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Homologue distributions of polychlorinated terphenyls by high-resolution gas chromatography and high-resolution mass spectrometry

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Abstract

The use of high-resolution gas chromatography–high-resolution mass spectrometry in the selected-ion monitoring mode (HRGC–HRMS-SIM) to study the distribution of polychlorinated terphenyls (PCTs) in commercial and environmental samples is proposed. Interferences in the detection and measurement of the $M^{+\cdot}$ ions due to chromatographic co-elution of PCT congeners were observed. In this paper, the interfering contribution of the $[M-2Cl]^+$ fragment from the terphenyl homologues with an additional two chlorine atoms was eliminated using HRMS at a resolving power between 30 000 and 35 000. Homologue distributions of PCTs in commercial mixtures, Aroclor 5460 and Leromoll 141, and in samples of shellfish from the Ebro Delta (Catalonia, Spain) are proposed.

1. Introduction

Polychlorinated terphenyls (PCTs) and polychlorinated biphenyls (PCBs) are structurally and toxicologically related classes of anthropogenic compounds that have been identified as potentially serious environmental hazards. They have certain physical properties such as high heat capacity, chemical stability and electrical properties that make them desirable for a number of industrial uses [1]; however, the application of PCTs has always been more limited than that of PCBs.

Reports on the determination of PCTs are rare in the literature, particularly when compared with those concerning PCBs. Nevertheless, they have been detected in river water [2], soils and sediments [3–6], biological samples [5,7–11], food packaging [12,13] and human tissue [7,14–16].

Analyses for PCTs have proved to be difficult because of the complexity of the mixtures and the high boiling points of the heavily chlorinated congeners. Poor resolution in gas chromatography using packed chromatographic columns prevented their determination with PCBs and related compounds in the 1970s. More recently, using open-tubular columns, stationary phase thermal stability problems and very long retention times detracted environmental analytical chemists from further research to confirm the presence of these pollutants in environmental samples.

Two additional problems have been found in

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the determination of PCTs by high-resolution gas chromatography: co-elution of the lower chlorinated PCT congeners with some PCBs and the unavailability of individual standards. The separation between the highly chlorinated PCBs and the low-chlorinated PCTs can be achieved using sufficiently long capillary columns and low-resolution mass spectrometry. Moreover, the unavailability of individual standards can be overcome by using Aroclor or other technical mixtures as secondary standards, but the compositions of these formulations are not known. Gas chromatography–mass spectrometry can be used to elucidate the composition of these mixtures but interferences in the measurement of the molecular ions were observed [15], preventing the identification of the homologues. In a previous paper [11], the approximate distribution of the homologues for Aroclor 5432, Aroclor 5460 and Leromoll 141 using low-resolution mass spectrometry was proposed.

The detection and measurement of the $M^{+\cdot}$ ions produced by a member of a given isomer group may be interfered with by the $[M-2Cl]^{+}$ fragment ions of homologues with two additional chlorine atoms [11,15]. To discriminate between the molecular and interfering ions, high-resolution mass spectrometry was necessary. In this work, the determination of PCTs was performed by high-resolution gas chromatography–high-resolution mass spectrometry (HRGC–HRMS) at a resolving power between 30 000 and 35 000, and the homologue distributions for Aroclor 5460 and Leromoll 141 were proposed. The presence of these compounds in samples of shellfish from the Ebro Delta (Catalonia, Spain) was investigated.

2. Experimental

2.1. Chemicals

Aroclor 5460 PCT mixture was purchased from Chem-Service (West Chester, PA, USA) and the commercial product Leromoll 141 was a gift from Dr. U.A.Th. Brinkman (Amsterdam, Netherlands). Standard solutions of PCT mixtures containing 10 mg/l of individual Aroclor 5460 and Leromoll 141 were prepared in isooctane for residue analysis (Carlo Erba, Milan, Italy).

