Element Specific Gas Chromatographic Analyses of Organochlorine Pesticides in the Presence of PCB's by Selective Cancellation of Interfering Peaks

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Polychlorinated biphenyl interference-free qualitative and quantitative gas chromatographic (gc) analyses of β-BHC, oxychlordane, heptachlor epoxide, p,p'-DDE, o,p-DDT, p,p'-DDD, p,p'-DDT, and Mirex in the 10–25 ng range have been carried out in the presence of approximately 10 to 20 times their concentrations of Aroclors 1232, 1248, 1254, and 1260 by the use of the Coulson electrolytic conductivity detector in the noncatalytic reductive mode. No modification of the detector system was necessary except to set the detector's reactor temperature at 660°. The results on individual analyses in most instances were within ±20% of the actual value.

The belated recognition of polychlorinated biphenyls (PCB's) as a source of potential threat to the ecosystem, coupled with their large-scale employment (about 600 million lb manufactured in the U. S. between 1960 and 1970), has resulted in the inadvertent introduction of enormous amounts of PCB's into the environment (Broadhurst, 1972; Jensen, 1966). Consequently, PCB's have been found in wildlife and humans in most of the so-called advanced regions of the world (Holmes et al., 1967; Koeman et al., 1969; Price and Welch, 1972; Risebrough and de Lappe, 1972; Risebrough et al., 1968; Widmark, 1967; Yobs, 1972).

There are a total of 210 PCB isomers with varying boiling points, gc retention times (Cook, 1972), and toxicities (Bitman et al., 1972; Hoopingarner et al., 1972; Zitko, 1972). They interfere in the gc determination of virtually all organochlorine pesticides (Fishbein, 1972; Reynolds, 1969; Zitko et al., 1971). This has given rise to much controversy in pesticide analyses (Reynolds, 1969) and may be the principal reason for the difficulty in recognizing PCB's as environmental contaminants.

Attempts to separate organochlorine pesticides from PCB's have largely been unsatisfactory. Existing methods of separation are either inefficient and time-consuming or subject to problems of reproducibility (Armor and Burke, 1970, 1971; Porter and Burke, 1971). Quantification of organochlorine pesticides has, thus, often been shrouded in clouds of uncertainty and controversy.

Recently, two methods have been reported for the rapid, interference-free detection of organochlorine pesticides known to be contaminated with PCB's.

The first method involves the irradiation of a pesticide–PCB mixture (Leavitt et al., 1973). It takes advantage of the fact that PCB's are photochemically degradable to mono- and dichlorobiphenyls (Ruzo et al., 1972), which have shorter gc retention times than many organochlorine pesticides or their photoproducts.

The second method calls for modification of the Coulson conductivity detector for gc and its operating parameters (Dolan et al., 1972). The paper discusses the detection of dieldrin and heptachlor in the 100-ng range in the presence of Aroclor 1254. No mention was made of any attempt to quantify the two pesticides studied.

The Coulson conductivity detector is a versatile element-specific gc detector (Coulson, 1966) which can be operated in the oxidative mode or in the reductive mode with or without a catalyst (Tracor, Inc., 1971). The proper choice of operating conditions may enable it to achieve selective cancellation of interfering peaks (SCIP).

In this paper, data are presented concerning the utility of the conductivity detector in the qualitative and quantitative analyses of organochlorine pesticides in the presence of PCB's.

EXPERIMENTAL SECTION

Materials. All organochlorine pesticides and Aroclors were analytical standards obtained from the Perrine Primate Laboratory, E.P.A., Perrine, Fla. They were used as received.

Gas Chromatograph. A Micro-Tek (Tracor, Inc.) Model 220 gas chromatograph equipped with a Coulson conductivity detector, Vycor glass inserts at the injection port for off-column injection, and U-shaped 6 ft × ¼ in. o.d. pyrex glass columns were used. The column packings (supplied by Perrine Primate Laboratory) were 1.5% OV-17/1.95% QF-1 on 60–80 Chromosorb W HP. Carrier gas flow rate was 70 ml/min.

