorinated naphthalenes manufactured by Koppers Company Inc.), were chosen as representative chlorinated naphthalenes for this study. Halowax 1014 is a mixture of tetra-, penta-, and hexachloronaphthalenes; Halowax 1051 is octachloronaphthalene; Halowax 1099 is a mixture of trichloro- and tetrachloronaphthalenes (1).

Gas chromatography of the Halowaxes showed that the GLC behavior of the chlorinated naphthalenes is similar to that of the organochlorine pesticides. Retention time and response data for the three Halowaxes on two columns with electron capture detection are given in Table 1. Gas chromatographic conditions are those used for organochlorine pesticide residue analysis (5). The components of Halowax 1014 chromatograph throughout the retention time region of the organochlorine pesticides (retention times relative to aldrin, 0.5 to 6). Halowax 1099 exhibits peaks in the region of early eluting pesticides (retention times relative to aldrin, 0.5 to 2), and Halowax 1051 chromatographs beyond the retention times of common pesticides (retention time relative to aldrin, 11).

Study of the Florisil column chromatographic cleanup (5) showed that Halowaxes 1014 and 1099 were completely eluted by 200 ml 6% ethyl ether-petroleum ether. Halowax 1051 was found in both eluates from successive 200 ml elutions with 6 and 15% ethyl ether-petroleum ether. A number of the organochlorine pesticides, including DDT and its analogs, are also eluted by 6% ethyl ether-petroleum ether.

Halowax 1014 was chosen for experiments to determine recovery through the Food and Drug Administration's multiresidue methods (5). Fifty µg Halowax 1014 was added to 100 g samples of fish, milk, and spinach, and the samples were extracted and cleaned up by the appropriate methods (5). Gas chromatography with electron capture detection (5) was used for the determination. Recoveries from fish, milk, and spinach were 67, 68, and 90%, respectively. Low recoveries of Halowax 1014 from fish and milk resulted from unfavorable partitioning between petroleum ether and acetonitrile. These results show that chlorinated naphthalenes would be recovered by the multipesticide residue methods

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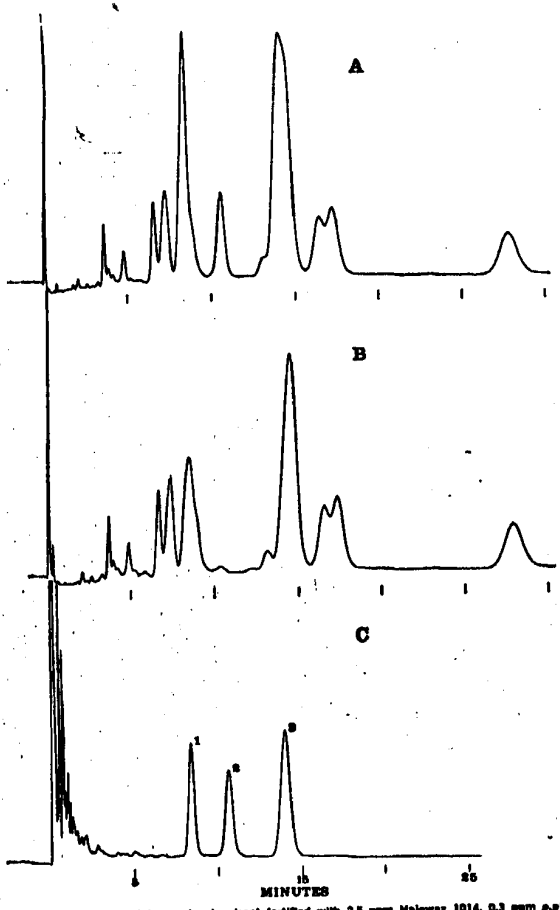


FIG. 1—GLC curves of brown trout extract fortified with 2.5 ppm Halowax 1014, 0.3 ppm p,p'-DDT, and 0.2 ppm p,p'-TDE and containing 0.19 ppm p,p'-DDE residue, before and after separation on silicic acid column. 1A: Before separation. 1B: Petroleum ether eluate from silicic acid column containing chlorinated naphthalene. 1C: Polar eluate from silicic acid column containing (1) p,p'-DDE, (2) p,p'-TDE, and (3) p,p'DDT. 10 mg sample injected for each curve. GLC conditions: same as those given in Table 1.



