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RECENT ADVANCES IN THE ANALYSIS OF POLYCHLORINATED BIPHENYLS IN ENVIRONMENTAL AND BIOLOGICAL MEDIA

E. D. PELLIZZARI*, M A MOSELEY and S D COOPER

Analytical and Chemical Sciences, Research Triangle Institute, Research Triangle Park, NC 27709 (U S A)

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CONTENTS

1 INTRODUCTION

Polychlorinated biphenyls (PCBs), terphenyls (PCTs) and quadphenyls (PCQs) had been manufactured as commercial mixtures [Aroclors (U.S.A.), Clophen (F.R.G) and Kanoclor (Japan)] for more than four decades before they were banned in the U.S.A. in 1976 Because of their long-term heavy usage as dielectric fluids, in transformers and capacitors, in hydraulic fluids, fire retardants, etc., and their persistence, PCBs have permeated into practically every environmental medium throughout the world[1]. Because of their ubiquity, PCBs have received considerable attention in recent years in the area of analytical measurements and toxicology

Since environmental pollution by PCBs first became apparent, many purification procedures, gas chromatographic (GC) systems, detectors and methods for quantifying GC responses have been reported for determining the contamination of environmental and biological samples[1–11]. However, until recent advances in analytical instrumentation, most of the conventional methodology yielded only semi-

quantitative data with virtually no qualitative or quantitative information on the PCB isomer composition in environmental or biological samples. The analytical problems are complicated by the fact that there are 209 individual chlorinated biphenyl isomers[12] spanning 10 homologous series (1–10 chlorine atoms per biphenyl). A commercial mixture itself (e.g., Aroclor) may contain as many as 60 chlorobiphenyl isomers[12].

The conventional quantification method is based on packed column GC and reports the PCB content in environmental and biological samples by referring it to a particular Aroclor mixture (e.g., Aroclor 1242, 1254 or 1260). The GC detector is first calibrated using commercial Aroclor mixtures, and then the appropriate commercial Aroclor profile is matched to the sample profile. Using the Webb and McCall technique or a variation of it the total PCB content is calculated[13]. This approach, however, is potentially subject to error.

Environmental contamination may be derived from Aroclor mixtures or from incidentally generated chlorobiphenyls whose profiles do not resemble Aroclor patterns[14] In either instance, the conventional quantification method is inadequate. As time passes, the "Aroclor patterns" undergo alteration in the environment, as selective weathering and biotransformation and bioaccumulation in living organisms perturb these patterns. The problem of Aroclor pattern dissimilarity will be further aggravated as PCB monitoring continues into the future.

The quantification problem is further exacerbated by the production of chlorobiphenyl isomers in chemical process streams, incineration, etc., via chemical or pyrolysis reactions that are not the same as the chemical reactions once used for the manufacture of Aroclors[14]. As incidental generation does not necessarily produce any fixed pattern of chlorobiphenyl isomers, the analyst cannot identify and quantify chlorobiphenyls based on pattern recognition from the packed column gas chromatogram. Hence the qualitative and quantitative analysis of PCBs in environmental and biological samples and in samples from process streams involves the difficult issue of having to detect, identify and quantify each individual isomer.

The accuracy of PCB determination in environmental, biological and process stream samples is, in addition to the reasons given above, also related to the degree of variability in the analytical response of each chlorobiphenyl isomer to the detector employed[1,15–18].

Recent theoretical and experimental studies have indicated that the biological properties of chlorobiphenyl isomers are significantly influenced by the number and biphenyl ring position of the chlorine atoms[19–23]. Because the toxicological properties vary considerably among isomers[19,20,23], more sophisticated methods capable of yielding information about the chemical composition at the isomeric level are required in order to be able precisely to investigate and assess the toxicological consequences of PCB pollution. Obviously, the ideal analytical procedure is one that identifies and measures each individual chlorobiphenyl isomer

This review examines the most recent advances during the period from 1971 to the present that strive to meet the objective of individual chlorobiphenyl isomer identification and quantification. The areas reviewed are (a) development of high-resolution GC, (b) improvement in detection systems, (c) availability of chlorobiphenyl isomer standards; and (d) application of state-of-the-art methods to the analysis of environmental and biological samples. It is beyond the scope of this review to include sampling techniques and isolation and purification methods for PCBs.

2 HIGH-RESOLUTION GAS CHROMATOGRAPHIC TECHNOLOGY

In order to analyze for 209 individual chlorobiphenyl isomers, the use of high-resolution chromatographic techniques is mandatory. In this respect, GC currently is far superior to high-resolution thin-layer and high-resolution liquid chromatography for PCB analysis. The relative merits of packed column (low resolution) *versus* capillary column (high resolution) GC analysis of PCBs have been succinctly reported by Mullin and Filkins[23]. Their work provided the impetus for further research into the determination of an optimum capillary column(s) for the analysis of individual isomers of PCBs, polybrominated biphenyls, pesticides and other halogenated hydrocarbons in biological and environmental samples.

2.1. Development of capillary columns

In addition to early research using metal capillaries[24], Mullin *et al.*[25], Bush, *et al.*[26], Nygren and Mattson[27] and Moseley and co-workers[28–30] have more recently reported on extensive investigations into five variables that affect glass and fused-silica capillary performance for the analysis of PCBs[28–30]. The variables studied were: (a) material of construction; (b) pre-treatment/deactivation procedures, (c) stationary phase type; (d) stationary phase film thickness; and (e) capillary dimensions. Evaluation criteria employed were (a) separation number (Trennzahl, *TZ*) between 2,2',4',5-tetrachlorobiphenyl and 2,2',4,4',6,6'-hexachlorobiphenyl; (b) resolution between 2,2',5,5'-tetrachlorobiphenyl and 2,2',4',5-tetrachlorobiphenyl; (c) height equivalent to an effective theoretical plate (HEETP) for 2,2',4', 5-tetrachlorobiphenyl; (d) adsorption characteristics; (e) thermal stability; and (f) general performance on an Aroclor 1242–1260 mixture (1:1, w/w).

Capillaries were made from Pyrex and soft glass, quartz, vitreous silica and fused-silica materials[28–31]. The objectives of these studies were to determine the most suitable material for construction, pre-treatment/deactivation and amenability to coating of a thin, uniform, stable film of stationary phase. It was recognized that these variables were not independent of each other. Except for the hydrocarbon $C_{87}H_{176}$ (C_{87}), all stationary phases evaluated could be successfully coated on the flexible silica capillaries[30]. Preference for the silica capillaries was attributed to their flexible nature, facilitating their assembly into gas chromatographs even by the novice. Thus, a major impediment to the use of capillaries by the analytical community had been removed.

Many pre-treatment/deactivation procedures were investigated as the raw construction material was not suitable for coating directly with stationary phase[28–30] The procedures studied were: (a) barium carbonate treatment, (b) Carbowax 20M; (c) Superox-4; (d) HCl etching; (e) persilylation; and (f) thermally induced polysiloxane (SE-52 or OV-101) bonding. The preferred methods were polysiloxane deactivation on silica and Pyrex and persilylation on Pyrex[28–30].

Although glass capillaries coated with C_{87} stationary phase provide excellent resolution of individual chlorobiphenyl isomers, use of C_{87} is limited by two factors —its temperature stability (*ca.* 220°C) and the inability to coat successfully a uniform film on silica. Because of the upper temperature limit, the C_{87}-coated capillaries have been inadequate for the analysis of PCTs, PCQ, PBBs and sample extracts that contain many impurities (*e.g.,* from fish). For these reasons, alternative stationary phases were sought.

There have been several reports on different stationary phases used in capillary GC for the analysis of PCBs[16,25,31-34]; however, until recently there was no concerted effort to evaluate stationary phases systematically[28-30]. Using the previously mentioned criteria, a matrix study design was performed in concert and while making a comparison of phase selectivity (McReynolds constants) to guide the overall investigation toward the "optimum" phase. Among the phases evaluated were C_{87}, SE-54, SP-2100, QF-1, SE-52, OV-101, Dexsil 410, Apiezon M and Apiezon L. Early results predicted (from McReynolds constants) that Apiezon M would most closely mimic the excellent separation pattern of C_{87}[30]. In fact, this correspondence was demonstrated experimentally[28]. Several advantages of Apiezon M will be discussed later. Finally, a complimentary stationary phase to Apiezon M was sought so that one phase could serve as a primary analytical column and the other as a reference column. SE-54-coated capillaries provided a significantly different resolution pattern to Apiezon M[28,29].

It has long been recognized that the thinner the stationary film the higher is the mass transfer coefficient The sample capacity, however, decreases. Research has been performed to determine a film thickness that possessed a very high mass transfer coefficient (as measured by HEETP), adequate sample capacity for the detection system to be employed and stability to long periods of usage[28-30]. Stability (to solvent and thermal shock) was imparted by immobilizing the film on the silica surface by a cross-linking/surface bonding reaction[29].

Two methods were reported that immobilized phases to silica[29]. One utilized a thermal technique (using SE-52), the other a dicumyl peroxide reaction (using SE-54). The first method easily produced the desired 0.025 μm film capillaries for use with electron-capture and negative ion chemical ionization (NICI) mass spectrometric (MS) detection of PCBs. These capillaries exhibited a bleed of 0.7 pA (flame-ionization detection) at 320°C[29]. The other method yielded thicker films (0.1 μm) for higher capacity for use with electron-impact MS.

An Apiezon M phase immobilized to silica has not been reported

Investigations on the resolution of PCBs indicated that a silica capillary, polysiloxane deactivated, 50 m × 0 2 mm I.D. in length, coated with Apiezon M (0.025 μm film) or SE-54 (0.025 μm film) was preferable[28-30]. An Apiezon M-coated silica capillary allowed the elution of PCBs to occur at temperatures approximately 30–40°C lower than other stationary phases[28-30] and was thermally stable to up to *ca.* 285°C.

2.2. Comparison of packed and capillary column profiles

The inherent differences between low- and high-resolution GC columns are exemplified by Figs. 1 and 2. Fig. 1 compares the profiles for a standard mixture of Aroclor 1242 and 1260. Fig. 2 depicts the profiles for a stack (stationary source) sample[35]. Both high-resolution analyses were performed on SE-54 fused-silica capillaries.

It is evident in Fig 2 that the low-resolution profile does not readily resemble a commercial Aroclor mixture. Therefore, it would be highly inaccurate to quantify the low-resolution profile using a commercial Aroclor standard for instrument calibration and the Webb and McCall method[13].

Several examples demonstrating the performance of Apiezon M silica capillaries will be discussed later.
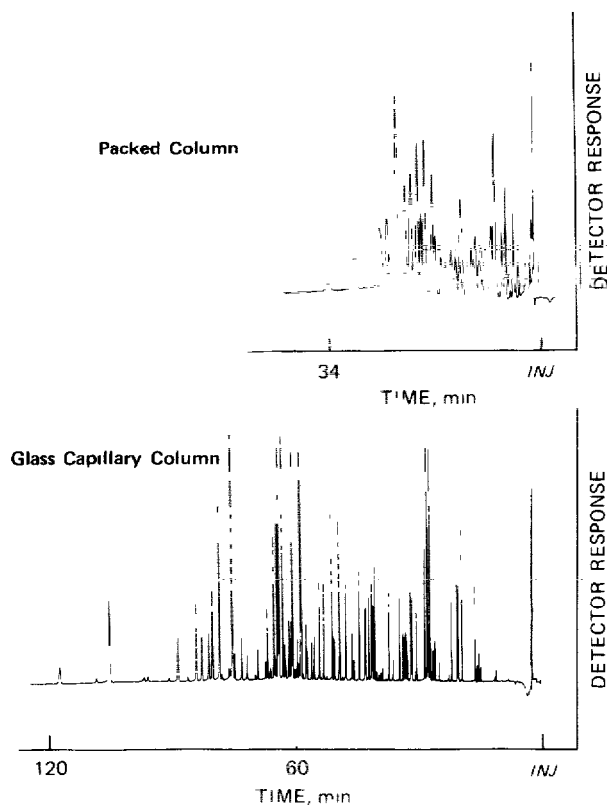
Fig 1. Chromatograms of Aroclor 1242–1260 Top, packed column, bottom, capillary

3 DETECTION SYSTEMS

3.1. Modes of detection

Use of several types of detectors in the analysis of PCBs has been reported over the years. A few of the more significant recent advances are noteworthy. These are electron capture, negative ion chemical ionization mass spectrometry (NICI-MS) and selected ion monitoring (SIM), a variant of electron-impact mass spectrometry.

3 2 Electron-capture detection

The electron-capture detector continues to be one of the most sensitive and hence valuable selective detectors for PCB detection. It is only recently, however, that its full potential has been realized and incorporated into commercial systems.

