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DETERMINATION OF CHLORINATED PESTICIDES AND POLYCHLORINATED BIPHENYLS BY DERIVATIZATION GAS CHROMATOGRAPHY

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SUMMARY

The determination of chlorinated pesticides and polychlorinated biphenyls (PCBs) in environmental samples is rapidly and efficiently achieved by the simultaneous use of gas chromatography and derivatization gas chromatography. The method is based on the different stabilities of chlorinated pesticides and PCBs towards magnesium oxide in a microreactor. Extracts of samples are injected twice, first into a regular gas chromatograph and then into a gas chromatograph equipped with a microreactor for derivatization. A "basic" chromatogram and a "derivatization" chromatogram are obtained and the combination of the two chromatograms provided a satisfactory solution.

INTRODUCTION

The determination of chlorinated pesticides and polychlorinated biphenyl (PCB) contaminants in the environment is usually carried out by application of gas chromatography (GC)[1,2]. GC has replaced thin-layer chromatography (TLC), which is not suitable for the detection of picogram amounts, and high-performance liquid chromatography (HPLC) is so far inapplicable to the determination of trace amounts of chlorinated compounds because the sensitivity of HPLC detectors is inadequate[3–5].

The GC determination of chlorinated pesticides together with PCBs is difficult, however. Chlorinated pesticides and PCBs are extracted together in routine residue analysis, and the GC retention times of several PCB peaks are almost identical with those of a number of peaks of chlorinated pesticides, notably of the DDT group. The PCB interference may vary, because the PCB mixtures used have different chlorine contents, but it is common for PCBs to be very similar to many chlorinated insecticides and the complete separation of chlorinated pesticides from PCBs is not possible by GC alone[6–10]. Fig. 1 illustrates the possibility of the interference of DDT-type compounds in the presence of PCBs.

Various liquid–solid column chromatographic techniques have been used prior to GLC detection for separating PCBs from chlorinated pesticides[11–13]. These procedures have the disadvantage in routine residue analysis that they require a con-

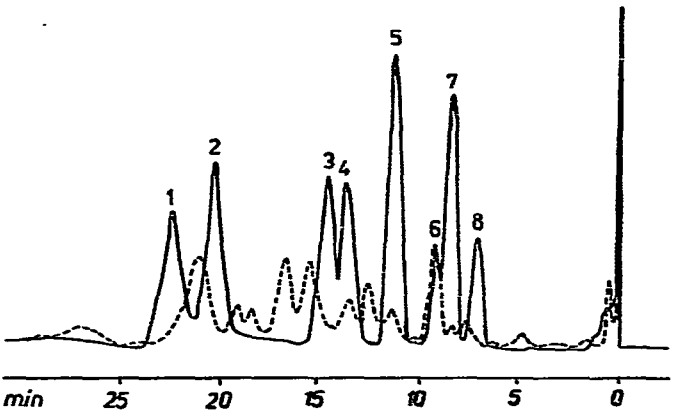

Fig. 1. Interference of DDT-type compounds in the presence of PCBs. GC column: 5% QF-1 on Gas-Chrom Q, 100–120 mesh. Solid line: 1 = *p,p'*-DDT; 2 = *p,p'*-DDD; 3 = *o,p*-DDT; 4 = *o,p*-DDD; 5 = *p,p'*-DDE; 6 = *p,p'*-DDMU; 7 = *o,p*-DDE; 8 = *o,p*-DDMU. Broken line: PCB Chlophen A 50.

siderable amount of time. Chemical derivatization of sample extracts[14] is very convenient in comparison with these methods. The extracts containing pesticides and PCBs, after the first injection into the gas chromatograph, are treated with derivatization reagents, the pesticides being converted into derivatives while the PCBs remain unchanged. Table I demonstrates the stability of chlorinated pesticides and PCBs towards reagents for chemical derivatization. The chemical derivatization of extracts is effected in separate test-tubes in the liquid phase. Many manipulations and a reaction time of about 30 min are necessary[15–18].

