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DETERMINATION OF POLYCHLORINATED ALKANES VIA CARBON SKELETON CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

Polychlorinated alkanes (PCAs) may be reduced to their respective hydrocarbon feedstocks by a simple on-column hydrodechlorination reaction. The reaction may be achieved with either palladium or platinum as catalyst over a wide range of operating conditions. The resultant hydrocarbon profiles are characteristic of the polychlorinated compounds from which they are derived. The presence of PCAs in plastic materials may thus be simply demonstrated via carbon skeleton capillary gas chromatography. The reproducibility of the alkane profiles obtained in this way suggests that quantitation by peak height summation is a real possibility. PCAs may be extracted from complex matrices by cyclic steam distillation and separated from likely interferents by thin-layer chromatography.

INTRODUCTION

The need to measure contamination of the environment by chlorinated aromatic hydrocarbons, particularly polychlorinated biphenyls (PCBs) together with *p,p'*-DDT and related compounds, prompted us to develop a wide variety of procedures employing thin-layer chromatography (TLC) and either packed or capillary gas chromatography (GC). Hydrodechlorination was used as a sample simplification technique[1–4]. Subsequently we used these techniques to determine the levels of organochlorine residues in river sediments[5], agricultural soils[6] and birds of prey[7].

However, the development of procedures for the analysis of polychlorinated alkanes (PCAs) has received little attention despite their widespread industrial use. These compounds are based on straight chain alkanes (C_{10}–C_{30}) and contain a known percentage of chlorine by weight. Among common tradenames for these compounds are Chlorowax, Chlorafin, Chlorez and Cereclor. It has been reported[8] that the annual production of PCAs is large and may well exceed that of PCBs. These chlorinated alkanes are used as secondary plasticisers, as additives for gear oils and as fire retardants.

Polychlorinated alkanes can migrate into the environment in the same manner as PCBs, but there are few data concerning their toxic properties[9]. However, bio-

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accumulation is thought to be slow relative to PCBs. Hitherto, studies on PCAs have been restricted because of their extremely complex composition and low response in the electron capture detector relative to organochlorine pesticides such as *p,p'*-DDT. Early work was performed with microcoulometric detection[10], but this detector is non-specific for PCAs. Recently a complex TLC procedure for the study of these compounds has been published[8] but the precision is poor.

Catalytic hydrodehalogenation is a convenient and easy way of removing halogen atoms under mild conditions and replacing them with hydrogen atoms. This reaction may be achieved under acidic, neutral or alkaline conditions, but bases may affect both the speed and selectivity of hydrodehalogenation[11,12]. Alternatively, hydrodechlorination may be achieved in a gas phase reaction by passage of an organochlorine compound over a heated metal catalyst (such as palladium or platinum) in a stream of hydrogen[13,14]. A similar reaction may be achieved in the liquid phase using "nickel boride" (NiB_2) generated *in situ* by reaction of sodium borohydride with alcoholic nickel chloride. By this reaction, chloroaromatic systems such as PCBs, polychlorinated naphthalenes (PCNs) and *p,p'*-DDT may be reduced (or partially reduced) to their respective hydrocarbons. Treatment of chloroaliphatic compounds with "nickel boride" in the presence of sodium borohydride affords no hydrodechlorination products[15].

Clearly there is a need for an analytical procedure that will permit the identification and quantitation of polychlorinated alkanes. We have previously, briefly, reported the application of carbon skeleton capillary GC^+ to the study of PCAs and now report fully our studies of these compounds by this technique.

EXPERIMENTAL

All solvents were redistilled before use. The standards used were PCBs (Monsanto, Newport, Great Britain), PCNs (Bayer, Leverkusen, G.F.R.), Cereclors and feedstocks (ICI, Macclesfield, Great Britain) and organochlorine pesticides (National Physical Laboratory, Teddington, Great Britain). Standards were prepared as 1000 ppm stock solutions and diluted as required.

Steam extraction

Typically, a sample (10 g: usually a soil or sediment) was blended with water (*ca.* 100 ml) to give a free running suspension which was then placed in a 250-ml round-bottomed flask. After fitting the extraction unit (Fig. 1), the sample was extracted for 12–14 h into 1 ml heptane. The heptane layer was collected, the apparatus washed with heptane (2 × 1 ml) and the extract and washings combined.