From a quantitative standpoint, one of the earlier limitations of the electron-capture detector was the non-linearity of response. Until the mid-1970s the electron-capture detector had a linear dynamic range of approximately 50–100. Several papers have dealt with the determination of the proper function that would yield a linear relationship with concentration[36,3]. It has been suggested that the response was logarithmic by analogy to light absorption[37] However, when the electron-cap-
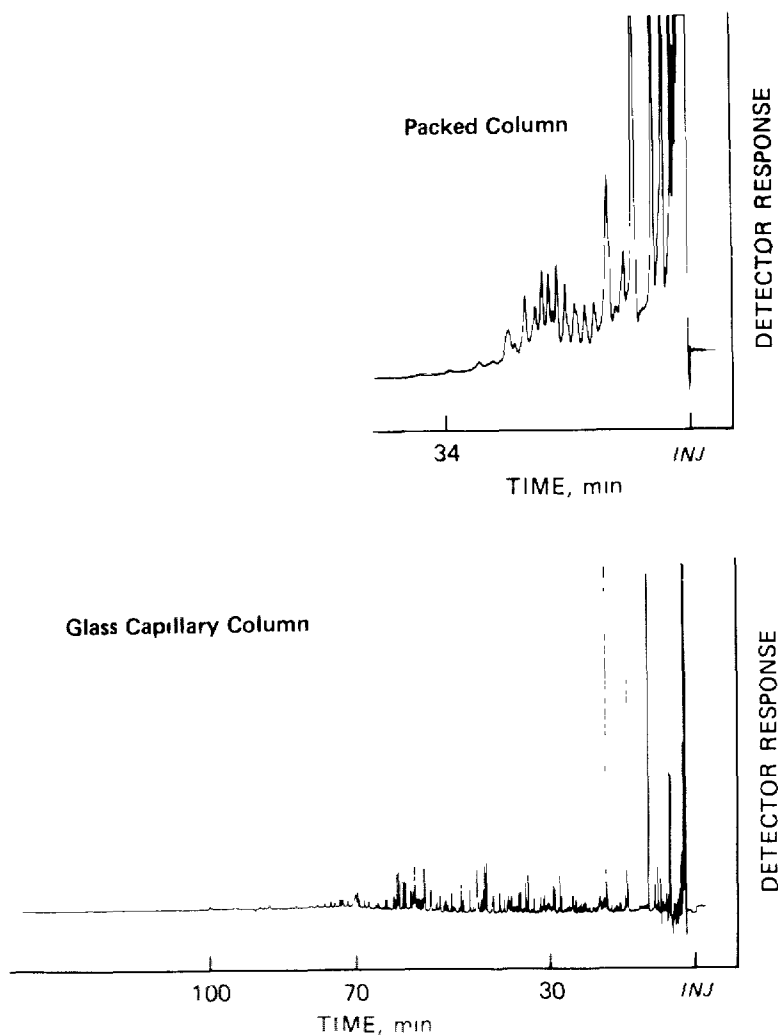
Fig 2 Chromatograms of stack sample Top, packed column, bottom, capillary.

ture detector was operated in the pulse samplmg mode the reactions occurred pri-marily in the field-free period. so that the analogy was not considered very appro-priate[37].

Once a valid kinetic model for the electron-capture processes for thermal re-actions had been derived by Wentworth and Chen[37] and research in atmospheric pressure ionization mass spectrometry gave direct evidence on negative and positive ion formation (under electron-capture conditions), the solution to electron-capture detector non-linearity was in hand. Attention was focused on the electron-capture detector's concentration dependence, which had been of great concern in analytical chemistry. Analysis of the kinetic model was carried out by numerical solution of differential equations. which disproved some of the early mathematical assump-tions[37].

As a result of the experimental work on electron-capture mechanisms, subsequent reports appeared describing an alternative method of linearization of response[38,39]. The fundamental principle was based on modulating the pulse frequency on the detector electrode so that the plasma current was maintained constant This function is given by

$$K_a = \frac{F - F_0}{F_0}$$

where F_0 is the frequency giving the base current in the absence of capturing species and F is the frequency giving the base current in the presence of a capturing species. Initially there were reports of a "break" in linearity, but with improved instrument design parameters this problem was eliminated[39]. Thus, the modern electron-capture detector utilizes modulated pulsed frequency to achieve a dynamic range of approximately four orders of magnitude, an improvement that is necessary for the analysis of PCBs in environmental and biological samples.

A second limitation was the cell volume of the electron-capture detector. This problem was not apparent until analysts began to investigate the use of high-resolution capillary columns[40]. The original cell volumes of 2–4 ml were adequate when used with packed columns with high flow-rates where the chromatographic peak shape and efficiency were preserved. A few isolated reports appeared that considered improved cell design, in particular low-volume cells, for use with capillaries. Electron-capture detector cell volumes between 250 and 500 μl utilizing a coaxial design still required a scavenger gas after the capillary column to reduce the residence time in the cell and preserve the ultra-high numbers of theoretical plates that were attainable by capillaries[40]. However, it is only recently that commercial GC systems have become routinely available with electron-capture detectors compatible with capillary flow-rates.

With these two parallel developments it became feasible to perform elegant quantitative electron-capture detection of PCBs.

3.3. Negative ion chemical ionization mass spectrometry

This detection method is a variant of positive ion chemical ionization mass spectrometry[41]. The associated electronics to regulate, focus and pass negative ions to an appropriately polarized electron multiplier were developed in the mid-1970s; however, it was not until recent years that ion source and reagent gas conditions were investigated for optimizing PCB analysis[30].

NICI-MS is uniquely suited to measuring trace amounts of polyhalogenated chemicals in environmental samples because of its high sensitivity for these chemicals and its virtual transparency to otherwise potentially interfering molecules[42]. It also provides, in addition to sensitivity, molecular ion information and thus a verification of the structural entity being measured, a highly desirable feature when examining complex environmental and biological samples.

NICI-MS is very closely analogous to electron-capture detection in that the ion-forming reactions are common to both. The ion-forming reactions that are important for polychlorinated molecules have been described[42]. They include: (a) the resident capture of thermal electrons; (b) chloride attachment, (c) deprotonation; and

(d) oxygen exchange. Because NICI-MS is a novel technique, the operating parameters that optimize the technique preferentially to one of the above mechanisms for PCB analysis have only recently been studied.

Investigations have been performed on the use of high-resolution GC in combination with NICI-MS while elucidating and characterizing instrumental parameters suitable for PCB analyses[30]. These investigations have included: (a) examination of the performance of two different ion-source designs, (b) the effect of source pressure on sensitivity and spectral signature; and (c) the effect of various reagent gases on sensitivity and fragmentation of PCB isomers. Compared with conventional electron-impact MS, less information about the structure of the compound is obtained. Therefore, the specific aim of the investigation was to study several moderating and reagent gases to enhance the formation of molecular anions of the individual chlorobiphenyl isomers or their dissociation to yield chloride-35 and -37 isotopic anions[30].

Reagent gas studies were conducted with methane, oxygen–nitrogen, nitrous oxide–nitrogen, nitrous oxide–methane, difluorodichloromethane and tetrafluoromethane This variety of reagent gases was necessary because a major problem encountered in the NICI-MS analysis of PCBs had been the lack of molecular weight information obtained for the lower molecular weight PCBs (C_1–C_6) under methane-moderated electron-capture conditions. As the lower molecular weight PCBs undergo dissociative electron capture to form Cl^- ions under these conditions, the use of a reagent gas that reacts chemically with individual chlorobiphenyl isomers rather than just moderating the electron energy led to the observation of useful molecular weight information in the spectral signature.

Field and co-workers[43,44] had observed that a mixture of nitrous oxide and methane produced abundant OH^- ions under negative ion conditions These ions were observed to react with a wide variety of compounds by proton abstraction to form $(M-H)^-$ ions. Therefore, this reagent gas mixture was studied in our laboratory as a likely candidate to provide molecular weight information for individual chlorobiphenyl isomers.

Experiments have been conducted with an LKB 2091 magnetic sector instrument with a relatively open source design Figs. 3–7 depict mass spectra of monochlorobiphenyl, trichlorobiphenyl, hexachlorobiphenyl, octachlorobiphenyl and decachlorobiphenyl obtained under nitrous oxide–methane NICI conditions. Nitrous oxide was introduced through a reagent gas inlet ($5 \cdot 10^{-5}$ Torr as measured at the Penning gauge) and methane ($3 \cdot 10^{-15}$ Torr) was passed into the ion source via a GC make-up line and separator Based on calculations made for positive ion methane CI, the actual source pressure exerted by both reagent gases was 0.2–0.3 Torr. The MS system was optimized for m/z 17 (OH^-). A 2-μl injection (ca. 10 pg) of a standard solution of PCBs was made with a 5:1 splitting ratio. As indicated in Fig. 3, the spectrum of 2-chlorobiphenyl exhibited $(M-H)$ ions The M^- peak at m/z 188 is no larger than expected from ^{13}C isotope abundance. In addition, very low intensity ions were found for the $(M-H+O)^-$ ion at m/z 203, $(M-H+N_2O)^-$ ion at m/z 231 and $(M-H+NO)^-$ ion at m/z 217.

The high-mass region for trichlorobiphenyl ($>m/z$ 40, Fig. 4) mass spectrum was dominated by the $(M-H)^-$ ions at m/z 255, 257 and 259. The M^- intensity was greater than predicted on the basis of ^{13}C isotope abundance (24% vs 13%), sug-
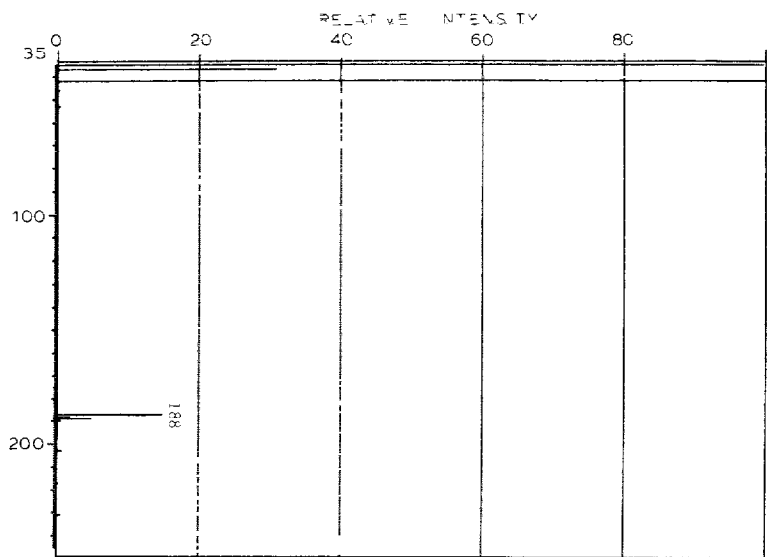
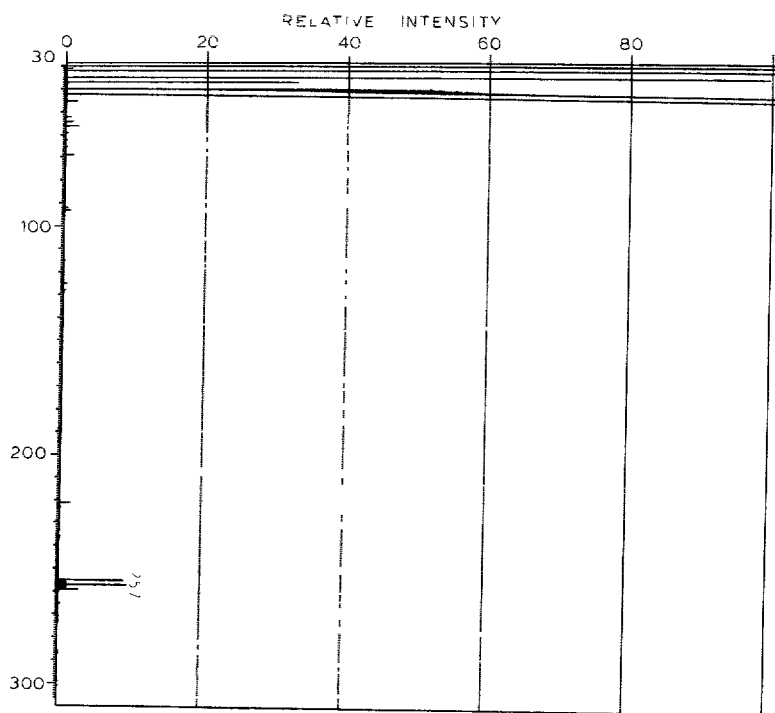Fig 3 N₂O–CH₄ NICI mass spectrum of monochlorobɩphenyl
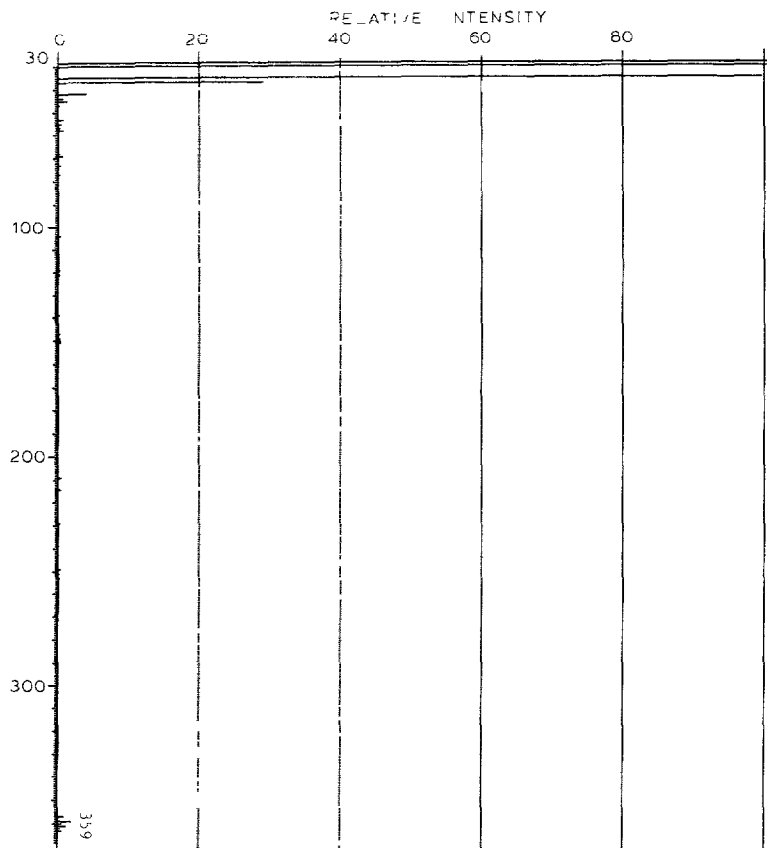
Fig. 4 N₂O–CH₄ NICI mass spectrum of trɩchlorobɩphenyl

