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CARBON SKELETON–GAS CHROMATOGRAPHIC TECHNIQUES AND THEIR APPLICATIONS

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SUMMARY

The hydrodechlorination reaction whereby organochlorine compounds such as DDT, polychlorinated biphenyls, polychlorinated naphthalenes and polychlorinated alkanes are converted to their respective hydrocarbons, 1,1'-diphenylethane, biphenyl, naphthalene and *n*-alkanes, may be performed by placement of the catalyst in the injection port of the gas chromatograph. This method is suitable for relatively simple samples. For more complex mixtures, that is, those where the parent hydrocarbons are present in addition to the polychlorinated species, a forked column arrangement, allowing with and without catalysis quantitation to be performed, is necessary. For capillary gas chromatography, a simple off-column catalytic reactor system may be used.

This technique is particularly useful for the study of very complex polychlorinated alkane compounds.

INTRODUCTION

The determination of organochlorine residues such as DDT, aldrin, dieldrin and lindane in environmental samples became a complex problem with the discovery of polychlorinated biphenyls (PCBs) in raptorial birds and fish[1]. The multicomponent nature of PCB compounds caused considerable interference with the analysis of other organochlorine species when determined by conventional methods such as gas–liquid chromatography–electron-capture detector (GLC–ECD)[2]. The detection of other complex organochlorine species such as, polychlorinated naphthalenes (PCNs)[3], polychlorinated terphenyls (PCTs)[4] and toxaphene[5] served only to further complicate the problem of interference. The considerable use now made of polychlorinated alkanes (PCAs), which are extremely complex mixtures of isomeric polychlorinated compounds adds an extra dimension to the scope for potential interference. PCAs have yet to be detected in the environment, though bio-accumulation is known to take place[6], possibly because the complexity of these compounds renders them unsuitable for study by conventional methods (GLC–ECD).

To combat the complex nature of environmental extracts a multistep extraction and fractionation procedure has been devised[7,8]. However, compounds such as

PCBs are sufficiently complex for some components to remain in the same fraction as compounds such as DDT[2]. An alternative approach[9,10] has been to perchlorinate organochlorine species especially PCBs but this procedure does not appear particularly useful for the determination of other species in the presence of PCBs.

A radical alternative to this conventional approach was suggested by Thompson and co-workers[11–14]. Passage of organic compounds containing sulphur, nitrogen, oxygen or halogens over a heated catalyst in a stream of hydrogen yielded the respective parent hydrocarbons containing the carbon skeletons of the various organic compounds studied. Subsequently Beroza[15] developed the technique for gas chromatographic (GC) use and Asai *et al.*[16] applied the procedure to the qualitative analysis of organochlorine pesticides (OCPs) and PCBs. Zimmerli[17] then used this technique of carbon skeleton–GC for the study of PCBs, PCT, PCNs and OCPs some of which were found to be present in biological samples.

We have recently refined the technique of carbon skeleton–GC to a simple and reliable procedure that is easy to perform with conventional GC equipment[18]. Alliance of the catalytic hydrodechlorination reaction to GC–mass spectrometry (MS), together with the use of gas–solid chromatography to provide column durability and high thermal stability, has produced an analytical system which is versatile[19], precise[20] and extremely sensitive[21].

We now report on the various methods by which carbon skeleton–GC may be achieved together with some preliminary results of the applicability of the technique to the study of PCAs which present considerable difficulties when studied by conventional GLC–ECD methods.

EXPERIMENTAL

Reagents

All solvents were redistilled before use. Standard solutions were prepared in hexane. PCBs (Monsanto, Newport, Great Britain), PCNs (Bayer, Leverkusen, G.F.R.), Cereclors (I.C.I., Macclesfield, Great Britain) and OCPs (National Physical Laboratory, Teddington, Great Britain) were used as received. Catalysts and columns were prepared and conditioned as previously described[18].