2.2. Apparatus

HRGC–HRMS analyses were performed on a Hewlett-Packard (Palo Alto, CA, USA) Model 5890 Series II gas chromatograph interfaced to a VG AutoSpec-Q (VG Instruments, Manchester, UK) with an OPUS 1.0 data system interface and DEC VAX 3100 Workstation for data processing. A DB-5 fused-silica column (J&W Scientific, Folsom, CA, USA) capillary column (60 m × 0.25 mm I.D., 0.25 μm film thickness) was used with helium as the carrier gas at a linear velocity of 25 cm/s. The temperature programme was from 90°C (held for 3 min) to 200°C (held for 1 min) at 20°C/min, and then from 200 to 310°C (held for 30 min) a 2.5°C/min. The injector temperature was kept at 275°C, using the splitless mode.

The HRGC–HRMS-selected ion monitoring (SIM) mode operating conditions were as follows: ion source and interface temperatures, 280 and 290°C, respectively; ionization energy, 70 eV (electron impact mode); monitored ions and the interfering ions as shown in Table 1. The resolving power was kept between 30 000 and 35 000 (10% valley definition), using m/z 404.9760 of pentafluorokerosene (PFK) as lockmass. SIM at an accelerating voltage of 8000 V, dwell time 80 ms and delay time 20 ms was used. The total scan cycle was 1.6 s. Verification of the resolution in the working mass range was obtained by measuring the PFK reference peaks on a mass-calibrated oscilloscope. The theoretical relative abundance of the isotopes of carbon (^{12}C, ^{13}C), hydrogen (^{1}H, ^{2}H, ^{3}H) and chlorine (^{35}Cl, ^{37}Cl), were taken into account in order to calculate the exact masses of PCTs. The two major molecular ions of each PCT homologue were used for mass monitoring.

For HRGC–low-resolution (LR) MS the full-scan mode at a resolving power of 1000 and a mass range between 100 to 750 m/z at 1 s per

decade were used. The working conditions for selected-ion monitoring (LRMS-SIM) were described in a previous paper [11].

3. Results and discussion

The EI mass spectra of the PCTs gave an intense molecular ion $M^{+\cdot}$, as can be seen in Fig. 1, where the full-scan EI spectrum of a nona-CT from Aroclor 5460 is given as an example. The molecular ion and the fragment ions showed the typical expected clustering due to the chlorine isotopes. In addition, a relatively intense fragment due to $[M-2Cl]^+$ and a small fragment ion due to $[M-Cl]^+$ appeared. The fragment $[M-2Cl]^+$ provided an interfering cluster for the molecular ion from the PCT homologues with two fewer chlorine atoms. In Fig. 2, the EI mass spectrum of the molecular region for hepta-CT is given.

For each formulation of PCTs the $[M-2Cl]^+$ interferences were important for the main homologues. Thus nona-CTs interfered with hepta-CTs and deca-CTs interfered with octa-CTs for Aroclor 5460. Leromoll 141 showed interferences from hepta-CTs with the penta-CTs and octa-CTs with the hexa-CTs. As an example, the hepta- and nona-CT LRMS-SIM profiles showing interference of nona-CTs with hepta-CTs for Aroclor 5460 are given in Fig. 3. To calculate the homologue distribution, no co-elution between homologues containing two additional chlorine atoms can be assumed and the contribution of the $[M-2Cl]^+$ can be eliminated. In a previous paper [11], the results obtained using this approach were given. To discriminate between the $M^{+\cdot}$ and the $[M-2Cl]^+$ ions, HRMS was required.

The selected ion monitored, the interfering ion for each homologue and the resolution, calculated at 10% valley definition, are given in Table 1. The nona-CTs molecular cluster ions that gave the mass which interfered with the hepta-CTs molecular ion are given as an example in Fig. 4. As can be observed, the loss of two chlorine atoms as two ^{35}Cl, two ^{37}Cl or one ^{35}Cl and one ^{37}Cl gave the same $[M-2Cl]^+$ cluster fragment. In order to avoid this interference, a resolution of 25 300 was required.