Fig 5 N_2O–CH_4 NICI mass spectrum of hexachlorobiphenyl

gesting that some stabilization of M^- was occurring. Also, $(M - Cl)^-$ ions were evident at m/z 221 and 223.

  For hexachlorobiphenyl (Fig. 5) the $(M - H)^-$ ions at m/z 357, 359, 361 and 363 were present. Also, a substantial abundance of M ions was observed (53% observed *vs.* 13% calculated as ^{13}C). Ion clusters for the loss of one chlorine (m/z 323) and two chlorine atoms (m/z 288) from the parent molecule were detected An interesting ion cluster formed by the loss of chlorine and the addition of oxygen, $(M - 19)^-$, was observed (m/z 338).

  The mass spectrum of octachlorobiphenyl (Fig 6) exhibited negligible hydrogen abstraction but was certainly dominated by M^- ions. As there are only two hydrogens available for abstraction on this PCB homolog, this result was unexpected.

  Decachlorobiphenyl (Fig 7) with no hydrogens available for abstraction yields a spectrum that is due to electron capture (formation of M^-) and Cl^-.

  The above observations for nitrous oxide–methane reagent gas indicated that verification of the molecular weight of the chlorobiphenyl isomer could be achieved in high-resolution GC–NICI-MS Further, the homogeneity of the GC peaks in complex mixture analysis could be established, as non-PCB substances or non-homolo-
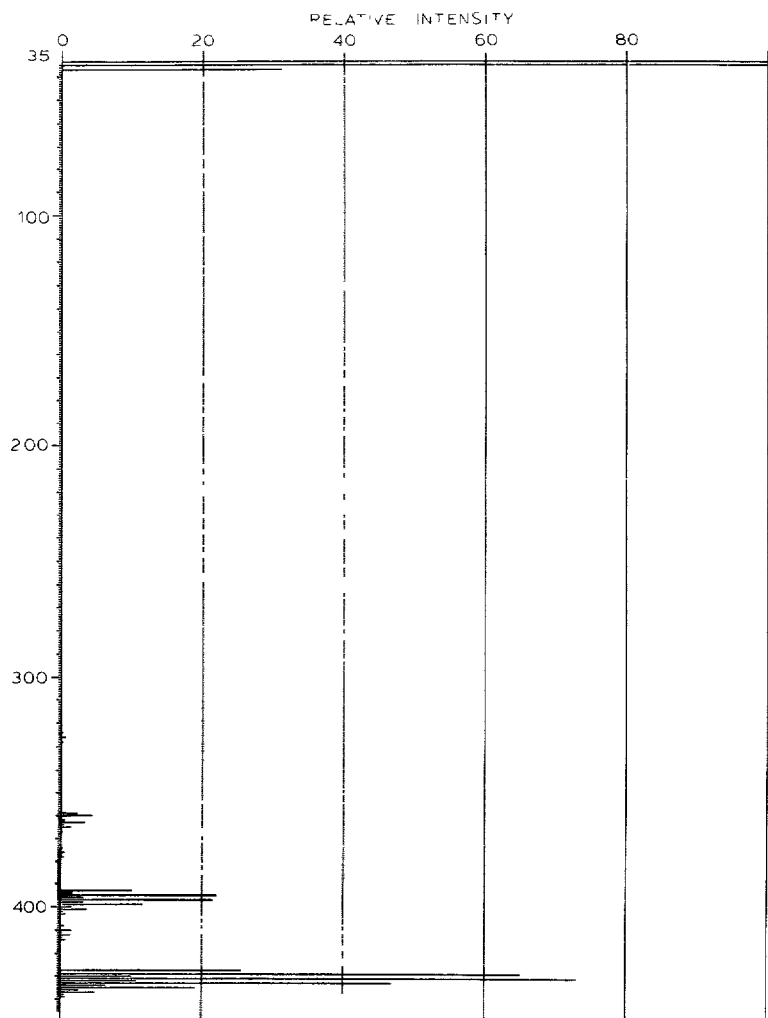
Fig 6 N_2O–CH_4 NICI mass spectrum of octachlorobiphenyl

gous PCB isomers can be distinguished. NICI-MS can thus provide molecular weight information, which has been one of the advantages claimed for EI-MS.

Another moderating gas typically used in NICI-MS has been methane[41]. Experiments on the effects of source pressure on sensitivity indicated that as the methane pressure increased so also did sensitivity[30]. As a compromise between maximum sensitivity and excessive pressure, a reagent gas pressure of $4 \cdot 10^{-5}$ Torr is normally employed (measured at the diffusion pump throat; the actual ion source pressure might be higher)

Of the reagent and moderating gases studied, methane provided one of the more sensitive modes of operation. However, the principal mechanism of reaction was dissociative electron capture, leading to m/z 35 and 37.
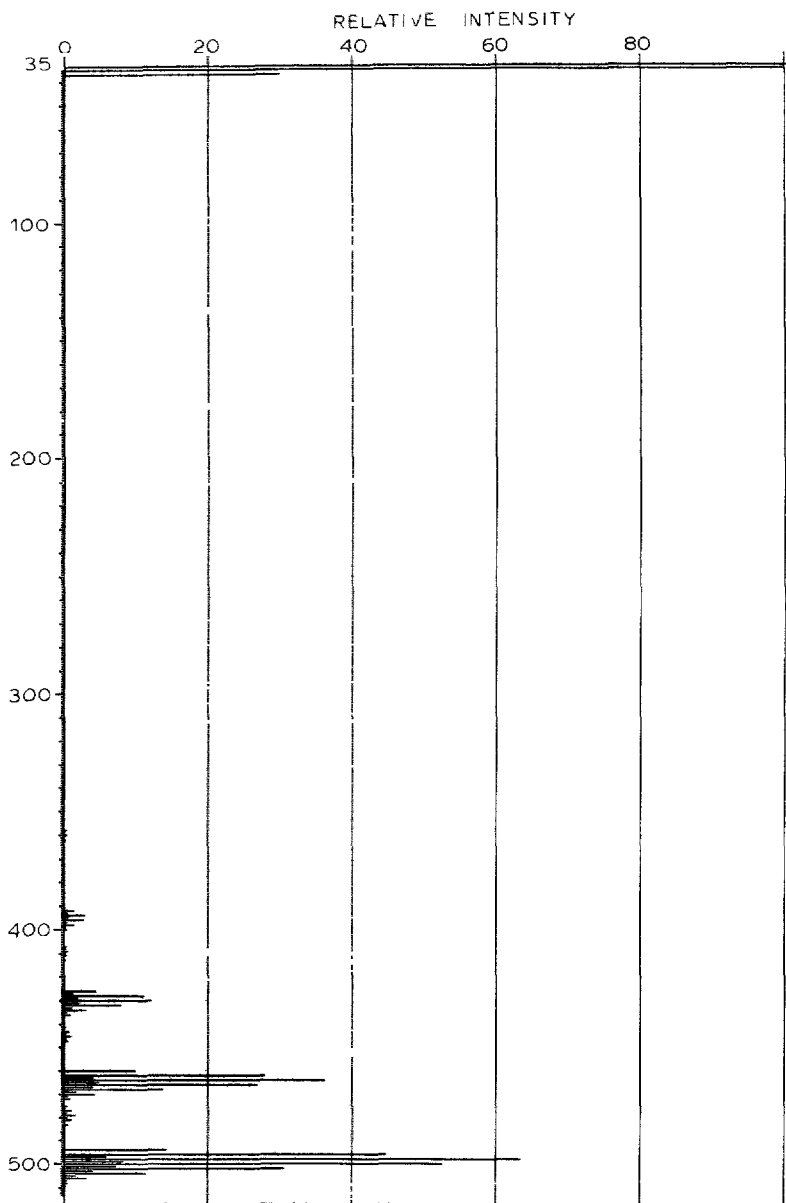
Fig 7. N$_2$O–CH$_4$ NICI mass spectrum of decachlorobiphenyl

The chemical thermodynamics in NICI-MS were also found to be affected by the physical design of the GC–MS source where the CI takes place. The experiments conducted with a relatively open and closed source designs gave parallel results. The principal feature of the open source was that it was less subject to filament carbonization and its sensitivity was maintained stable for a few weeks. Considerable absolute differences in the limits of detection were observed between two different in-

strument makes One system was clearly capable of detecting in the high femtogram region, whereas the other required two orders of magnitude more PCB material.

3.4. Selected ion monitoring utilizing EI-MS

Electron-impact mass spectrometry has been a very popular analytical tool, in addition to the electron-capture detector, as a GC detector for PCBs. The use of the conventional scanning mode suffers from an inadequate limit of detection for chlorobiphenyl isomers. The limits of detection between EI-MS and ECD may differ by as much as three orders of magnitude[30]. For this reason, EI-MS *per se* has not been as widely used unless there are large amounts of PCBs present in environmental and biological samples[45-56]. There have been reports, however, of a specialized application of EI-MS. Selected ion monitoring (SIM) had been primarily developed for drug analysis, but recently it has been applied to verifying and quantifying PCBs[45-48]. Improved limits of detection were achieved.

Another variant of EI-MS has been limited mass scanning (LMS). The use of SIM (programmed mode) and LMS permits the spectrometer to spend more time transmitting through the analyzer to the electron multiplier ions of interest to yield lower limits of detection[46]. Both of these techniques were under computer control and were also available to the analyst when operating in the NICI-MS mode.

3.5. Pulsed positive ion–negative ion chemical ionization (PPINICI) mass spectrometry

During the past few years PPINICI has been available; rapid switching between positive and negative CI (12 kHz) allows simultaneous information to be acquired[30]. Little research has been performed on its optimization and application to PCB analysis.

3.6 Combination of high-resolution gas chromatography and ultrasensitive detection

Figs 1 and 2 depict the combination of state-of-the-art high-resolution chromatography and electron-capture detection It is clearly evident from these profiles that modern electron-capture detectors are designed to preserve the high resolution that capillary columns are now capable of delivering.

The direct coupling of high-resolution GC capillaries with the ion source of mass spectrometers has also been successfully accomplished The flexible nature of silica capillaries has greatly facilitated this accomplishment, as most MS systems are not well engineered to accept the rigid glass capillaries.