Gas chromatography

GC separations were carried out on Pye Series 104 gas chromatographs fitted with either a dual-channel flame-ionisation detector (FID), a Ni^{63} ECD or interfaced to a VG Micromass 16B2 mass spectrometer via a single stage jet separator. Columns were either 2% RbCl on Chromosorb G (60–80 mesh) or 3% SE-30 Ultraphase (Phase Separations. Queensferry, Great Britain), on Gas-Chrom Q (Jones Chromatography, Glamorgan, Great Britain) (85–100 mesh) as required. N.B. 2% RbCl columns should not be used with ECDs. The carrier gas (hydrogen) flow-rate was 30 ml/min for GC–MS studies and 40 ml/min for normal GC studies. No hydrogen need be fed directly to the flame of the FID when this type of chromatography is performed. The column effluent (carrier gas) mixed with the correct amount of air (approximately 8-fold excess) sustains the flame in the detector.

Capillary GC was performed on a Carlo Erba (Erba Science, Swindon, Great Britain) 2150 Series instrument fitted with a Grob splitless injector. The follow-

ing parameters: column, 50 m 1% OV-1, nitrogen flow-rate, 2 ml/min; injection temperature, 275°; injection volume, 1 μl; temperature programme: 50° hold 3 min, increase 6° min^{-1} to 250°, then 8° min^{-1} to 300°, hold 3 min were used.

MS conditions were: interface temperature 280°, source temperature 200°, ionisation voltage 55 eV. Compounds were identified by comparison of mass spectra and retention time with authentic samples.

Catalysis equipment

Injection point heaters were modified by rewinding the heating element such that a temperature range of 50–350° was available. The power supply was a variable current transformer. The capillary catalysis system (Fig. 3) was constructed from a wide bore (5 mm) glass tube (10 cm length) packed with glass wool for insulation, containing a heating element wound round a central glass tube and aluminium liner (7 mm I.D.) sealed at both ends with a heat resistant cement.

RESULTS AND DISCUSSION

The principle of carbon skeleton–GC requires the removal of heteroatoms such as halide, nitrogen, oxygen or sulphur which are usually present as functional groups, *e.g.*, $-NH_2$, –OH, –SH from organic compounds accompanied by their replacements with hydrogen atoms such that the hydrocarbon species so generated retains the structure, *i.e.*, carbon skeleton, of the original species. The removal of functional groups promotes ease of chromatographic separation and eliminates the need for a separate chemical derivatization step. For example, where the original species are halo-organic compounds such as PCBs or polybrominated biphenyls catalytic hydrodehalogenation provides considerable matrix simplification as a single product (biphenyl) results from a complex mixture of isomeric and polyhalogenated biphenyl compounds. The removal of functional groups is achieved by passage of the organic compound in the vapour phase over a heated catalyst (usually a transition metal such as palladium or platinum) in a stream of hydrogen. It is therefore a heterogeneous, *i.e.*, gas–solid reaction which probably requires adsorption of the organic species onto the catalyst surface prior to chemical reaction. For a discussion of the possible mechanisms involved in this reaction see refs. 22 and 23. The technique is most commonly applied to the analysis of OCPs.

Equipment

We have previously reported[18] that carbon skeleton–GC may be performed by extending the GC column outside the GC oven such that the catalyst is contained in this external part of the column and thus heated by a separate small oven. Subsequent experiments have shown that this length of catalyst (about 10 cm) is unnecessary. In the arrangement displayed in Fig. 1 the catalyst (approximate length 2 cm) is contained in that portion of the column which is heated by the injection point heater. This procedure thus requires no modification of the GC column, neither does it necessitate a separate catalyst oven system. For experimental purposes however, we have modified the windings and power supply control to the injection point heater in order to achieve greater control over a wider temperature range. It should be stressed however, that for routine use involving, for example, a palladium

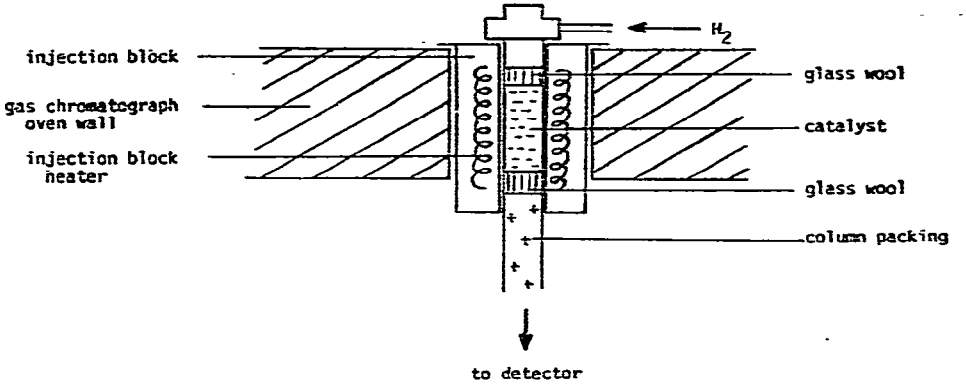

Fig. 1. Arrangement for on-column catalytic hydrodechlorination using injection point heater as reactor oven.