Thin-layer chromatography

Chlorinated alkanes may be separated from co-extracted material on silica gel G containing HF254 indicator. After development with *n*-hexane, the spots were visualised by spraying with silver nitrate in ethanol ($AgNO_3$, 0.85 g: ethanol, 100 ml). The dark grey-brown colour develops slowly (several hours). Plates were activated (110°C, 3 h) just prior to use. Typical R_F values were: Cerelors, 0–0.3; bi-, tri- and tetracyclic aromatic hydrocarbons (PAHs), 0.35–0.6; PCNs, 0.7–0.85; PCBs, 0.6–0.7; polychlorinated terphenyls (PCTs), 0.5–0.65 and alkanes 0.9–1.0. For environmental extracts, the section of the plate corresponding to R_F values of 0.0–0.3 was removed

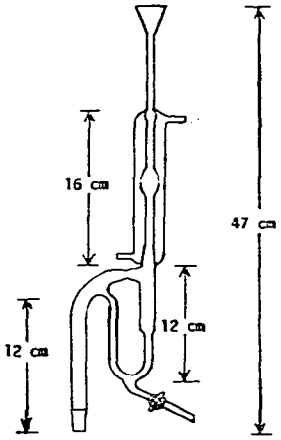

Fig. 1. Small scale apparatus for cyclic steam extraction.

and the PCAs re-extracted. Having established the R_F values of interest, silver nitrate was not used for sample extracts. Re-extraction of PCAs from the silica gel was achieved with diethyl ether.

Capillary gas chromatography

A Carlo Erba (Erba Science, Swindon, Great Britain) 2150 Series capillary gas chromatograph fitted with a Grob splitless injection system and flame ionisation detector was used. The column was coated with either OV-1 on Carbowax 20M (20 m) or SE-30 on silanised (HMDS) glass (20 m), by standard procedures. Typical operating conditions were: flow-rate 1.5 ml min^{-1}; detector temperature 275°C; amplifier × 16; splitless time 30 sec; and injection volume 1 μl.

Catalyst preparation

Palladium chloride (0.5 g) (Johnson Matthey, Royston, Great Britain) was dissolved in hot 5% v/v acetic acid (50 ml) and Chromosorb P (9.5 g, 80–100 mesh; Jones Chromatography, Glamorgan, Great Britain) was added. The pH was adjusted to 7.1 with sodium hydroxide. Evaporation of the solvent and drying (110°C, 12 h) yielded the catalyst (3% palladium).

In a similar manner a 5% platinum catalyst was prepared. Catalysts were conditioned and mounted in the capillary gas chromatograph as previously described[5].

RESULTS AND DISCUSSION

The measurement of trace amounts of organic contaminants in samples of environmental origin is a multistep procedure. These steps may be broadly defined as: (1) removal of the compound(s) of interest from the matrix; (2) simplification of the extract and (3) qualitative and quantitative determination of the target compound(s). The removal of PCAs from samples (except from those containing greater than *ca.* 10% oil/fat) may be accomplished simply via cyclic steam distillation. Sim-

plification of the resultant extract may easily be achieved by TLC on silica gel G. Qualitative and quantitative measurements are made by hydrodechlorinating the PCAs to their respective hydrocarbon feedstocks over a palladium or a platinum catalyst. The resultant characteristic profiles of *n*-alkanes indicate the presence of a PCA residue. Quantitation follows via peak height calibration against standards or by use of an internal standard such as *n*-$C_{18}H_{38}$.

Steam extraction

For development of procedures for the determination of polychlorinated alkanes a compound (Cereclor S52) based on an *n*-C_{14}–C_{17} alkane feedstock was used. However, the methods described are also applicable to compounds based on *n*-C_{10}–C_{13} and *n*-C_{22}–C_{30} feedstocks. Many chloroaromatic compounds such as polychlorinated biphenyls and *p,p'*-DDT may be recovered in high yield from environmental matrices such as river-water, sediments and biota by steam distillation[16]. Using a 1/3rd scale version of this apparatus we have extracted organochlorine compounds from river sediments[5], agricultural soils[6], raptorial[7] and mammalian[17] tissue. However, this design proved inadequate for the removal of PCAs. The relatively long distillation path involved coupled with the low volatility of polychlorinated alkanes relative to chloroaromatic compounds presumably results in a poor extraction efficiency. Instead a carefully insulated, modified version of a design by Franklin and Keyzer[18] was used (Fig. 1). The function of this apparatus is to remove from an aqueous sample or a sample blended with water, by steam entrainment, volatile organic components which condense and partition into a small (*ca.* 1-ml) volume of an organic solvent (heptane) which is less dense than water. After a suitable extraction period the solvent and remaining water can be drawn off. The organic layer is separated, dried over anhydrous sodium sulphate and after fractionation by TLC is suitable for GC analysis.