Fig. 8 depicts an example of analysis of an Aroclor 1016–1254–1260 mixture (2.5:2.0 1 0, w/w) utilizing an Apiezon M coating (0.025 μm film), a PSD silica capillary and NICI-MS detection. Table 1 lists the operating conditions, which were optimized for dissociative electron capture (*i.e.*, enhancement of m/z 35 and 37). The mass chromatogram (m/z 35) exemplifies the close similarity between the proportional response for individual chlorobiphenyl isomers under methane NICI conditions and those obtained with electron-capture detection. An expanded version of this chromatogram is given in Figs. 9–11 Chromatographic peaks 3, 35 and 103 are the internal standards. 1,2-dichloronaphthalene, 1,2,3,4-tetrachloronaphthalene and octachloronaphthalene, respectively. The chromatographic peaks depicted in Figs. 9–11 indicate ideal symmetry and thus the chromatography was preserved. The peak
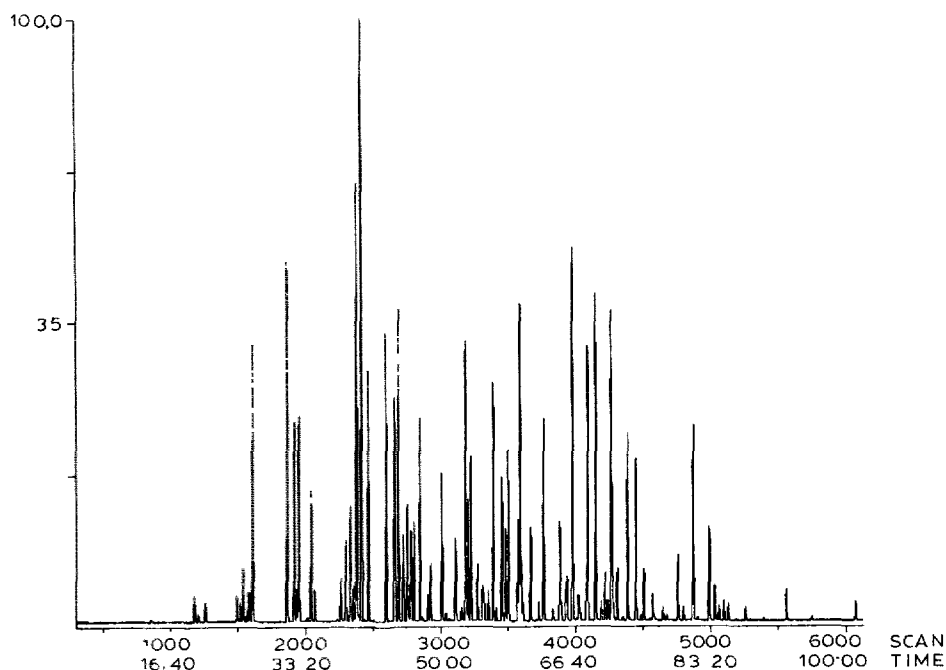
Fig. 8 Mass chromatogram $(m/z$ 35) of Arocior 1016–1254–1260 obtained by CH_4 NICI-MS.

TABLE 1

CAPILLARY GC–NICI-MS OPERATING CONDITIONS (FINNIGAN 4021)

| Mode	Parameter	Condition
GC	Capillary:	Fused silica
	I.D	0 23 mm
	Length	45 m
	Deactivation	Polysiloxane
	Stationary phase	Apiezon M
	Film thickness	0 025 μm
	He carrier gas	0 6 ml/min (32 cm/sec)
	Splitless/split	40 sec, 10 1
	Temperature	100°C (0 1 min) to 260°C at 1.5°C/min
MS	Reagent gas:	Methane
	Fore-pressure	0.2 Torr
	High-vacuum pressure	4 2 10^{-5} Torr
	Manifold temperature	120°C
	Ionizer temperature	260°C
	Emission current	0 5 mA
	Electron energy	70 eV
	Scan cycle	1 0 sec
	Scan range	30–700 daltons
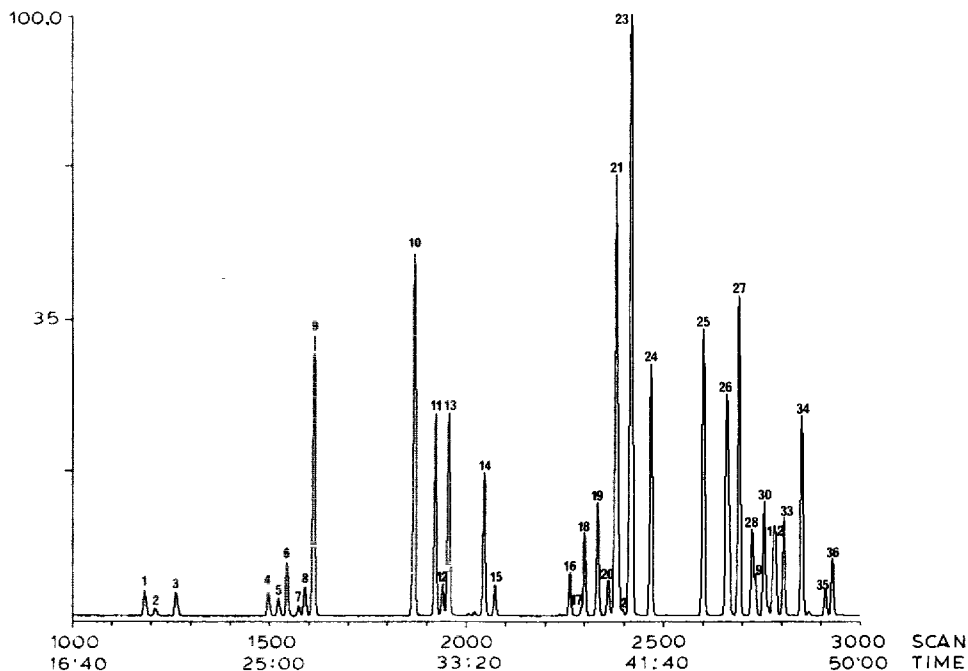
Fig 9 Mass chromatogram (m/z 35) of Aroclor 1016–1254–1260 obtained by CH_4 NICI-MS (Fig 8 expanded). Peak No 3 is the internal standard, 1,2-dichloronaphthalene
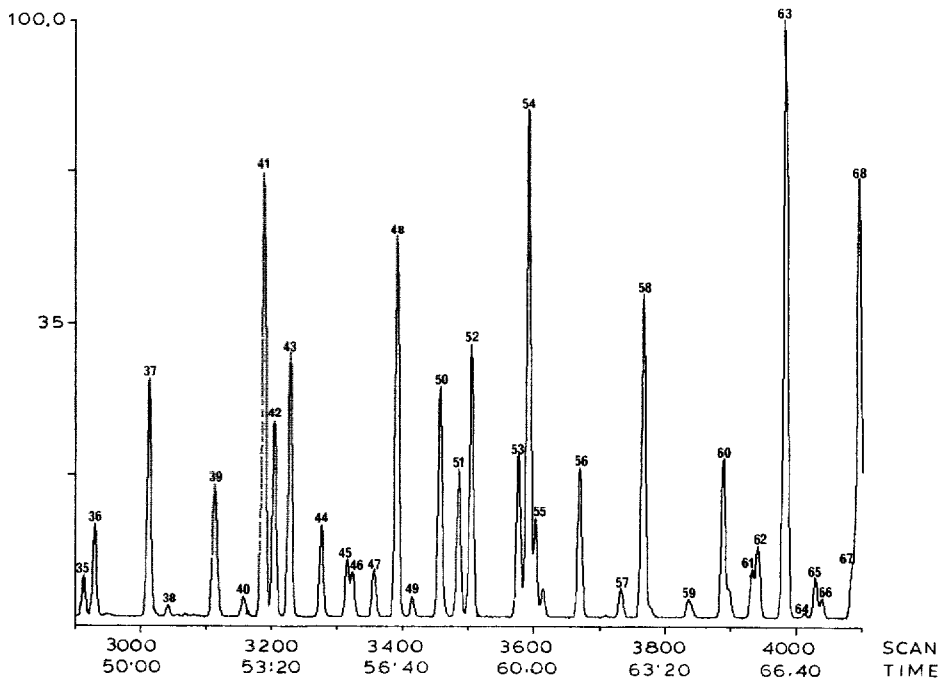

Fig 10 Mass chromatogram (m/z 35) of Aroclor 1016–1254–1260 obtained by CH_4 NICI-MS (Fig 8 expanded, middle portion) Peak No 35 is the internal standard, 1,2,3,4-tetrachloronaphthalene
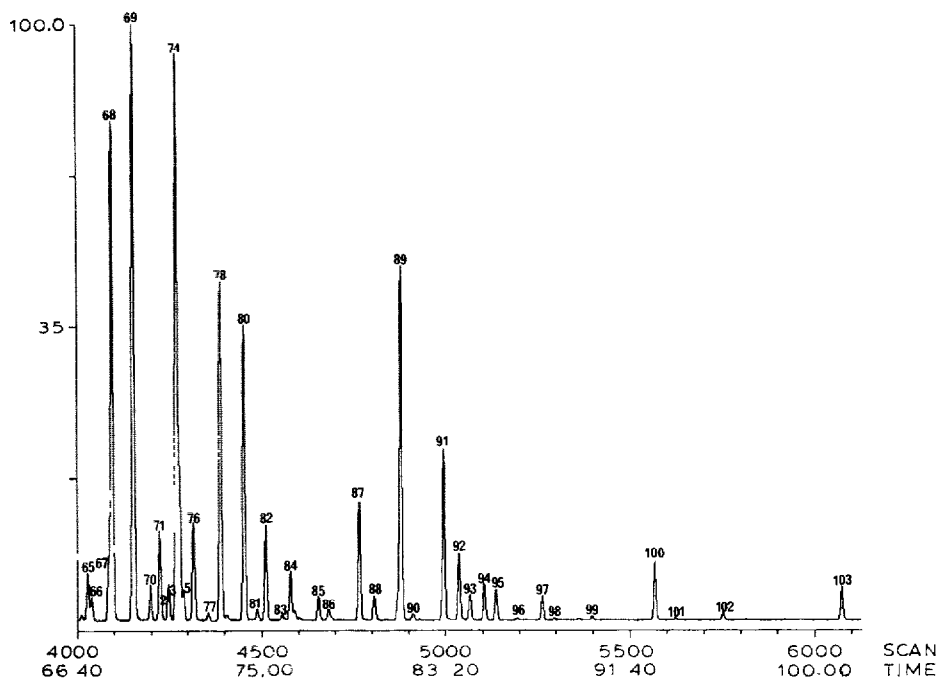
Fig 11 Mass chromatogram (m z 35) of Aroclor 1016–1254–1260 obtained by CH_4 NICI-MS (Fig 8 expanded, later portion). Peak No 103 is the internal standard, octachloronaphthalene.

residence times are generally 7–8 sec. Because the electron-capture detector and NICI-MS profiles are superimposable, the numbering scheme shown in Figs 9–11 was standardized for our characterization research and for our cross-referencing and verification efforts.

Another means of representing NICI-MS information is depicted in Figs. 12 and 13. The upper trace is the one shown in Fig. 8 but it is considerably reduced. The remaining profiles in Fig 12 are mass chromatograms for m/z 188 (Cl_1), 222 (Cl_2), 256 (Cl_3), 292 (Cl_4) and 326 (Cl_5) representing the five homologous series. It is important to note that under methane NICI conditions the intensity of molecular anions for Cl_1–Cl_5 was very weak to non-existent It is more appropriate to use nitrous oxide–methane for detecting which homolog is represented by a chromatographic peak. Fig. 13 shows mass chromatograms for m/z 360 (Cl_6), 394 (Cl_7), 428 (Cl_8), 462 (Cl_9) and 496 (Cl_{10} not detected) for the remaining homologous series. In this instance all of the chlorobiphenyl isomers were detected in the Aroclor mixture.