catalyst at 300° or a platinum catalyst at 200° this modification is unnecessary. The reduced amount of catalyst had no effect upon the efficiency of performance which appeared to be solely a function of temperature under the conditions normally employed (hydrogen flow-rate 30 ml/min). Presumably this observation reflected the high surface loading of hydrogen present[24] on the catalyst relative to the amount of organochlorine compound which was injected.

For complex samples, that is, those samples where the parent hydrocarbon of the compound under investigation (*e.g.*, an OCP) is present in addition to the chlorinated derivatives the apparatus displayed in Fig. 1 is not recommended. Its use would require the measurement of the concentration of hydrocarbon without catalysis followed by measurement with catalysis. The difference between the two levels may then be related to the concentration of the chlorinated species present. This time consuming procedure may be avoided by use of the column design illustrated in Fig. 2. The injection end of the column is modified to give two arms each of which passes through one of the injection point heating devices of a dual column gas chromatograph. A single gas flow (to avoid regulating two gas streams to approximately the same rate) is split into two and fed to the two arms of the column. Into one arm is packed the catalyst and the other is left empty except for a glass wool plug. The temperatures of the two arms are independently controlled by two injection point heaters. The column packing was usually 2% RbCl on Chromosorb G (60–80 mesh) and, in consequence, column bleed was negligible. Baseline drift was thus insignificant even though only a single column was used. A baseline shift of only *ca.* 10% f.s.d. was observed for the temperature range 50–300°. It should be emphasised that when hydrogen is used as a carrier gas the prevention of even small gas leaks is particularly important since small carrier gas leaks cause baseline drift during long temperature programmed runs. High quality septa should therefore be used and changed regularly since this is the most likely cause of leaks. Using this forked or V-column technique we have successfully analysed for PCBs and PCNs in complex environmental extracts[21] where both biphenyl and naphthalene were present at significant levels prior to catalysis together with a wide range of other polynuclear aromatic hydrocarbons. Injection onto the non-catalyst arm allowed measurement of the background levels of

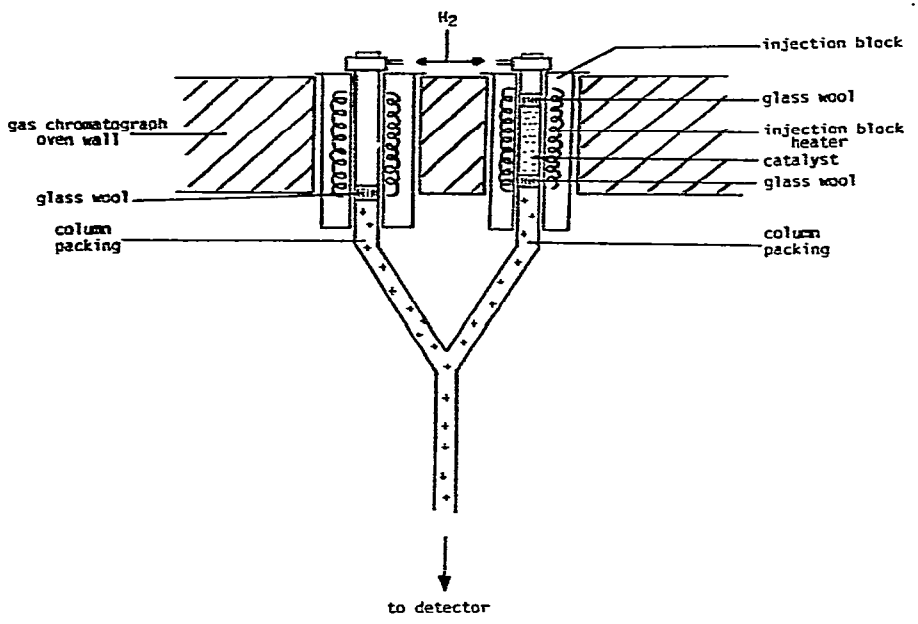

Fig. 2. Twin oven arrangement for with and without catalysis determination of hydrocarbons such as naphthalene and biphenyl.

these two hydrocarbons. Injection onto the catalyst gave the total concentration of the respective hydrocarbons. Identification and quantification was achieved using a mass spectrometer as a selective detector.