Operating Parameters. The operating parameters of the Coulson conductivity detector for gc in the noncatalytic reductive mode are as follows: conductivity bridge voltage, 30 V; conductivity bridge attenuation, 1; furnace (reactor) temperature, 660–840°; transfer block temperature, 250°; hydrogen flow rate through reactor, 40 ml/min; nitrogen flow rate through reactor, 100 ml/min; gas chromatograph column temperature, 200°; sample size, 5 μl.

All operating parameters, except for the reactor temperature, were kept constant for all the experiments.

RESULTS AND DISCUSSION

The Coulson electrolytic conductivity detector gives sharp symmetric peaks much like those observed for other detector systems. The magnitude of detector response is a function of the conductivity of the species being analyzed.

Organochlorine compounds can be noncatalytically reduced at high temperatures to hydrogen chloride and methane with hydrogen in a quartz tube (the reactor). Hydrogen chloride elicits excellent detector response, while methane is inert to the detector. By varying the reactor temperature and/or reactor gas ratios or flow rate, a variety of pyrolytic products, often nonconducting, may be obtained (Tracor, Inc., 1971). Thus, in a mixture of organochlorine compounds, some could be rendered undetectable while the rest are still readily detectable by appropriate manipulation of operating parameters.

A good linear relationship was observed for peak height vs. pesticide concentration at both 830° and 660° for β-BHC, oxychlordane, heptachlor epoxide, p,p'-DDE, o,p-DDT, p,p'-DDD, p,p'-DDT, and Mirex. Typical results are shown in Figures 1 and 2. Furthermore, the detector

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Table I. Detector Reproducibility at Various Temperatures

	Detector response[a]			
Pesticides	830°	800°	710°	660°
β-BHC	113 ± 5	85 ± 3	95 ± 19	75 ± 10
Oxychlordane	66 ± 2	70 ± 5	80 ± 8	74 ± 10
Heptachlor epoxide	68 ± 3	77 ± 3	85 ± 7	77 ± 8
p,p'-DDE	80 ± 2	50 ± 6	43 ± 14	16 ± 6
o,p-DDT	34 ± 2	33 ± 2	29 ± 7	22 ± 1
p,p'-DDD	28 ± 1	19 ± 2	20 ± 7	12 ± 4
p,p'-DDT	44 ± 1	41 ± 2	39 ± 10	31 ± 5
Mirex	65 ± 3	79 ± 7	71 ± 4	39 ± 4

[a] Arbitrary units; average of at least three determinations ±50% of range.

Table II. Approximate Lower Limit of Detection of Some Organochlorine Pesticides[a]

Pesticides	Lower detection limit,[b] ng
β-BHC	1.2
Oxychlordane	1.4
Heptachlor epoxide	1.7
p,p'-DDE	4.1
o,p-DDT	2.5
p,p'-DDD	3.0
p,p'-DDT	4.2
Mirex	3.0

[a] Reactor temperature at 830°; all other operating parameters as in Experimental Section. [b] Limit of detection arbitrarily set at 3% of full scale.
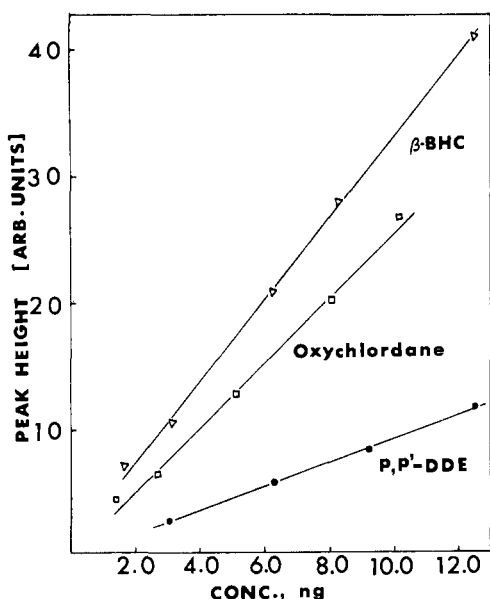

Figure 1. Typical data for peak height vs. concentration for some organochlorine pesticides at 830°.