3.7. Variation of detector responses

A common problem with electron-capture, NICI-MS and EI-MS (SIM, LMS) detectors is the large variation that has been observed between the individual chlorobiphenyl isomers, both within and between homologous series[1,15–18]. The relative response factors (RRFs) for a few individual chlorobiphenyl isomers obtained with high-resolution GC-ECD (HRGC-ECD) have been reported[18]. Most isomers have
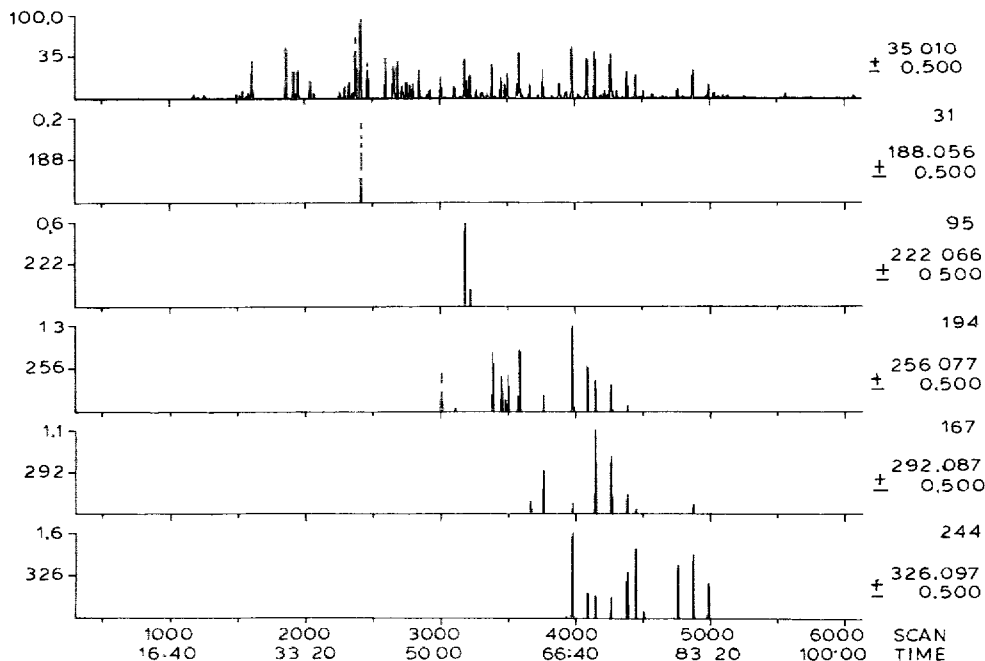
Fig 12 Mass chromatogram for parent ions of each PCB homologue (Cl$_1$–Cl$_5$) in Aroclor 1016–1254–1260 mixture
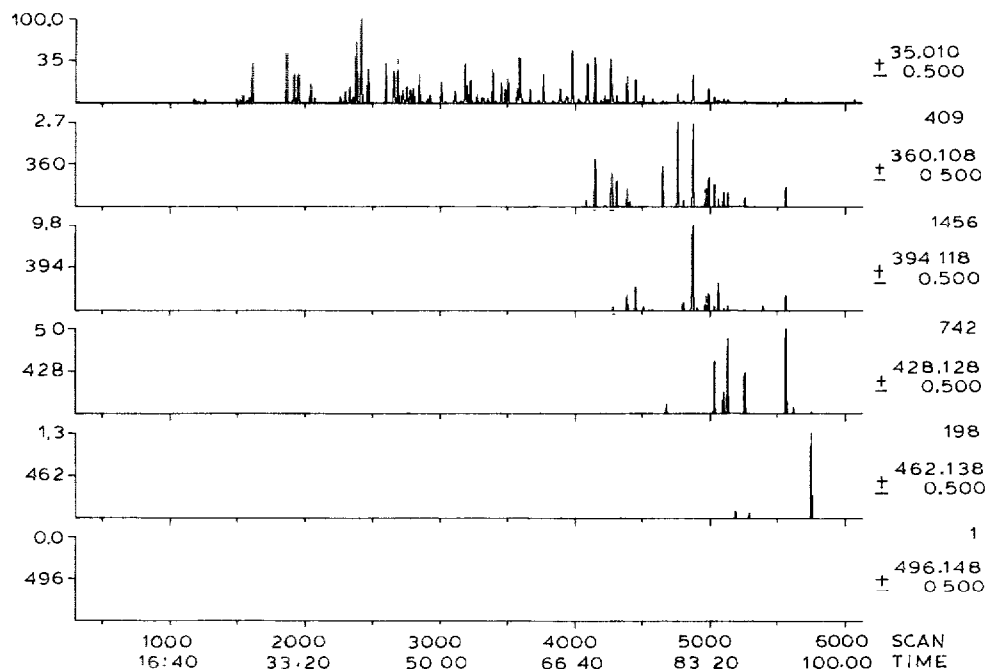
Fig 13. Mass chromatogram for parent ions of each PCB homologue (Cl$_6$–Cl$_{10}$) in Aroclor 1016–1254–1260 mixture

TABLE 2

RELATIVE RESPONSE FACTORS FOR INDIVIDUAL PCB ISOMERS USING HRGC–ECD

Homologue (No.)	PCB isomer No	RRF* (relative to OCN)		SE-54 column				Apiezon M column
				RRF (relative to MBB)		RRF (relative to TBB)		RRF (relative to DCN)
		Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean
1-Cl (3)	001	27 319	4 4	13 344	1 5	24.956	2 4	5 965
	002	47 158	5 2	20 152	3 7	38.534	3 9	9 435
	003	55 970	2 3	22 950	5 7	43.296	7 3	10 735
2-Cl (12)	004	10 696	15 2	4 798	10 2	9.153	11 5	2 703
	005	12 659	2 5	5 189	5 0	9.788	6 6	1 628
	006	2 622	1 5	2 851	1 3	5.556	2 5	1 049
	007	2 266	1 8	1.047	1 1	2.013	2 0	0 465
	008	3 958	2 6	2.040	0 3	3.836	1 5	0 798
	009	3 711	3 8	1 726	0 6	3.293	1 1	0 719
	010	5 202	0 0	2 054	0 8	3.920	1 9	0 717
	011	8 519	1 8	3 653	1 4	6.399	1 2	2 054
	012	4 322	4 8	2 211	1 1	4.162	1 4	0 929
	013	7 495	1 5	2 851	1 3	5.556	2 5	1 049
	014	4 956	3 4	2 395	1 3	4.578	1 9	0 987
	015	5 620	3 0	2 678	2 2	5.151	3 1	1 104
3-Cl (24)	016	2 678	3.0	1 087	1 1	2 088	1 9	0.378
	017	2 085	3.1	1 079	1.6	2 029	2 8	0.418
	018	2 543	6.0	1 129	3.1	2 152	3 2	0.651
	019	4 283	3 2	2 193	1.0	4 125	2 2	0.871
	020	1 344	3 6	0 670	2.5	1 260	3 5	0 283
	021	1 157	4 5	0 516	1.0	0 986	0 4	0.221
	022	0 757	5 5	0 341	3.1	0 627	1.5	0 139
	023	1 056	7 0	0 435	0 5	0 843	0.9	0 273
	024	2 198	3 6	0 480	0 5	1 627	1.4	0 273
	025	4.734	5 5	2 043	1 6	3 736	0.7	0 806
	026	2.001	2 5	1 046	0 7	1 969	1.9	0 388
	027	3.067	4 0	1 324	1 9	2 423	4.1	0 490
	028	1.449	8 3	0.747	0 6	1 433	0 9	0 315
	029	2.137	2 6	0.844	1 6	1 611	1.4	0 273
	030	0.742	4 8	0.392	0 3	0 743	0 4	0 155
	031	2 130	5 5	1 100	1 6	2 096	2 8	0 439
	032	2 633	4 9	1 136	0 7	2 079	1 7	0 421
	033	2 600	2 1	1 113	0 8	2 098	2 4	0 370
	034	1 144	3 2	0 590	0 5	1.109	1 5	0 231
	035	2 319	3 2	1 188	2 9	2.234	4 0	0 472
	036	1 351	21.7	0 780	1 7	1.428	3 5	0 319
	037	3 880	4.2	1 615	1 3	2 984	0 9	
	038	1 216	4.1	0 647	1 4	1 227	1 7	0 252
	039	3 813	3 1	2 000	1 1	3 768	0 3	0 778

	RRF (relative to TCN)		Statistics of RRFs (relative to OCN) for homologue					
			Range		Mean	Standard deviation	RSD (%)	N
RSD (%)	Mean	RSD (%)	Low	High				
0 8	27 695	1 4	27 319	55 970	43 482	14 675	33 7	3
2 9	46 291	1 6						
3 2	47 269	1 4						
1 7	11 929	2 3	2.266	12 659	6 002	3 225	53 7	12
7 1	7 171	7 3						
1 2	4 315	0 9						
4 7	1 986	0 5						
2 6	3 766	0 7						
1 3	3 452	0 7						
0 8	2 961	2 8						
3 3	9 941	1 1						
0 6	4.393	1 3						
1 2	4 315	0 9						
2 9	4.626	2 0						
4 1	4 178	0 6						
1 0	1 555	0.6	0 657	4 734	2 217	1 117	50 4	24
2 0	1 975	0.5						
1.9	2 872	2 7						
1.9	4 111	0 7						
2.3	1 336	0 3						
2 5	1 085	1 3						
1 4	0 649	0 1						
0 7	1 192	1 4						
0 7	1.192	1 4						
4 2	3.356	4 1						
0 9	1 862	5 7						
2 4	2 040	6 3						
1 3	1 801	1 2						
0 7	1 192	1.4						
0.5	0 686	2 2						
3.3	2 489	1 4						
2.8	1 753	5 5						
1 7	1 755	1 0						
2 0	1 088	0 7						
2 6	2 226	0 8						
6 7	1.327	1 4						
	—	—						
4 0	1 114	4.4						
0 9	3 690	0.4						

TABLE 2 *(continued)*

Homologue (No.)	PCB isomer No	RRF* (relative to OCN)		SE-54 column				Apiezon M column
				RRF (relative to MBB)		RRF (relative to TBB)		RRF (relative to DCN)
		Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean
4-Cl (42)	040	1 525	3 8	0 707	0.9	1 353	0 8	0.278
	041	1.688	3 0	0 879	2.2	1 652	1 2	0.336
	042	1 465	4 1	0 747	1.1	1 375	2 0	0 317
	043	0 331	4 4	0 138	2.2	0 273	2 0	0 045
	044	2 184	3 3	0 758	1.4	1 485	1 7	0 353
	045	2 319	5 1	0 996	1 2	1 909	2 4	0 339
	046	0 866	0 0					0 209
	047	1 219	4 4	0.584	5 4	1 102	6 1	0 247
	048	1 831	4.1	0 888	2 7	1 749	2 5	0 371
	049	1 713	9 2	0 691	8 3	1 330	8 9	0 270
	050	0 876	5 5					0 375
	051	1 200	1.9	1 428	0 8	2.784	2 0	0 480
	052	1 400	6.7	0 679	2 9	1 294	3 3	0 328
	053	2 156	5.3	1 054	1 4	1 876	2 7	0 424
	054	2 409	3.7	1 224	1 2	2 356	1 7	0 503
	055	1 481	4.2	0 663	2 5	1 237	2 8	0 282
	056	1 239	2.2	0 622	0 8	1 170	0 8	0 259
	057	1 405	3 4	0 742	1 0	1.399	0 3	0 284
	058	2 338	2.8	0 835	0 7	–	–	0 640
	059	1 405	3 4	0 742	1 0	1.399	0 3	0 284
	060	1 464	0 4	0 626	2 4	1 196	2 6	0 221
	061	0 990	4 0	0 450	1 0	0.860	0 1	0 185
	062	1 031	5 4	0 535	1.4	1 026	2 6	0 197
	063	1 209	2 3	0 656	2.3	1 236	2 0	0 246
	064	1.209	2 3	0 656	2.3	1 236	2 0	0.246
	065	1.090	3 5	0 502	1.6	0 957	0 6	0.213
	066	1.765	4 1	0 724	0 73	1 366	9 0	0.148
	067	1.405	3 4	0 742	1 0	1 399	0 3	0.284
	068	1.635	4 3	0 760	0 4	1 405	1.7	
	069	1 683	3 1	0.585	0 9	1 146	1.5	0 271
	070	1 377	3 3	0 616	1 6	1 151	2.1	0.159
	071	2 605	4 6	1.089	1 9	2 147	1.8	0 444
	072	1 114	6 9	0.491	8 3	0 944	7.4	0 279
	073	1 547	3 2	0.796	2 5	1 498	3.6	0 313
	074	1 209	2.3	0 656	2 3	1.236	2 0	0 246
	075	1 286	4.1	0 650	0 9	1.198	1 9	0 273
	076	1 707	6.6	0 861	0 9	1.670	1 5	0 313
	077	2 036	34 7	0 758	35 0	1.327	34 8	0 544
	078	1 481	4 2	0 663	2 5	1.237	2 8	0 282
	080	2 020	2 6	0 835	0.7	–	–	
	080	0 587	14 5					0 252
	081	1.008	12 7	0 490	12.5	0 922	13 5	0 219

| | | | Statistics of RRFs (relative to OCN) for homologue | | | | | |
| | RRF (relative to TCN) | | Range | | Mean | Standard deviation | RSD (%) | N |
RSD (%)	Mean	RSD (%)	Low	High				
1 5	1 366	0 3	0.331	2 605	1 488	0 490	32.9	42
2 5	1.585	0 4						
1 1	1.477	0 7						
2 6	0 207	3 7						
1 8	1 859	0 9						
0 8	1 605	1 2						
3 5	0 969	5 1						
2.5	1 087	0.3						
4.9	1 722	3.6						
19.8	1 151	17.2						
1.9	1 871	1.1						
1.0	1 975	0.6						
1.8	1 448	1.9						
2 6	1 867	3 6						
1 1	2 179	1.3						
5 9	1 231	0.8						
2 9	1 220	0 5						
1 4	1 347	1 0						
3 6	2 972	0 7						
1 4	1 347	1 0						
10 3	1 037	12 5						
1 6	0 910	0 3						
2 1	0.933	0 3						
2 4	1.124	0 3						
2 4	1.124	0 3						
1 4	1 026	1 0						
4 0	0 652	5 0						
1 4	1 347	1 0						
1 7	1 430	0 8						
6 8	0 703	5 6						
2.7	2 063	0.6						
2.4	1 208	0.5						
2.1	1 475	0 7						
2.4	1 124	0.3						
3.3	1 547	0.5						
1.8	1 366	0.6						
1.0	2 635	2.1						
5.9	1 231	0.8						
15 6	1 259	16 5						
3 1	1 035	1 5						