We have, as yet, been unable to modify the injection point of a capillary gas chromatograph to perform on-column catalytic conversions. However, the apparatus shown in Fig. 3 is suitable for the catalysis of samples prior to study by capillary GC. An aliquot (*ca.* 50 μl) is injected onto the catalyst over about 20 sec. The sample is swept through the catalyst and condenses in the cooled trap. A second injection of solvent (50 μl) is then made to flush any residual material from the apparatus into the trap. The trapped sample is then adjusted to known volume (normally 100 μl, *i.e.*, a two-fold dilution) and may be used for injection into the capillary gas chromatograph. This procedure, though effective, is not ideal. Recovery of organochlorine species such as PCB are only about 80–85% using the flushing procedure and only about 70–75% if a second injection of solvent is not made. Losses probably accrue from two sources. Less volatile material may condense on the colder parts of the trap before reaching the solvent at the bottom thus representing a loss to the solution. Extra injections of solvent may reduce this but may result in unacceptable dilution of the sample. A second possibility is incomplete conversion due to the relatively large sample volume (50 μl) employed.

That a dramatic simplification of a chromatogram may be achieved by this process is demonstrated in Fig. 4. Fig. 4A is the capillary gas chromatogram of a mixture of six organochlorine species of which two (a PCB and a PCN) are complex mixtures. Upon re-chromatographing the sample after micro-catalytic hydrodechlorination Fig. 4B was obtained. The simplified nature of the trace allows easy identifica-

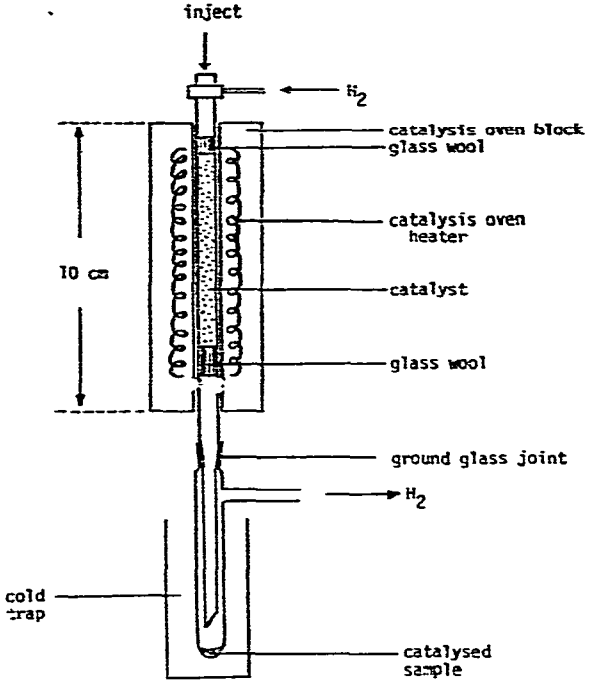

Fig. 3. Catalysis oven and trap arrangement for hydrodechlorination of samples (≈50 μl) prior to analysis by capillary GC.

tion of peaks due to naphthalene (1), from the PCN, to biphenyl (2) from the PCB and to diphenylethane (3) from DDT, DDE and TDE.

Application

A particular example where these techniques have proved useful for the study of compounds which represent a complex problem for GLC–ECD methods is the PCAs.