TABLE I

STABILITY OF CHLORINATED PESTICIDES AND PCBs

Substance	*Treatment with conc. H_2SO_4**	*Treatment with ethanolic KOH**
Aldrin	+	+
Dieldrin	−	+
Endrin	−	+
Endosulfan	−	−
HCH isomers	+	−
PCBs	+	+
p,p'-DDT	+	→*p,p'*-DDE
o,p-DDT	+	→*o,p*-DDE
p,p'-DDE	+	+
o,p-DDE	+	+
p,p'-DDD	+	→*p,p'*-DDMU
o,p-DDD	+	→*o,p*-DDMU
p,p'-DDMU	+	+
o,p-DDMU	+	+

* + = unchanged; − = decomposed (products of decomposition are not detected); → = dehydrochlorination to the olefin.

DERIVATIZATION BY THE MICROREACTOR TECHNIQUE

Derivatization chromatography proved to be a convenient method. Derivatization should be effected directly in the gaseous phase in a microreactor situated before the GC column[19]. Rapid derivatization in the gaseous phase for the determination of DDT metabolites and PCBs was first carried out in 1973 by means of catalytic reduction (carbon skeleton chromatography with hydrogen as carrier gas). This method has the disadvantage that a flame-ionization detector (FID) is used, which has insufficient sensitivity[20,21]. We have investigated the heat stability and reactivity of pesticides and PCBs to alkaline earth metal oxides in a microreactor, and used nitrogen as the carrier gas in order to make use of the high sensitivity of the electron-capture detector (ECD) for the detection of the resulting compounds. We found that only pre-heated magnesium oxide effects the rapid and quantitative dehydrochlorination of saturated DDT metabolites to the corresponding DDT olefins[22]. The derivatization products immediately obtained in the gaseous phase by means of the microreactor (with nitrogen as the carrier gas and magnesium oxide as the catalyst) are comparable with the products of chemical derivatization with an alkali in the liquid phase, and substances that are stable to treatment with alkali are also not decomposed in the microreactor (*cf.*, Table I). These results were used in a convenient on-line technique for the rapid, efficient and sensitive determination of chlorinated pesticides and PCBs.

EXPERIMENTAL

Two gas chromatographs (Chromatron GCHF 18.3-6) with an all-glass system and an ECD were used. One chromatograph was equipped with a microreactor for the derivatization GC (Fig. 2). The microreactor was screwed on to the inlet system of the gas chromatograph and was furnished with a glass tube for the catalyst. The reactor tube was heated by a resistance regulated by a thermocouple and a temperature control unit. The chromatographic conditions of both gas chromatographs were the same. We recommend the liquid phase QF-1 for the determination of DDT-type compounds and PCBs[23,24] and the mixed liquid phase 1.5% OV-17–1.95% QF-1 for the separation of chlorinated pesticides[25,26].

For derivatization GC, the magnesium oxide catalyst is placed in the glass tube of the microreactor. Magnesium oxide undergoes a 10% loss in weight on pre-heating, and we recommend its use without pre-heating; 40 mg of magnesium oxide produces a quantitative reaction, but this should be checked before the analysis and the amount varied if necessary. The microreactor was used for several months with no decrease in the activity of the magnesium oxide.

For the GC determination, aliquots of sample extracts are injected into both gas chromatographs. The injection into the first chromatograph gives a "basic" gas chromatogram and that into the second chromatograph, equipped with the microreactor, gives a "derivatization" gas chromatogram. The sample extracts are obtained by digestion with perchloric acid–acetic acid[27], extraction with *n*-hexane and clean-up with sulphuric acid.[28,29]

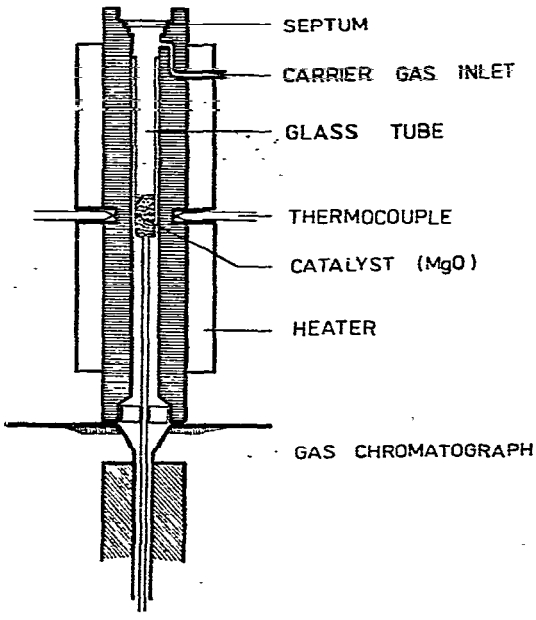

Fig. 2. Microreactor for derivatization gas chromatography.