TABLE 2 *(continued)*

Homologue (No)	PCB isomer No	RRF* (relative to OCN)		SE-54 column				Apiezon M column
				RRF (relative to MBB)		RRF (relative to TBB)		RRF (relative to DCN)
		Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean
5-Cl (46)	082	1 242	3 2	0 588	3 9	1 106	3 1	0 124
	083	1 802	5 9	0 686	7 8	1 338	8 9	0 264
	084	1 802	5 9	0 686	7 8	1 338	8 9	0.314
	085	1 325	5 5	0 580	2 4	1 048	1 6	0 265
	086	1 073	6 0	0 553	3 3	1 053	2 7	0.222
	087	0 934	5 4	0 494	1 4	0 951	1 0	0.183
	088	1 249	6 1	0 605	0 7	1 156	0 5	0 248
	089	0 830	2 7	0 359	3 4	0 656	5 1	0 099
	090	2 305	7 7	0 480	3 8	1 630	4 0	0 321
	091	1 824	5.6	0 798	2 3	1 442	2 9	0 335
	092	1 790	5 9	0 834	2 8	1 644	2 1	0 382
	093	1 727	3 7	0 598	1 6	1 172	1 5	0.280
	094	3 071	9 8	0 936	7 3	1 782	6 7	0.370
	095	1 654	4 6	0 939	1 4	1 792	0 3	0.352
	096	2 093	3 6	1 015	0 9	1 941	1 0	0 415
	097	1 614	3 1	0 655	0 5	1 258	1.9	0 264
	098	1 329	2 1	0 684	0 8	1 288	1 0	0 263
	099	2 305	7 7	0 480	3 8	1 630	4 0	0 289
	100	1.437	3 9	0.598	0 6	1 105	0 3	0 235
	101	1 847	2 1	0.835	0 5	1 574	1 4	0 270
	102	3 071	9 8	0 936	7 3	1.782	6 7	0 370
	103	1 329	3 9	0 688	1 9	1 268	3 4	0 282
	104	3 704	3 4	1 658	0 6	3 095	1 8	0 378
	105	1 285	2.1	0 651	1 5	1 225	1 8	0 260
	106	1 058	2 7	0 554	2.0	1 045	1 0	0.216
	107	1 026	2 5					0 247
	108	1 142	1 6	0 625	2 3	1 177	0.9	0 230
	109	0.931	5 0	0 442	2 9	0 843	2 4	0 172
	110	1.087	2 3					0 262
	111	1 295	2 0	0 705	2 2	1.328	0 9	0 263
	112	1 111	4 8	0 582	0 7	1.088	0 5	0 223
	113	1 017	7.6	0 547	1 2	1 020	1 5	0.186
	114	0 947	1.4	0 419	1.6	0 735	1 2	0.222
	115	1 251	3 5	0 434	1 5	0 851	1.2	0 202
	116	0 510	6 6	0 271	1 4	0 513	1.0	0 106
	117	1.078	5 7	0 459	2 0	1 027	1 4	0 224
	118	1 238	2 5	0.657	3 5	1.236	2 3	0 236
	119	1 276	5 6	0 559	3 2	1.009	2 0	0 245
	120	1 295	2.0	0 705	2 2	1 328	0 9	0 263
	121	1 270	3 8	0 589	0.8	1 127	0 4	0.232
	122	1 644	2 9	0 853	2.5	1 625	2.3	0.338
	123	1 189	5 4	0 598	6 8	1 119	7.8	0 251
	124	1 078	3 1	0 512	3 2	0 977	1 8	0 204
	125	0 753	28 5	0.359	3 4	0 656	5 1	0 238
	126	2 491	5 0	1 201	7 4	2.297	7 3	0 498
	127	1 142	1.6	0 625	2 3	1 177	0 9	0 230

			Statistics of RRFs (relative to OCN) for homologue					
	RRF (relative to TCN)		_Range_		_Mean_	_Standard deviation_	_RSD (%)_	_N_
RSD (%)	_Mean_	_RSD (%)_	_Low_	_High_				
2 3	0.545	3 1	0.510	3 704	1 489	0 640	43 046	46
1 5	1.166	1 9						
0.7	1 292	0 6						
3.6	1 083	1 5						
3.4	1 258	0.4						
4 3	0 793	2.3						
4 0	1 162	2 0						
6 6	0 410	1 6						
0 9	1 398	0 8						
2 1	1 369	0 6						
6 7	1 773	4 6						
1 5	1 473	0 8						
3.6	2 070	0 6						
1 5	1 453	2 1						
3 8	1 944	3 2						
1 5	1 166	1 9						
1 3	1.262	6 0						
4 9	1 261	6 4						
2.0	1 343	0 5						
2.2	1 238	0.8						
3.6	2 070	0 6						
1.4	1 313	1 1						
1 5	1.811	1 5						
2.3	1 246	6 1						
0.8	1 026	0 5						
3 3	1 147	0.6						
2 9	1 049	0 8						
4 5	0 847	4 2						
3 0	1 216	0 3						
2.7	1 199	0 3						
3 2	1 034	3 2						
7 2	0 889	8 0						
2 2	1 075	0 6						
1 3	1.064	0 3						
2 6	0 469	3 4						
1.9	1 038	0 5						
2 5	1 131	7 3						
3 0	1 001	1 2						
2 7	1.199	0 3						
1 5	1 138	0 4						
3.6	1 913	0 5						
0 5	1 167	1 2						
3 0	0 981	2 6						
5 3	0 994	10 1						
4 8	2 336	3 3						
2.9	1 049	0.8						

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TABLE 2 *(continued)*

Homologue (No)	PCB isomer No	RRF* (relative to OCN)		SE-54 column				Apiezon M column
		Mean	RSD (%)	RRF (relative to MBB)		RRF (relative to TBB)		RRF (relative to DCN)
				Mean	RSD (%)	Mean	RSD (%)	Mean
6-Cl (42)	128	1 309	29 7	0 808	29.2	1 517	27 4	0.215
	129	0 987	3.4	0 520	1.6	0 992	0 9	0 249
	130	1 423	3.9	0 762	1.3	1 407	2 4	0 261
	231	0 919	1.9	1 153	1.0	2.019	0 6	0 218
	132	1 423	2 4	0 743	1 2	1.387	2 0	0 271
	133	0 827	8 4					0 259
	134	1 213	2 2	0.631	0 5	1.186	1 1	0 242
	135	1.564	1 8	0.595	1 9	1 149	2 9	0 259
	136	1.538	3 3	0 803	1 7	1 480	2 8	0 323
	137	1.055	3 2	0 489	1 8	0 934	1 3	0 193
	138	1 161	2 9	0 601	2 5	1 107	1.8	0 249
	139	1 253	3 4	0 582	1 3	1 112	0.5	0 229
	140	1 179	7 2	0 604	4 8	1 160	6.2	0.229
	141	0 475	6 7	0 259	2 1	0 490	1 8	0.096
	142	0 993	3 8	0 509	1 0	0 960	1.8	0.207
	143	1 196	3 4	0 583	3.1	1 114	3.2	0.236
	144	1 277	3.9	0 664	1.0	1 265	2 0	0.261
	145	1 539	2.7	0 801	1.8	1 581	0 9	0.318
	146	2 521	1 1	0 996	1.4	1 900	0 9	0 436
	147	1 260	5.8	0 674	0.8	1.242	1 8	0 263
	148	2 258	8 2	1 049	4.8	1 939	5 5	0.362
	149	1 564	1.8	0 595	1.9	1 159	2 9	0.557
	150	2 045	2.6	1 105	0.6	2.063	2 5	0 370
	151	1 011	3.8	0 473	1.3	0 901	0 1	0.246
	152	1 441	3 1	0 754	3.5	1.421	2 5	0 295
	153	1 606	4 7	0 499	3 6	0.950	3 3	0 148
	154	1 502	4.0	0 524	1.8	1.027	1 1	0 241
	155	2 158	5.7	0 926	1 5	1.776	3 0	0 315
	156	0 993	2 0	0 511	2 4	0.953	2 4	0 193
	157	1 118	5 7	0 556	1 3	1.065	2 9	0 227
	158	0 954	9 1	0 463	3 2	0.883	1 6	0 176
	159	1 227	7 3	0 616	5 1	1.181	6 6	0 246
	160	0 846	5 7	0 403	3 0	0.770	2 9	0 172
	161	1.010	2 2	0.279	2 7	0.914	1 1	0 192
	162	0 838	5 3	0 502	10 5	0.988	9 7	0 116
	163	1 271	2 3	0.659	1 5	1.231	2 0	0 244
	164	1 294	3 1	0.661	2 9	1.166	1 3	0 247
	165	1 677	3 5	0 720	1 8	1.381	2 2	0 197
	166	0 971	9 7	0 485	2 7	0.926	1 3	0 173
	167	1 195	5 3	0 502	10 5	0.988	9 7	0 116
	168	1 046	3 1	0.525	1 6	1.003	1 8	0 198
	169	1 428	3 2	0.678	5 4	1.297	5 5	0 291

| | RRF (relative to TCN) | | Statistics of RRFs (relative to OCN) for homologue | | | | | |
| | | | Range | | Mean | Standard deviation | RSD (%) | N |
RSD (%)	Mean	RSD (%)	Low	High				
5 5	0 932	4 5	0.475	2 521	1 286	0 402	31.342	42
4 1	1.028	0 9						
4 5	1.235	5 6						
1 2	1.056	2 1						
1 7	1 296	0 6						
8 0	1 280	6 9						
3 0	1 142	0 6						
8 0	1 280	6 9						
1 6	1 530	1 4						
1.9	0 949	0 8						
2.7	1 161	2.0						
1.7	1 122	0.6						
1.1	1 084	1.1						
11.6	0 422	10.1						
4.3	1 174	1.0						
2 6	1 104	2 5						
3 7	1 480	0 3						
0 4	1 506	0 2						
3 2	1 801	0 7						
1 2	1 246	1 0						
1 4	1 712	2 0						
19 8	2 675	19 6						
1 3	1.771	0 9						
2 0	1.087	2 6						
0 9	1.398	0 5						
14 5	0.641	16 2						
1 7	1.270	0 7						
1 1	1.493	0 9						
1 8	0.924	0 8						
2 7	1.077	1 1						
9 5	0.846	9 3						
2 6	1.164	0 9						
4 2	0.804	1 8						
2 1	0.290	1 7						
3 1	0.537	0 7						
1 7	1.168	0 7						
2 9	1 184	2 4						
1 8	0.934	0 4						
10 1	0.831	9 8						
3 1	0.537	0 7						
3 4	0.929	3 5						
4 9	1 365	2 3						

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TABLE 2 *(continued)*

Homologue (No)	PCB isomer No	RRF* (relative to OCN)		SE-54 column				Apiezon M column
				RRF (relative to MBB)		RRF (relative to TBB)		RRF (relative to DCN)
		Mean	RSD (%)	Mean	RSD (%)	Mean	RSD (%)	Mean
7-Cl (24)	170	1 698	3 6	0 466	2 5	0 858	3 1	0 414
	171	1 033	3 6	0 542	1 3	1 032	2 2	0 209
	172	1 722	2 3	0 802	2 1	1 482	3 5	0 253
	173	0 852	6 4	0 452	1 5	0 833	0 9	0 180
	174	1.344	6 4	0 724	1 3	1 333	0 8	0 279
	175	9.084	2 0	2.868	26 1	5.406	26 8	1 809
	176	0.652	4 9					0 279
	177	0 292	1 9	0 314	1 8	0.595	1 3	0 057
	178	2 418	3 1	1 007	0 6	1.861	0 9	0 403
	179	1 203	9 9	0 624	0.3	1 153	0 5	0 269
	180	1 113	4 1	0 516	1.1	0 984	0 8	0.274
	181	1 142	2.6	0 437	2.0	0 846	0 7	0.161
	182	1 123	6 7	0 596	1.6	1 097	0 6	0.237
	183	1 305	6 3	0 648	1 4	1 194	0.9	0 221
	184	0 978	2 8	0 499	1 5	0 959	1.7	0 203
	185	0 813	1 9	0 441	3 3	0 841	2.2	0 167
	186	0 964	0 7	3 121	13 7	5 466	13 5	0 226
	187	0 904	10 8	0 376	10 7	0 659	10 4	0 223
	188	1 444	6 1	0 770	0 7	1 418	1 8	0 303
	189	1 993	3 2	0.830	7 0	1 534	9 0	0 036
	190	0.862	1 4	0 429	1 6	0 808	0 7	0 178
	191	0 490	2 5	0 253	2 6	0 480	2 1	0 106
	192	0 736	5 3	0 379	0.9	0 698	2 1	0.161
	193	0 868	1 5	0 295	2.2	0 517	2 1	0.165
8-Cl (12)	194	0 967	1 5	0 533	0 7	1 005	1 7	0 196
	195	2 376	1 4	1 124	3 7	2 141	2 5	0 574
	196	1.263	3 1	0.582	1 9	1 113	1 1	0 233
	197	1.116	4 1	0 537	1 2	1.034	0 4	0 251
	198	0 831	32 9	0 415	36 4	0.807	37 0	0 232
	199	0 969	2 4	0 443	0.5	0 852	1 8	0.201
	200	2 261	3.2	1 124	1 8	2 071	2 5	0.505
	201	1 655	3.2	0 760	1 9	1 454	1.1	0 306
	202	1 244	2 7	0 692	1 3	1 303	1.5	0 223
	203	0 910	3 3	0 399	4 8	0 721	5 5	0 201
	204	2.595	5 0	1.433	4 0	2 699	2 5	0 471
	205	0 883	1 8	0 415	4 1	0.783	5 7	0 184
9-Cl (3)	206	0 953	1 8	0 329	1.2	0 645	1 5	0.155
	207	0 764	3 5	0 378	1 1	0 725	1.9	0 260
	208	1 032	1 5	0 473	2 0	0 890	0.8	0 092
10-Cl (1)	209	0.659	2 2	0 335	2 9	0 638	1 7	0 264