Using this equipment and Cereclor S52 as a typical polychlorinated alkane, the usual extraction time of 2–4 h was insufficient to afford good recovery. The optimal extraction time was found to be 12–16 h, with good insulation of the equipment over the distillation pathlength.

To measure the recovery by this procedure it was necessary to establish the precise formulation of the PCAs used. Microanalytical data for the compounds used are given in Table I. The amount of chloroalkane recovered was determined by first converting (by carbon skeleton GC) it into its parent feedstock and then comparing the peak heights with those of standard feedstock solutions. The percentage of chlorine present in the sample had to be known accurately so that the amount of hydrocarbon produced by the catalytic hydrodechlorination could be predicted. The difference between the predicted value and the observed value gives the conversion efficiency of the catalytic step. The difference between samples catalytically hydrodechlorinated before and after steam extraction gave the percentage recovery. The percentage recovery for a typical PCA (Cereclor S52) was thus calculated to be 93% (mean of six measurements; R.S.D. 4%). The conversion efficiency was measured as 100%. Recovery for a typical chloroalkane based on a C_{10}–C_{13} feedstock was 80% measured against an internal standard (*n*-$C_{18}H_{38}$). This lower figure possibly reflects losses in the extraction step due to the higher volatility of these compounds. Recoveries of PCAs based on the C_{22}–C_{30} feedstock were apparently not good (es-

TABLE I

MICROANALYTICAL MEASUREMENTS FOR POLYCHLORINATED ALKANES

Sample	*% C*	*% H*	*% Cl*	*Literature value[20] (% Cl)*
C_{10}–C_{13}	84.2	16.00	–	–
C_{14}–C_{17}	85.1	15.5	–	–
C_{22}–C_{30}	85.3	15.4	–	–
56 L	38.2	5.5	56.2	56
S52	43.1	6.2	51.2	52
63 L	33.7	4.3	62.1	63
65 L	32.8	3.8	62.3	65
70 L	28.1	3.2	70.0	70
54	41.2	5.7	53.5	54
50 LV	44.1	6.7	49.1	50
S58	37.1	5.1	59.6	58
48	45.8	6.7	47.5	49
42	51.1	7.9	41.8	42
51 L	43.5	6.5	51.6	52
S45	48.0	7.6	45.2	45
70	27.1	3.0	70.6	70

timated at 55–65%), although this figure could reflect the difficulty of quantitating compounds by summation of peak heights of nine components (C_{22}–C_{30}).

Particularly noteworthy are the ratios of the various alkanes achieved after hydrodechlorination as these provided a "fingerprint" for the presence of a polychlorinated alkane residue in a sample. The ratios established were 1:4.7:4.1:3.6 for compounds based on the C_{14}–C_{17} feedstock and 1:7.3:6.8:2.2 for compounds based on the C_{10}–C_{13} feedstock. The production of a set of hydrocarbons in this ratio by carbon skeleton GC treatment of an extract from an environmental sample strongly indicates the presence of a chloroalkane residue in that sample. This is clearly demonstrated in Fig. 2 which illustrates a capillary GC trace of the three alkane feed-

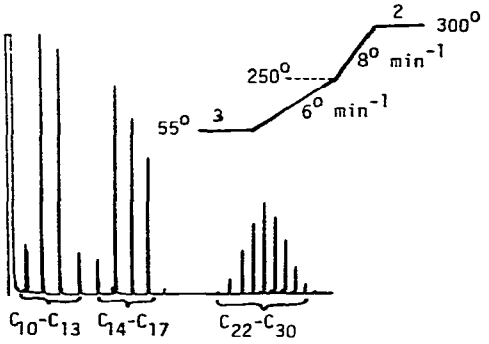

Fig. 2. Chromatogram (OV-1 capillary column) of the three hydrocarbon feedstocks C_{10}–C_{13}, C_{14}–C_{17} and C_{22}–C_{30}. Time periods indicated (2, 3) are given in min.

stocks C_{10}–C_{13}, C_{14}–C_{17} and C_{22}–C_{30}. Fig 3 displays the results of catalytic hydrodechlorination of 50 LV (C_{10}–C_{13}), S52 (C_{14}–C_{17}) and 54 (C_{22}–C_{30}). For comparison, Fig. 4 shows a chromatogram of a mixture of these three chloroalkanes without catalysis.