Table III. Approximate Lower Limit of Detection of Some Common Aroclors (PCB's)[a]

Aroclor	Lower detection limit,[b] ng
1232	26
1248	24
1254	22
1260	42

[a] Reactor temperature at 830°; all other operating parameters as in Experimental Section. [b] Limit of detection arbitrarily set at 4% of full scale of the most intense peak.
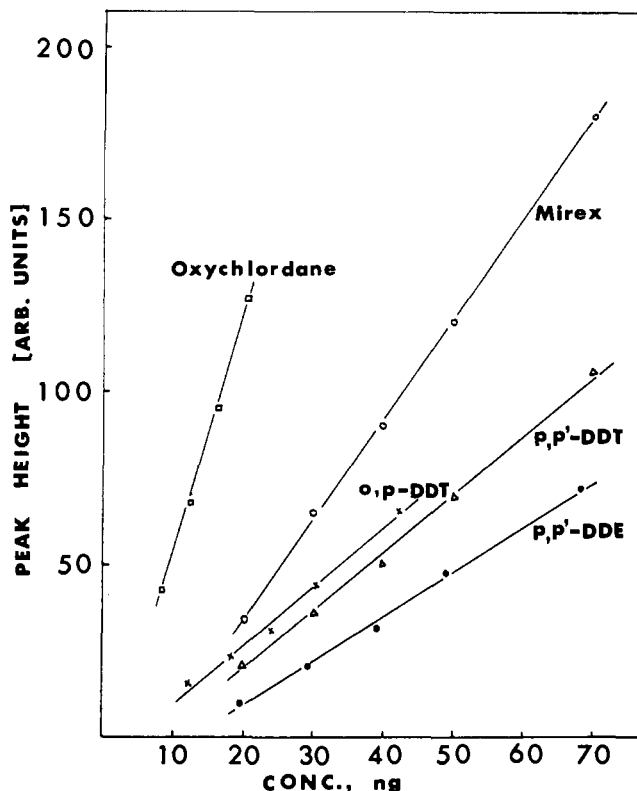

Figure 2. Typical data for peak height vs. concentration for some organochlorine pesticides at 660°.

III. These limits are arbitrarily set at 3% of full scale for the pesticides (single gc peak) and at 4% of the most intense peak of a particular Aroclor (multiple gc peaks). As in other detection systems, the sensitivity may vary from day to day, and the limits should only be viewed as approximate values.

It was observed that at 660°, the pesticides elicited almost the same detector response as at 830°. Of the pesticides studied, p,p'-DDE displayed the largest decrease in detector response and reproducibility. PCB's, which differ from the other pesticides in that they contain only phenyl chlorines, cannot be detected at 660° at the 200-ng level. By setting the detector temperature at 660°, and all other parameters being the same as in the Experimental Section, it is possible to carry out interference-free qualitative and quantitative analyses of the eight pesticides in the presence of the various Aroclors. Examples of the effect of reactor temperature on pesticides and PCB's are shown in Figures 3 and 4. In each figure, A is the chromatogram of an Aroclor, B is the chromatogram of a mixture of β-BHC, oxychlordane, heptachlor epoxide, p,p'-DDE, o,p-DDT, p,p'-DDD, p,p'-DDT, and Mirex, C is the chromatogram of the pesticide-Aroclor mixture at 830°, and D is the chromatogram of the pesticide-Aroclor mix-

exhibited good reproducibility between 830° and 710° for organochlorine pesticides. At 660°, there was a slight decrease in reproducibility, but in most instances it was within ±20% although, as would be expected, the range may be somewhat larger for smaller peaks (Table I).

The lower limits of detection of the eight organochlorine pesticides and the four Aroclors studied have been determined, and the results are summarized in Tables II and

Table IV. Determination of Pesticide Concentration in the Presence of Various Aroclors at 660°