* These values were obtained by averaging the RRFs obtained from the two columns in most instances

			Statistics of RRFs (relative to OCN) for homologue					
RRF (relative to TCN)			*Range*		*Mean*	*Standard deviation*	*RSD (%)*	*N*
RSD (%)	*Mean*	*RSD (%)*	*Low*	*High*				
5 0	1 823	2 6	0.292	9 084	1.452	1 695	116 7	24
4.2	1 185	0 9						
1.8	1 196	2.9						
1.2	0 850	0.5						
1 2	1 320	0 2						
2 1	8 690	6 9						
3 1	1 393	1 2						
3 0	0 250	1 5						
2 5	2.306	0 4						
3 2	1.539	1 0						
2 3	1 207	3 2						
2 5	0 707	1.2						
2.8	1 122	2.4						
1 8	1 164	0.8						
2 5	0 881	0 9						
2 7	0 736	3 3						
2 4	1.095	0 7						
3 9	1 079	1 7						
1 0	1 434	0 4						
3.3	0 206	1.1						
2 3	0 855	5.6						
2 5	0 468	0 9						
1 3	0 760	0 4						
2 6	0.799	0 9						
4.0	0 850	3 1	0.831	2 595	1 423	0 640	45.0	12
2.7	2 532	4.0						
2 1	1 142	0 9						
3 3	1 088	1 7						
2 4	0 928	1 6						
5 8	0.861	1 7						
3 1	2.353	2 5						
2 0	1 501	0 8						
3.0	1 061	0.9						
3 7	0 470	5 1						
3 6	2 235	1 4						
3 5	0 810	1 4						
1 8	0 815	1 0	0.764	1 032	0.916	0 138	15.1	3
3.7	1 039	2 3						
1 7	0 405	0.7						
4 5	1 055	2 9						

been analyzed on SE-54 and Apiezon M fused-silica capillaries and the RRF compared (Table 2) The RRF was calculated as follows:

$$RRF = \frac{Amt_i}{A_i} \cdot \frac{A_{i\,s}}{Amt_{i\,s.}}$$

where RRF = relative response factor for PCB isomer i; Amt, = amount of PCB isomer i injected; A_i = peak area, $A_{i\,s}$ = peak area for internal standard; $Amt_{i\,s}$ = amount of internal standard.

The relative standard deviation for the RRFs within a homologous series ranged from 32 to 117%. Thus, for accurate quantification of individual chlorobiphenyl isomers by HRGC–ECD, the appropriate RRF must be employed. The largest variation is observed with the Cl_7 homologous series. As additional chlorine substituents are introduced on to the biphenyl nucleus, the limits of detection do not significantly decrease and the response variation decreases as ring substitution pattern no longer plays a large role in determining the magnitude of response This is not the case, of course, with the lower homologous series where the ring substitution pattern and number of chlorine substituents are important determinants of electron-capture detector response.

In a parallel study, the relative molar response (RMR, for m/z 35) has been determined for individual chlorobiphenyl isomers using high-resolution GC–NICI-MS. The operating conditions were as previously given in Table 1. The RMR was calculated as follows:

$$RMR_i = \frac{A_i}{A_{i\,s}} \cdot \frac{MW_i}{MW_{i\,s.}} \cdot \frac{Amt_{i\,s}}{Amt_i}$$

where A_i = peak area of PCB isomer i; $A_{i\,s}$ = peak area of internal standard; MW_i = molecular weight of PCB isomer i; $MW_{i\,s}$ = molecular weight of internal standard, $Amt_{i\,s}$ = amount of internal standard; Amt_i = amount of PCB isomer i.

The relative standard deviation for the RMR_i values within a homologous series ranged from 33 to 125% (Table 3). It is apparent that appropriate RMR factors must be employed for accurate quantification.

A summary comparison of response factors is given in Table 4 for electron-capture, NCI-MS and EI-MS (SIM) detection. Literature values for EI-MS were normalized to the lowest response within a homologous series. Thus, a comparison between homologs was not possible[45] On the other hand, it can readily be seen that EI-MS exhibited the lowest relative standard deviation within a homologous series when compared with ECD and NICI-MS. Some caution is needed in this comparison as the number of chlorobiphenyl isomers used in the study was small This observation is consistent with the expectation that EI-MS produces the smallest variation of response between chlorobiphenyl isomers No comparable data for positive ion chemical ionization have been reported: however, the variations in responses should be similar to EI-MS.

The extreme RRF_i values determined with electron-capture detection were approximately 190:1. The range of RRF values was not as large as reported by other investigators[1,15–18]. This difference may reflect differences amongst instrumental systems.

The extreme RMR$_i$ values (the calculation includes MW) determined with NICI-MS were approximately 320·1.

The importance of using appropriate response factors for quantifying individual chlorobiphenyl isomers is evident from the above observations.

4 CHLOROBIPHENYL ISOMERS AND INSTRUMENT CALIBRATION

4 1 Primary standards

The issue of instrument calibration for chlorobiphenyl isomer quantification in environmental, biological and process stream samples has been recognized, and for this reason the synthesis of the individual isomers was performed[57].

Primary standards have been also needed for establishing reference data (spectral) banks for NICI-MS, EI-MS, FTIR, etc., for use in qualitative analysis or for verification purposes. They have been needed to establish relative retention indices to standardized fused-silica capillary GC (FSCGC) operating conditions.

The large-scale synthesis of chlorobiphenyl isomers would obviously be an expensive proposition, particularly if the supply must accommodate the needs of many analytical laboratories performing isomer quantification in environmental, biological and process stream samples. Hence research on devising alternative techniques for instrument calibration has been needed.

4.2. Secondary standards

One approach has been to determine whether a secondary standard for calibrating instruments for quantification could be used so that this secondary standard could be widely distributed among laboratories involved in chlorobiphenyl isomer analysis. The initial availability of the primary standards (209) has been the key to developing a secondary standard.

Two approaches have been investigated One is the characterization of an Aroclor "cocktail" using primary standards[58-63]; the other employs a "clustering" of similar response factors to derive a small subset of chlorobiphenyls from the 209 primary standards, with a chlorobiphenyl serving as a surrogate for several isomers[64]. Each of these concepts is discussed here

4.3. Characterization of Aroclor mixtures

As ample amounts of various commercial Aroclors have been available for distribution, the use of an Aroclor "cocktail" that was thoroughly characterized with respect to isomer speciation and amount has been studied.

An Aroclor 1016–1254–1260 mixture (2.5:2 0·1 0, w/w) was used. For characterization the use of relative retention time data for primary standards and matching with those in the Aroclor cocktail mixture for three different HRGC–ECD systems and one HRGC–NICI-MS system were employed In addition, the molecular ions and mass spectra obtained from HRGC–NICI-MS and HRGC–EI-MS analysis of the Aroclor cocktail mixture were used to establish the identities of the components in each of the chromatographic peaks.

A more complete Aroclor cocktail characterization (qualitatively and quantitatively) would be desirable and allow its use as a secondary standard for instrument

TABLE 3

RELATIVE MOLAR RESPONSES (m/z 35) FOR INDIVIDUAL PCB ISOMERS USING GLASS CAPILLARY GC–NICI-MS

Homologue (No)[*]	PCB isomer No [**]	RRF₁	(RSD, %)	Range	Mean ± S D (RSD, %)	N[***]
1Cl (3)	1	0 356	(6 8)[§]	0 091–0 356	0 184 ± 0 15 (81)	3
	2	0 105	(6 2)			
	3	0 091	(5 0)			
2Cl (12)	5	0 574	(10)[§]	0 574–4.223	1 662 ± 1 23 (74)	8
	7	4 223	(11)			
	9	2 064	(0 6)			
	10	2 430	(4 4)			
	11	0 574	(4.6)			
	12	1 452	(5.0)			
	14	1 209	(1.3)			
	15	0.773	(1 0)			
3Cl (24)	18	0.340	(12)[§§]	0.340–5 143	1 378 ± 1.72 (125)	7
	21	0.842	(3 1)			
	22	5.143	(2 6)			
	26	0.623	(3 1)			
	29	0.462	(4 3)			
	30	1.686	(4 4)			
	31	0.555	(1 9)			
4Cl (42)	40	1 240	(6 3)[§§]	0 048–2 013	0.971 ± 0 48 (50)	6
	42	1 208	(3 0)			
	44	0 920	(4 7)			
	47	1 447	(2 5)			
	53	0 048	(16)			
	54	0 358	(0 5)			
	55	0 779	(5 3)			
	60	2 013	(1 9)			
	61	1 562	(2 3)			
	65	0 789	(0 6)			
	69	1 055	(4 6)			
	70	0 989	(8 4)			
	72	0 840	(18)			
	75	1 038	(1 7)			
	77	0 364	(3 9)			
	81	0 893	(1 7)			
5Cl (46)	85	1 077	(2 0)[§§§]	0 465–1.216	0 805 ± 0 27 (33)	12
	87	0 564	(8 0)			
	93	0 528	(4.6)			
	101	0 818	(8 0)			
	106	1 123	(4 8)			
	112	0 667	(3 1)			
	114	1 137	(4 0)			
	116	1 216	(1.8)			
	117	0 839	(2.5)			
	118	0 465	(8 4)			
	121	0 634	(5.5)			
	122	0 591	(2.3)			

TABLE 3 *(continued)*

Homologue (No.)[*]	PCB isomer No.[**]	RRF_i	(RSD, %)	Range	Mean ± S D (RSD, %)	N[***]
6Cl (42)	128	1 011	(4 8)[§§§]	0 369–1.440	0 817 ± 0 29 (36)	16
	129	0 901	(8.4)			
	131	1.256	(4.8)			
	133	0.559	(2 7)			
	136	0.396	(4 9)			
	137	0 911	(4 6)			
	139	0 747	(4 1)			
	141	1 440	(8 6)			
	147	1 042	(6 8)			
	151	1 030	(7 3)			
	155	0.369	(2.9)			
	159	0.525	(0 7)			
	160	0.735	(2 5)			
	161	0 719	(2 3)			
	163	0 688	(4 4)			
	165	0 738	(3 9)			
7Cl (24)	170	0.451	(10)	0.236–1.192	0 703 ± 0.30 (43)	13
	173	0 659	(0 4)			
	175	0 305	(2 5)			
	180	0 679	(11)			
	184	0 708	(7 0)			
	185	0 755	(16)			
	186	0 236	(4 9)			
	187	1 102	(11)			
	188	0.503	(5 1)			
	191	1.192	(3 0)			
	192	0.542	(5 0)			
	193	1.096	(8 0)			
8Cl (12)	194	0 637	(1.3)[§§§]	0 241–1 116	9 573 ± 0 26 (46)	8
	196	0 608	(3.9)			
	197	1 116	(9 0)			
	199	0 393	(6 3)			
	200	0 486	(6 8)			
	201	0 413	(5 3)			
	202	0 692	(5 9)			
	204	0 241	(9 1)			
9Cl (3)	206	0.431	(8 0)[§§§]	0 066–0 565	0.354 ± 0 26 (73)	3
	207	0.066	(26)			
	208	0.565	(20)			
10Cl (1)	209	0 418	(7 5)[§§§]	—	—	—

[*] (No.) = number of theoretical isomers possible.
[**] See ref 58 for assignments
[***] N = number of isomers studied, each isomer was measured in triplicate
[§] Internal standard = 1,2-dichloronaphthalene.
[§§] Internal standard = 1,2,3,4 tetrachloronaphthalene
[§§§] Internal standard = octachloronaphthalene