RESULTS

A "basic" chromatogram of an extract of a fish sample is shown in Fig. 3. The peaks of γ-HCH and DDT metabolites appear, but the background suffers from interference from peaks of PCBs.

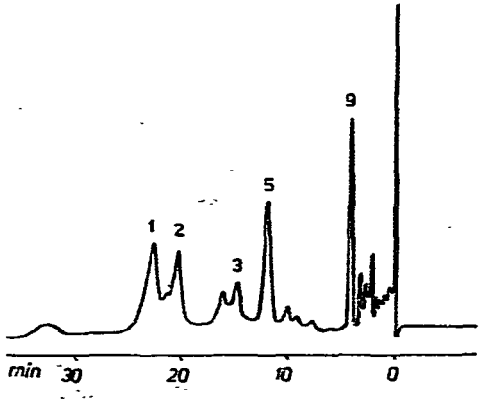

Fig. 3. "Basic" chromatogram of an extract of a fish sample. GC conditions: 5% QF-1 on Gas-Chrom Q, 100–120 mesh; glass column, 1.6 m × 3 mm I.D.; carrier gas, nitrogen at a flow-rate of 60 ml/min; detector, ECD. Peaks: 1 = *p,p'*-DDT; 2 = *p,p'*-DDD; 3 = *o,p*-DDT; 5 = *pp,'*-DDE; 9 = γ-HCH.

Fig. 4 shows the "derivatization" gas chromatogram of the same extract obtained by the procedure described above. After derivatization, the peaks of γ-HCH and the saturated DDT metabolites disappeared. The saturated DDT metabolites (*p,p'*-DDT, *p,p'*-DDD and *o,p*-DDT) are converted quantitatively into the corresponding DDT olefins (*p,p'*-DDE, *p,p'*-DDMU and *o,p*-DDE). The main peak in the "derivatization" gas chromatogram represents the sum of *p,p'*-DDT and *p,p'*-DDE from the "basic" chromatogram and is often sufficient for the determination of the total DDT content. The content of PCBs can be calculated in the "derivatization" gas chromatogram without interference effects due to saturated DDT metabolites.

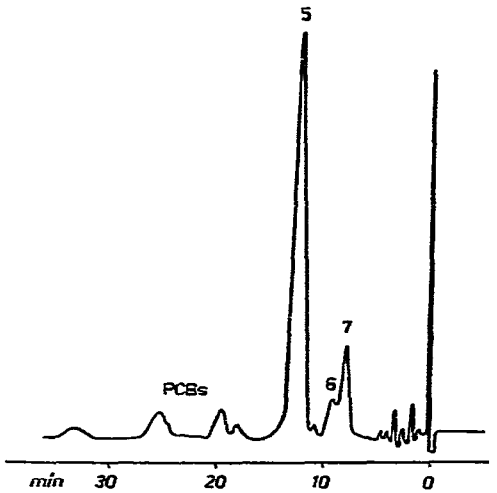

Fig. 4. "Derivatization" gas chromatogram of an extract of a fish sample from Fig. 3. GC conditions as in Fig. 3. Conditions for derivatization: temperature of microreactor, 225°; catalyst, magnesium oxide. Peaks: 5 = *p,p'*-DDE; 6 = *p,p'*-DDMU; 7 = *o,p*-DDE.

CONCLUSIONS

Derivatization in the gaseous phase by application of the microreactor (on-line) technique is convenient in comparison with chemical derivatization in the liquid phase (off-line technique). We used the different stabilities of chlorinated pesticides and PCBs towards magnesium oxide in a microreactor for derivatization GC. In our method, only two injections are needed for the determination of chlorinated pesticides and PCBs. After the first injection into a regular chromatograph, the "basic" gas chromatogram shows the presence and distribution of chlorinated pesticides and PCBs in the sample. A second injection into a gas chromatograph equipped with a microreactor (with magnesium oxide as catalyst) provides a "derivatization" gas chromatogram. By interpretation of the two chromatograms it is possible to eliminate peak interferences.

Derivatization gas chromatography provides the immediately efficient derivatization that is necessary in trace residue analysis[30,31]. The rapid, precise and sensitive determination of trace amounts of compounds is achieved by the simultaneous use of GC and derivatization GC.

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