| Mixture of pesticide–Aroclor	Determined pesticide concentration, ng				Actual pesticide concentration, ng
Aroclor (actual concn)	1232 (262.5 ng)	1248 (144.8 ng)	1254 (184.5 ng)	1260 (200.0 ng)	
β-BHC	10.5	10.0	9.8	10.2	10.2
Oxychlordane	10.2	9.5	10.2	8.7	10.2
Heptachlor epoxide	10.3	9.8	9.8	9.0	10.0
p,p'-DDE	27.0	24.5	24.7	21.0	24.5
o,p-DDT	16.1	14.6	15.6	17.4	15.1
p,p'-DDD	14.1	15.2	15.2	13.0	15.2
p,p'-DDT	24.2	26.2	24.4	21.4	25.0
Mirex	25.0	24.2	23.5	24.2	25.0
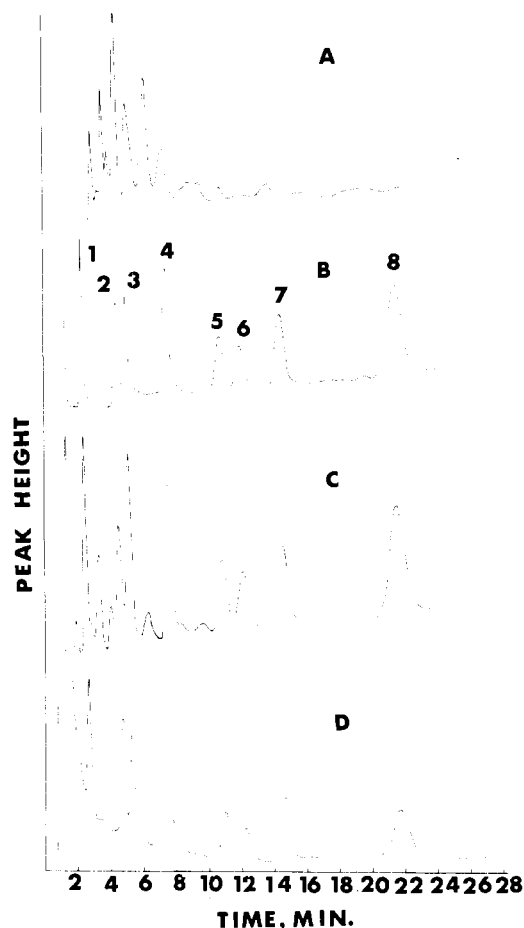
Figure 3. Gas chromatograms of PCB's (Aroclors) and pesticides using the Coulson conductivity detector. The detector's reactor temperature was set at 830° for A through C, and at 660° for D. A, Aroclor 1248 (144.8 ng). B, pesticide mixture: 1. β-BHC (10.2 ng); 2. oxychlordane (10.2 ng); 3. heptachlor epoxide (10.0 ng); 4. p,p'-DDE (24.5 ng); 5. o,p-DDT (15.1 ng); 6. p,p'-DDD (15.2 ng); 7. p,p'-DDT (25.0 ng); 8. Mirex (25.0 ng). C, mixture of A and B at 830°. D, mixture of A and B at 660°.
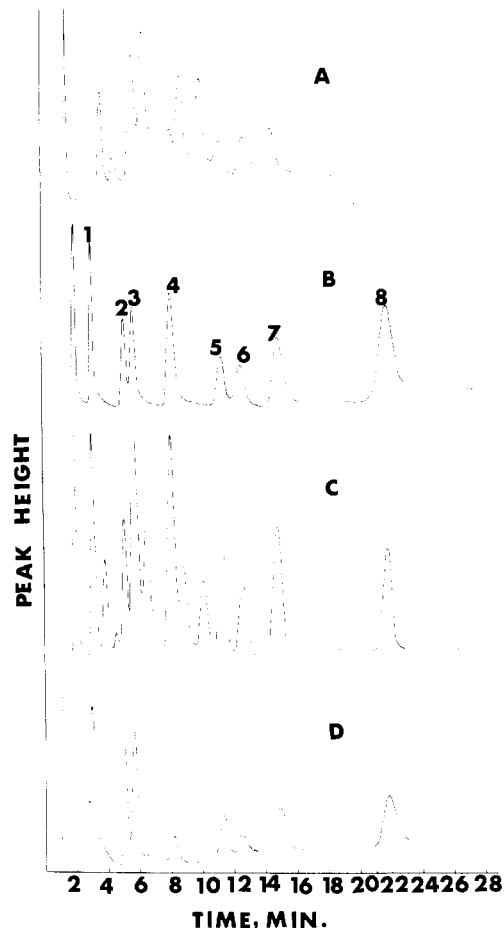
Figure 4. Gas chromatograms of PCB's (Aroclors) and pesticides using the Coulson conductivity detector. The detector's reactor temperature was set at 830° for A through C, and at 660° for D. A, Aroclor 1254 (184.5 ng). B, Pesticide mixture: 1. β-BHC (10.2 ng); 2. oxychlordane (10.2 ng); 3. heptachlor epoxide (10.0 ng); 4. p,p'-DDE (24.5 ng); 5. o,p-DDT (15.1 ng); 6. p,p'-DDD (15.2 ng); 7. p,p'-DDT (25.0 ng); 8. Mirex (25.0 ng). C, mixture of A and B at 830°. D, mixture of A and B at 660°.