TABLE 4

COMPARISON OF RELATIVE RESPONSE FACTORS BETWEEN GLASS CAPILLARY GC-ECD, GC–EI-MS (MOLECULAR ION) AND GLASS CAPILLARY GC–NICI-MS (m/z 35) FOR HOMOLOGOUS SERIES OF PCBs

Homologous series	Glass capillary GC ECD*			Glass capillary GC NICI-MS*			GC-EI-MS**		
	Range***	Mean ± S D (RSD, %)	N§	Range***	Mean ± S D (RSD, %)	N§	Range§§	Mean ± S D (RSD, %)	N§
1Cl(3)§§§	27.319–55 970	43 48 ± 14 67 (34)	3	0.456–1 787	0 924 ± 0 75 (81)	3	1 000–1 090	1 050 ± 0.04 (3.8)	3
2Cl(12)	2 666–12 659	6.00 ± 3.22 (54)	9	2 881 21 199	8.343 ± 6.17 (74)	8	1 000–2 062	1 736 ± 0 30 (17)	10
3Cl(24)	0 657–4.734	2 22 ± 1 12 (50)	9	0 721–10.901	2 921 ± 3 64 (125)	7	1 000–1 627	1 400 ± 0 24 (17)	9
4Cl(42)	0 331–2 605	1 49 ± 0 49 (33)	31	0 102–4 267	2 058 ± 1.02 (50)	16	1 000–2 146	1 549 ± 0 33 (21)	11
5Cl(46)	0 510–3 704	1 49 ± 0 64 (43)	35	0 465–1 216	0 805 ± 0 27 (33)	12	1 000–1 013	1 004 ± 0 01 (0 7)	3
6Cl(42)	0 475–2 521	1 29 ± 0 40 (31)	37	0 369–1 440	0 817 ± 0 29 (36)	16	1 000–1 321	1 153 ± 0 11 (9 6)	7
7Cl(24)	0 292-9 084	1.45 ± 1 69 (117)	21	0 236–1 192	0 703 ± 0 30 (43)	13	–	–	0
8Cl(12)	0.831 -2 595	1 42 ± 0 64 (45)	10	0 241–1 116	0 573 ± 0 26 (46)	8	1.000–1.359	1 179 ± 0 25 (22)	2
9Cl(3)	0 764- 1 032	0.92 ± 0 14 (15)	3	0 066–0 565	0.354 ± 0 26 (73)	3	–	–	0
10Cl(1)	–	1 168	1	–	0 418	1	–	–	0
	Overall· 0 292–55 97 (≈190.1)			Overall 0 066–21 199 (≈320·1)					

* From Tables 2 and 3, respectively
** From ref 45
*** All values are relative to octachloronaphthalene
§ N = number of PCB isomers included in measurement.
§§ Responses were relative to lowest response for each group
§§§ Values in parentheses are numbers of theoretical isomers possible

calibration, provided that identical high-resolution chromatographic conditions are employed in sample analysis as used for the Aroclor characterization.

4.4. Clustered secondary standard

Another reported approach is the development of a secondary standard that contains a small subset of individual chlorobiphenyl isomers that can be used to develop instrument responses for all PCBs of interest[64].

5. APPLICATION TO THE ANALYSIS OF PCBs AND PPBs IN ENVIRONMENTAL AND BIO-LOGICAL SAMPLES

With these recent parallel developments, laboratories have begun to characterize and quantify chlorobiphenyl isomers in environmental[65-72], biological[73-77] and process stream samples. A few examples of the combined state-of-the-art technology described above are discussed here.

The benefit of high-resolution GC over conventional packed column GC for analysis of sera and adipose tissue is exemplified by Figs. 14 and 15, respectively[77]. Fig. 14 depicts the profile for a human serum sample extract chromatographed on a packed column (top) and a capillary (bottom). Improved resolution and hence a better signal-to-noise ratio are achieved with high-resolution GC. Fig 15 shows that the low-resolution profile has many hidden isomers in its chromatographic peaks, which are revealed by high-resolution GC.

Identification of specific chlorobiphenyl isomers in human tissues may be important for two reasons: for the assessment of long-term persistence and for the evaluation of potential health effects as suggested by toxicological studies on individual isomers. Recently, the disposition of PCB isomers in occupationally exposed persons has been reported[78]. The concentrations of PCBs in adipose tissue and plasma were related to the duration and intensity of exposure in the workplace. It was reported that PCB levels in adipose tissue were proportional to those in plasma (total PCB ratio 190:1). The distribution of specific chlorobiphenyl isomers between plasma and adipose tissue was reported, however, to be related to specific ring position substitution, differing among isomers

These state-of-the-art techniques are currently being applied to the analysis of samples of rainwater, surface water, sediment, fish, human milk, maternal cord blood, etc.[35].

Finally, an area of considerable activity involves the development of computerized data analysis systems. With the use of automated gas chromatographs, a considerable amount of data are generated when using FSCGC.

Computerization is not only being introduced to facilitate calculations of PCB isomer and total PCB levels in samples, but is also being developed to assist in answering comparative questions about samples[79]. Questions relating to biotransformation, distribution and fate through an ecosystem and sources require sophisticated pattern recognition techniques for comparing and relating PCB information between environmental and biological samples[79]
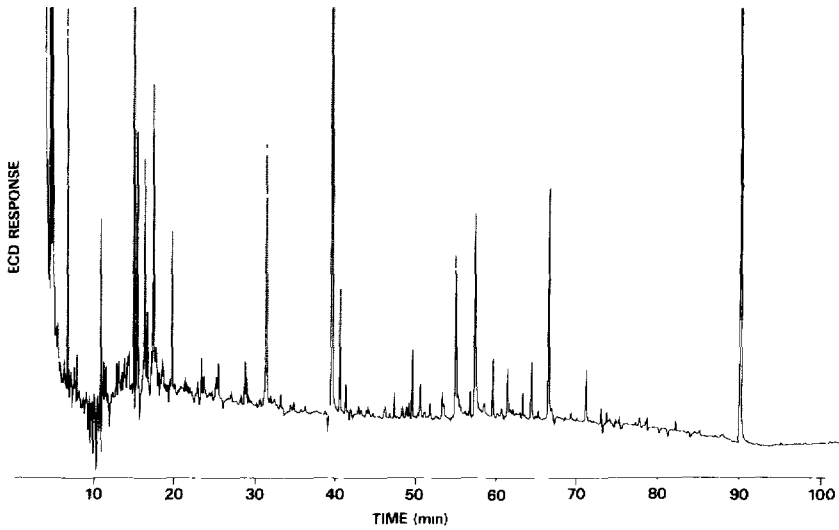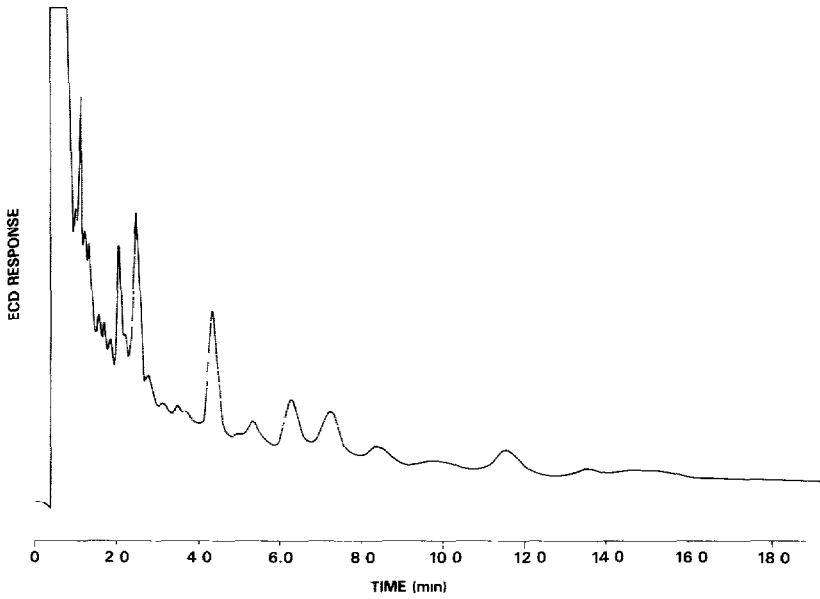
Fig 14 Chromatograms of human serum sample Top, packed column; bottom, capillary

6 CONCLUSION

Significant studies have been performed during the past 10 years in developing:
(a) high-resolution GC capillaries tailor-made for PCB analysis; (b) ultra-sensitive
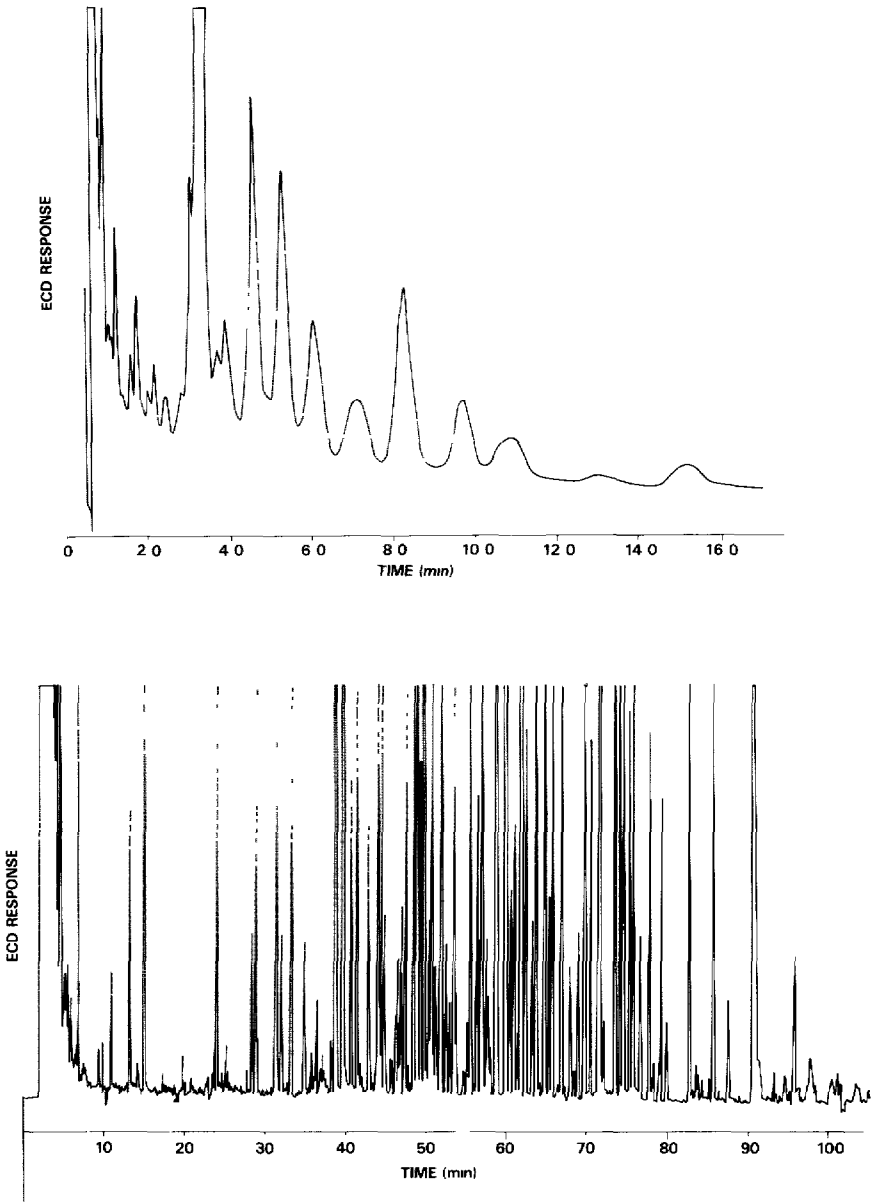electron-capture detectors compatible with capillary column flow-rates; (c) an ex-

Fig 15 Chromatograms of human adipose tissue Top, packed column, bottom, capillary.

panded linear dynamic range of operation for the electron-capture detector; (d) the operating conditions for NICI-MS necessary to measure and characterize PCBs in environmental and biological samples, and (e) the development of primary and secondary PCB standards for calibration of instrumentation. Research in the last area continues as more work needs to be done. Investigators are just beginning to reap

the fruits of their labor by applying this advanced analytical methodology to real-world problems.

7. ACKNOWLEDGEMENTS

8. SUMMARY

Analytical advances in the detection, identification and quantification of poly-chlorinated biphenyl isomers (PCBs) are reviewed. High-resolution gas chromatography, with specific reference to capillary column development and support "phases", methodologies, detector systems and the comparative advantages and limitations of each combination, is covered. Problems associated with instrument calibration, general non-availability of primary PCB standards and the use of secondary standards are discussed. Typical applications of these newer methods to environmental, biological and process stream samples are presented

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