PCA mixtures are marketed in Great Britain by I.C.I. under the brand name "Cereclor" and in the U.S.A. by Hooker (Stamford, Conn.), Hercules (Wilmington, Del.) and Dover Chemical (Dover, Ohio) under the brand names CP40, Chorafin 40 and Chlorez 700, respectively. Cereclors are prepared by chlorination of a hydrocarbon fraction up to a known weight of chlorine in a similar manner to the preparation of PCBs. Three hydrocarbon fractions are used, C_{10}–C_{13}, C_{14}–C_{17} and C_{22}–C_{30}. The relative ratios of the components for the first two fractions are 1, 6.7, 6, 1.9 and 1, 4.2, 3.6, 3.0 based on peak area. It was more difficult to establish an accurate distribution for the C_{22}–C_{30} fraction on a RbCl packed column. By far the most commonly used Cereclor is S52 which contains 52% by weight of chlorine. It is prepared from the C_{14}–C_{17} hydrocarbon fraction. PCAs may be used as a cheaper substitute for phthalate plasticizers and should thus be ubiquitous in the environment. Other common uses include extreme pressures additives for gear oils and metal working lubricants, and flame retardant additives for paints, plastics, rubber and textiles.

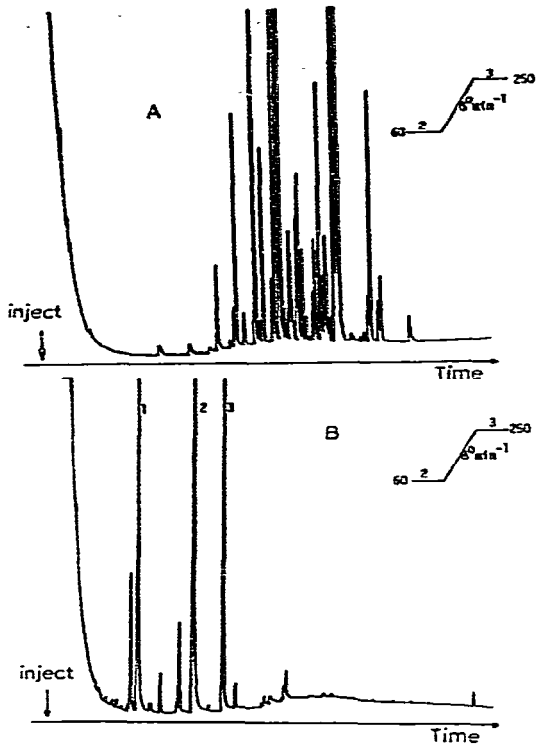

Fig. 4. Capillary GC traces of a mixture of Arochlor 1248 (10 ppm), D88 (a PCN) (10 ppm), aldrin (4.75 ppm), dieldrin (5 ppm), heptachlor (5.25 ppm), p,p′-DDT (4.25 ppm), p,p′-DDE (4.75 ppm) and p,p′-TDE (4.50 ppm) before catalysis (A) and after catalysis (B). Peaks: 1 = naphthalene, 2 = biphenyl, 3 = diphenylethane. Injection, 1 μl.

PCAs are reported to be non-toxic, non-accumulative and rapidly excreted but the analytical methods employed to reach these conclusions are not well defined. However, the non-aromatic nature of these compounds suggests that they may well give less cause for concern than their aromatic counterparts the PCBs and PCNs. The difficulties involved in studying PCAs by conventional GLC methods are shown in Fig. 5. Fig. 5A represents the chromatogram of S52 using an FID and Fig. 5B is the chromatogram obtained using an ECD. Obviously accurate quantitation is extremely difficult and qualitative identification is unlikely, if even a few co-eluting species, such as other organochlorine compounds are present. Fig. 5C is the FID chromatogram of S52 obtained by capillary GC. Fig. 5D is the FID trace of the hydrocarbon feedstock from which S52 is made. Fig. 5E is the trace obtained when S52 is injected onto a 3% palladium catalyst at 200°. Using this catalytic hydrodechlorination technique we have successfully converted some 13 different Cereclors back to their respective hydrocarbon feedstocks[25]. The presence of a PCA residue in a sample may thus easily be demonstrated by conversion back to the parent hydrocarbon accompanied by pattern recognition of the peaks so obtained. We have observed no interference when this is carried out in the presence of PCBs and PCNs (Fig. 5F). Detection at the ppm level may thus be obtained on a conventional gas chromatograph fitted

with an FID. Detection at the 10^{-9}g/g level or less may be achieved using GC–MS in the selective ion monitoring mode using high abundance fragments such as C_5, C_6 and C_7. A full account of the separation and determination of PCAs in complex mixtures will appear elsewhere[25]. Steam extraction after the method of Veith and Kiwus[26] employing a semi-micro extraction unit based on a design by Franklin and Keyzer[27] has successfully removed Cereclors from aqueous environmental samples.