ture at 660°. At 830°, the Aroclors clearly interfere with the pesticides, whereas at 660° it is evident that there is no PCB interference, since B and D are qualitatively the same. At 660°, the pesticide concentrations can readily be determined by comparison with standards run at 660°. Typical results are summarized in Table IV. Since the Aroclors are not detectable under these conditions in the 200-ng range, which is many times higher than ordinarily encountered, this method would appear to have wide applicability.

Within the limits of the capabilities set forth herein,

the Coulson detector appears to be a good, simple, and versatile tool for analyses requiring selective cancellation of interfering peaks. Specifically, it has been found useful for qualitative and quantitative analyses of organochlorine pesticides in the presence of PCB's without the uncertainty of PCB interference.

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Defluorination of Wagnerite Coproduced with Magnesium Phosphate Fertilizer

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Magnesium phosphate fertilizer (MGP), produced by the reaction between molten dehydrated carnallite and rock phosphate, consists mostly of trimagnesium phosphate ($Mg_3(PO_4)_2$) and wagnerite (Mg_2PO_4F), with lesser amounts of fluorapatite, MgF_2, MgO, and $CaCO_3$. Wagnerite is insoluble in water or in citric acid and can not be used as a fertilizer. The raw MGP has been submitted to a defluorination process. The experiments consisted of passing a flow of 3 l./ min of either air, oxygen, or nitrogen carrying 0.33 g/min of water over 2 g of MGP placed in an alumina boat inside an electrically heated tube furnace. Calcination was done at temperatures between 800–1000° for 1–12 hr. Complete defluorination of wagnerite was achieved after calcination at 1000° for 4 hr. The wagnerite decomposed to trimagnesium phosphate and magnesium oxide, increasing the citric acid solubility of MGP from 66 to 90%.

The agricultural value of a phosphate fertilizer is related to the percentage of P_2O_5 which is soluble in water or in 2% citric acid. The most important source for P_2O_5 is rock phosphate, which is composed mainly of francolite. The latter is chemically stable and its P_2O_5 content is only partially available to the plants. The fluorapatite structure may be broken either by acid treatment, as used for the manufacture of superphosphates, or by thermal treatment (Sauchelli, 1963). There are two different classes of thermal treatments. One is the defluorination of sintered rock in the presence of water vapor and silica at temperatures higher than 1300° (Elmore et al., 1942; Reynolds et al., 1934). The other is fusing the rock with different materials, such as silicates or sulfates, at temperatures higher than 1400°, followed by rapid cooling. The fluorine is not completely eliminated by this kind of treatment (Boylan and Larson, 1957; Bridger and Boylan, 1953; Walthall and Bridger, 1943).

A more recent method of producing soluble phosphates is by thermally reacting the rock with magnesium chlorides. The process was developed by IMI, Israel (Baniel et

al., 1965) and tried by Israel Chemicals Limited in a pilot plant in Sodom (Helberg and Zisner, 1972). The magnesium phosphate fertilizer (MGP) thus obtained, which is a mixture of soluble trimagnesium phosphate and insoluble wagnerite, served as raw material for the defluorination experiments reported in this work.

The aim of the present work was to study the defluorination process of the wagnerite in order to increase the amount of available phosphate in the MGP fertilizer. The HF which is liberated can be recovered and utilized. In the present work, the recovery of HF was not studied.

APPARATUS

All defluorination studies were performed in an experimental setup shown in Figure 1. The raw material was placed in an alumina boat (10) in a gas flow of 3 l./min, carrying with it 0.33 g of water/min. The water temperature at (6) was kept at 50 ± 1°. The temperature in the furnace was measured with Pt-Pt 10% Rh thermocouple (9) and kept within ±5° of the experimental temperature.

PROCEDURE

MGP produced at Sodom was sieved and only the fraction between 60 and 200 mesh was used in the investigation. A charge of about 2 g of MGP was placed in a boat.

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