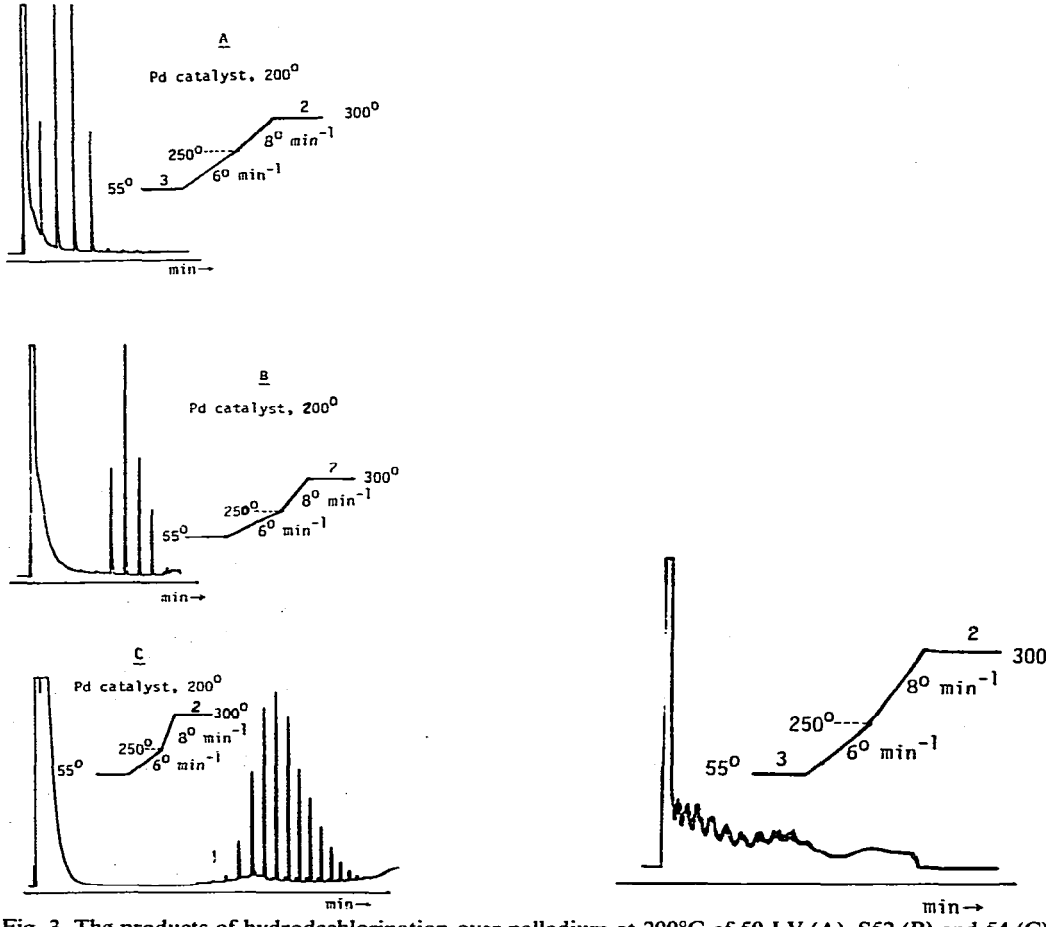

Fig. 3. The products of hydrodechlorination over palladium at 200°C of 50 LV (A), S52 (B) and 54 (C). Time periods indicated (2, 3) are given in min.

Fig. 4. Chromatogram (OV-1 capillary column) of 50 LV, S52 and 54 without catalytic hydrodechlorination. Time periods indicated (2, 3) are given in min.