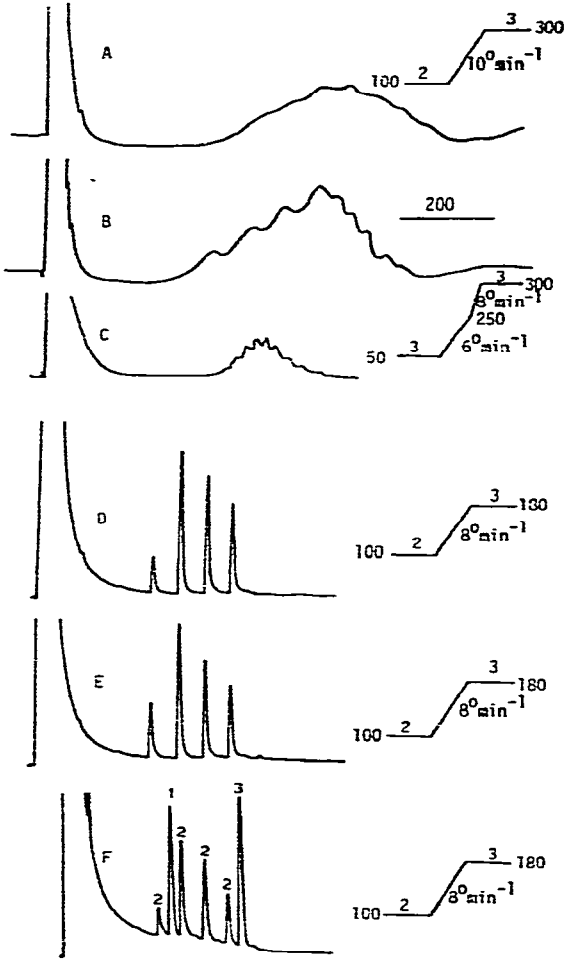

Fig. 5. (A) Chromatogram of Cereclor S52 (1 μl, 400 ppm) using an FID. Temperature programme diagrammatically illustrated is: initial temperature 100°, hold 2 min, then increase at 10° min^{-1} until 300°; then hold at 300° for 3 min. Column 3% SE-30 on Gas-Chrom Q. (B) Chromatogram of Cereclor S52 (1 μl, 10 ppm) using an ECD. Temperature 200°. Column 1.95% OV-17, 1.5% QF-1 on Gas-Chrom Q. (C) Capillary chromatogram of Cereclor S52 (1 μl, 200 ppm) using FID. Column 1% OV-101, 50 m. Flow-rate 2 ml/min. (D) Chromatogram of hydrocarbon feedstock (1 μl, 200 ppm) for Cereclor S52 using an FID. Column 3% SE-30 on Gas-Chrom Q. (E) Chromatogram of Cereclor S52 (1 μl, 400 ppm) catalysed over 3% palladium at 200°. Detector FID, column 2% RbCl on Chromosorb G, (60–80 mesh). (F) Chromatogram of Cereclor S52 (400 ppm), Arochlor 1248 (300 ppm) and a polychlorinated naphthalene (D88) (300 ppm) after catalysis on 3% palladium at 200°. Detector FID. Column 2% RbCl on Chromosorb G. Peaks: 1 = naphthalene, 2 = C_{14}–C_{17} alkanes, 3 = biphenyl.

CONCLUSIONS

On column catalytic hydrodechlorination of organochlorine compounds may be performed by simple modifications to conventional GC equipment. The determination of exceedingly complex PCA mixtures which are currently being used as low cost plasticisers in place of phthalate esters may be achieved using a 3% palladium catalyst at 200°. No interference from other organochlorine species has been observed. Potential interference from alkanes may be prevented by thin-layer chromatographic fractionation of extracts on silica gel G Type 60 and elution with hexane. Cereclors have R_F values of the order of 0.1 whereas alkanes have R_F values from 0.9–1.0 relative to the solvent front.

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