Table 1. GLC data for

| Compound | Response, ng Approx. Amt for ½ FSD | Rate |
|---|---|---|
| Halowax 1099 | 25 | 0.45, 0.79, 1.16, 1.88 |
| Halowax 1014 | 25 | 0.45, 1.57, 3.99, |
| Halowax 1051 | 10 | 11.3 |

[a] GLC columns: glass, 80-100 mesh Chromosorb QF-1 on 80-100 mesh Chro ditions: $N_2$ flow, 120 ml/m perature, 200°C; injector t design electron capture to produce ½ full scale d chlor epoxide when full s

and thus could interfe organochlorine pestici

The silicic acid col dure developed for s ganochlorine pesticide separation of the chlo pesticides. Fifty μg 1051, and 1000 were acid columns. Silicic a columns were eluted a Burke (4). Each Halow from the column by th

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Table 1. GLC data for chlorinated naphthalenes[a]

| Compound | Response, ng | Retention Times Relative to Aldrin | |
|---|---|---|---|
| | Approx. Amt for ½ FSD | 10% DC-200 Column | 1:1 10% DC-200/15% QF-1 Column |
| Halowax 1099 | 25 | 0.45, 0.57, 0.65, 0.71, 0.79, 0.86, 0.91, 1.04, 1.14, 1.23, 1.44, 1.57, 1.89 | 0.49, 0.65, 0.73, 0.82, 0.96, 1.14, 1.26, 1.46, 1.67, 1.96 |
| Halowax 1014 | 25 | 0.45, 0.79, 1.04, 1.43, 1.57, 1.82, 2.85, 3.12, 3.58, 3.73, 6.0 | 0.49, 0.83, 1.15, 1.45, 1.61, 1.93, 2.80, 3.16, 3.68, 3.84, 6.9 |
| Halowax 1051 | 10 | 11.9 | 10.8 |

[a] GLC columns: glass, 6' × 4 mm id; 10% DC-200 on 80-100 mesh Chromosorb W-HP, and 1:1 10% DC-200/15% QF-1 on 80-100 mesh Chromosorb W-HP. Operating conditions: $N_2$ flow, 120 ml/min; column and detector temperature, 200°C; injector temperature, 225°C. Concentric design electron capture detector operated at dc voltage to produce ½ full scale deflection (FSD) for 1 ng heptachlor epoxide when full scale deflection is $1 \times 10^{-9}$ amp.

and thus could interfere in the determination of organochlorine pesticides.

The silicic acid column chromatographic procedure developed for separating PCB from organochlorine pesticides (4) was evaluated for separation of the chlorinated naphthalenes from pesticides. Fifty μg each of Halowaxes 1014, 1051, and 1099 were placed on individual silicic acid columns. Silicic acid was prepared and the columns were eluted as described by Armour and Burke (4). Each Halowax was completely eluted from the column by the 250 ml petroleum ether eluant; PCB are recovered in this eluate. No Halowax was found in the acetonitrile-hexane-methylene chloride eluate; most of the common organochlorine pesticides are recovered in this eluate.

Figure 1 shows the silicic acid column separation of Halowax 1014 from *p,p'*-DDT, *p,p'*-TDE, and *p,p'*-DDE. Halowax 1014 (50 μg), *p,p'*-DDT (6 μg), and *p,p'*-TDE (4 μg) were added to a cleaned up extract of brown trout equivalent to 20 g. The trout contained a residue of 0.19 ppm *p,p'*-DDE. The fortified Florisil column eluate was placed on the silicic acid column and eluted with petroleum ether and acetonitrile-hexane-methylene chloride as described above. Each eluate was analyzed by gas chromatography with electron capture detection. Recovery of Halowax 1014 was 91% in the petroleum ether eluate; *p,p'*-DDT and *p,p'*-TDE recoveries were 100 and 91%, respectively, in the acetonitrile-hexane-methylene chloride eluate. The residue of *p,p'*-DDE was also completely separated into the second eluate.

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## References

(1) Halowax® Chlorinated Naphthalenes, Technical Bulletin, Koppers Co., Inc., Tar Products Division, Pittsburgh, Pa.

(2) Aroclor® Plasticizers, Technical Bulletin O/PL-300, Monsanto Co., St. Louis, Mo.

(3) Risebrough, R. W., Reiche, P., and Olcott, H. S., *Bull. Environ. Contam. Toxicol.* 4, 192–201 (1969).

(4) Armour, J. A., and Burke, J. A., *JAOAC* 53, 761–768 (1970).

(5) *Pesticide Analytical Manual*, Vol. I, Food and Drug Administration, Washington, D.C., 1969.

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