The temperature of the catalyst, *i.e.*, the injection port temperature, for the conversion of chloroaliphatics is less critical than for chloroaromatic compounds. Below 180°C, conversion efficiency is not good and profiles are distorted. Between 180 and 300°C good conversion is obtained with reproducible profiles. Above 300°C there is some evidence for thermolysis and/or isomerisation. It is important however to select an injection port temperature at which the sample is vaporised efficiently. Thus 200°C is suitable for compounds based on C_{10}–C_{13} and C_{14}–C_{17} feedstocks, 250°C for compounds based on the C_{22}–C_{30} feedstock. Alternatively, a temperature

of 250°C should be adequate for compounds based on all three feedstocks and for both 3% palladium and 5% platinum catalysts.

The facility of this reaction is somewhat surprising as no double bonds or aromatic systems are present to activate the carbon–chlorine bond via electron donation[19]. However, the linearity of these compounds enables them to align parallel with the surface and thus many chlorine atoms are adsorbed simultaneously onto the surface. Presumably, therefore, the strength of adsorption of PCAs onto the catalysts is quite high. The lack of isomerisation upon catalysis reinforces this concept of a strongly adsorbed species held in a particular orientation.

We have demonstrated the versatility of this technique by converting all thirteen commercially available chloroalkanes into their respective feedstocks. All these compounds may be studied either by the use of conventional packed columns with pre-column catalysis[3] or by the use of carbon skeleton capillary GC[4]. Thus the full range of polychlorinated alkanes commercially available to us may be conveniently classified according to hydrocarbon feedstock (Table II).

TABLE II

CLASSIFICATION OF POLYCHLORINATED ALKANES BY FEEDSTOCK TYPE

C_{10}–C_{13}	C_{14}–C_{17}	C_{22}–C_{30}
50 LV	S52	42
56 L	S45	48
63 L	S58	54
65 L	51 L	70
70 L		

Sample simplification: TLC

Although steam extraction provides a quicker and simpler way of removing compounds of interest from a matrix than does solvent extraction, the co-extraction of potential interferents still occurs. The criterion for preferential partition into heptane is hydrophobicity— a property possessed by many classes of organic compounds such as paraffins, polycyclic aromatic hydrocarbons, esters (including phthalates), organochlorine pesticides such as *p,p'*-DDE and γ-BHC, together with other industrial organochlorine compounds such as polychlorinated biphenyls. All these classes of compounds may be present in environmental samples. Compounds such as phenols, alcohols and triglycerides are not extracted and thus pose no problem. As the determination step for PCAs requires their conversion into *n*-alkanes, it is particularly important that *n*-alkanes be removed from the sample prior to catalysis. Thin-layer chromatography separates PCAs from alkanes and also from many other compounds likely to be present in the sample. The chromatographic separation of a selection of typical compounds which may be present is shown in Fig. 5. The PCA mixtures selected represent one from each feedstock. The complexity of these mixtures is reflected in the spreading of the spot. Clearly none of the likely co-extracted organochlorine compounds will cause interference in any subsequent carbon skeleton determination. The presence of some polycyclic aromatics in the chloroalkane fraction is possible but these will not cause interference. The likely aromatic compounds

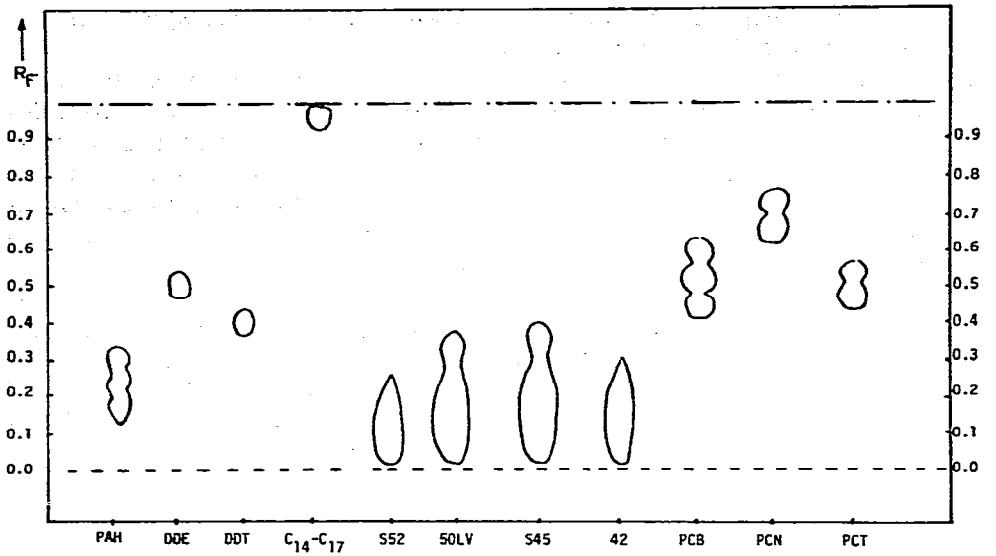

Fig. 5. TLC separation of PCAs from other classes of compound likely to be co-extracted from environmental samples. PAH = Polycyclic aromatic hydrocarbons such as naphthalene, phenanthrene and pyrene.

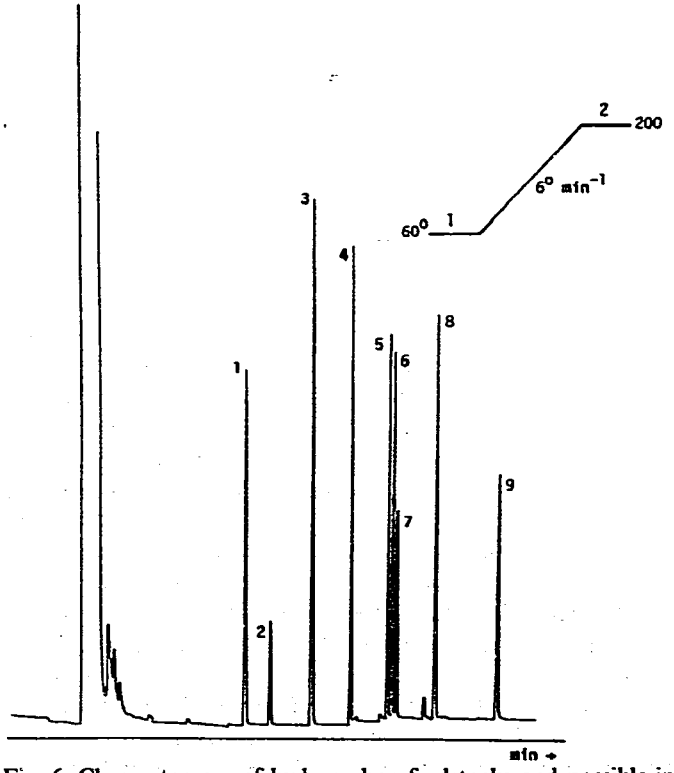

Fig. 6. Chromatogram of hydrocarbon feedstocks and possible interfering compounds. Peaks: 1 = biphenyl; 2 = *n*-C_{14}; 3 = *n*-C_{15}; 4 = *n*-C_{16}; 5 = *n*-C_{17}; 6 = phenanthrene; 7 = anthracene; 8 = *o*-terphenyl; 9 = pyrene. Time periods indicated (1, 2) are given in min.

present are the bi- and tricyclic compounds such as naphthalene, biphenyl and phenanthrene. Fig. 6 shows a capillary GC trace of these compounds chromatographed with the C_{14}–C_{17} feedstock and clearly demonstrates that interference does not occur.

We have applied this technique to the rapid screening of plastics for the presence of chlorinated alkanes. Thus a small portion (*ca.* 1 g) of the material under study is shaken (10 min) with hexane (3 ml) and aliquots (1–2 μl) of the hexane extract are chromatographed with and without catalysis. The presence of PCAs in rubberised floor tiles[4] and their absence in laboratory plastic tubing may thus be quickly demonstrated. However, examination of a recent batch of floor covering material suggests a change in composition of the hydrocarbon feedstock. The dominant species now appears to be n-C_{17} and not n-C_{15}. This is being investigated further. Likewise, results of the measurement of PCAs in environmental samples (estuarine sediments) will appear elsewhere.

CONCLUSIONS

PCA compounds may be removed from complex matrices by cyclic steam extraction. Such compounds may be reliably and quantitatively converted into their respective hydrocarbon precursors by catalysis over supported palladium and platinum catalysts. The preferred catalyst for this reaction is 3% palladium maintained at 200°C. Carbon skeleton capillary GC may thus be used to detect and quantify polychlorinated alkanes in extracts obtained from environmental and industrial samples. TLC on silica gel G may be used as a sample fractionation procedure prior to chromatographic determination in the former case.

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