The use of the resolution indicated in Table 1 allowed the elimination of the MS interference

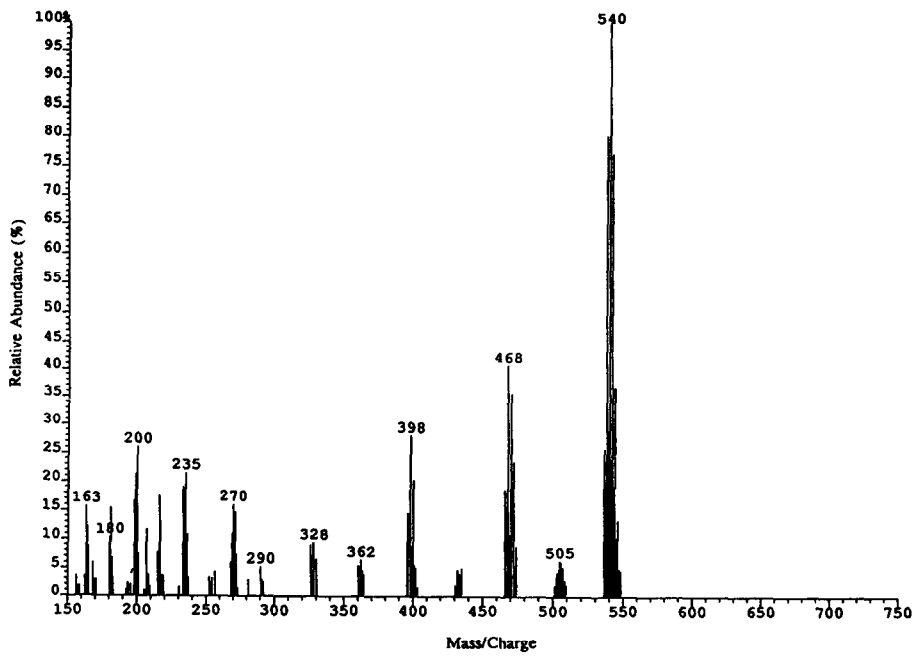

Fig. 1. Mass spectrum of a nonachloroterphenyl in Aroclor 5460.

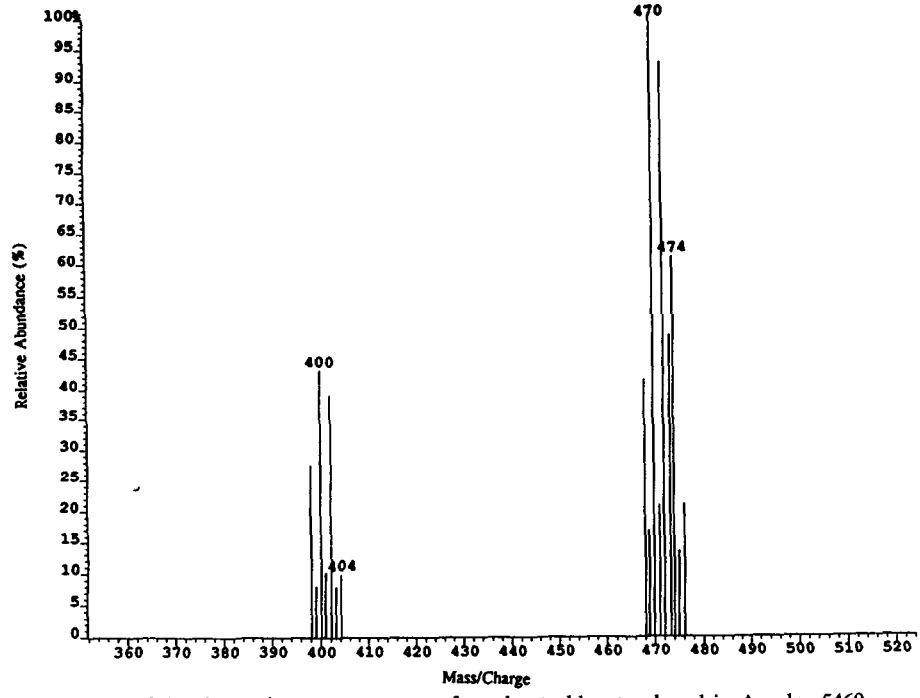

Fig. 2. Molecular region mass spectrum for a heptachloroterphenyl in Aroclor 5460.

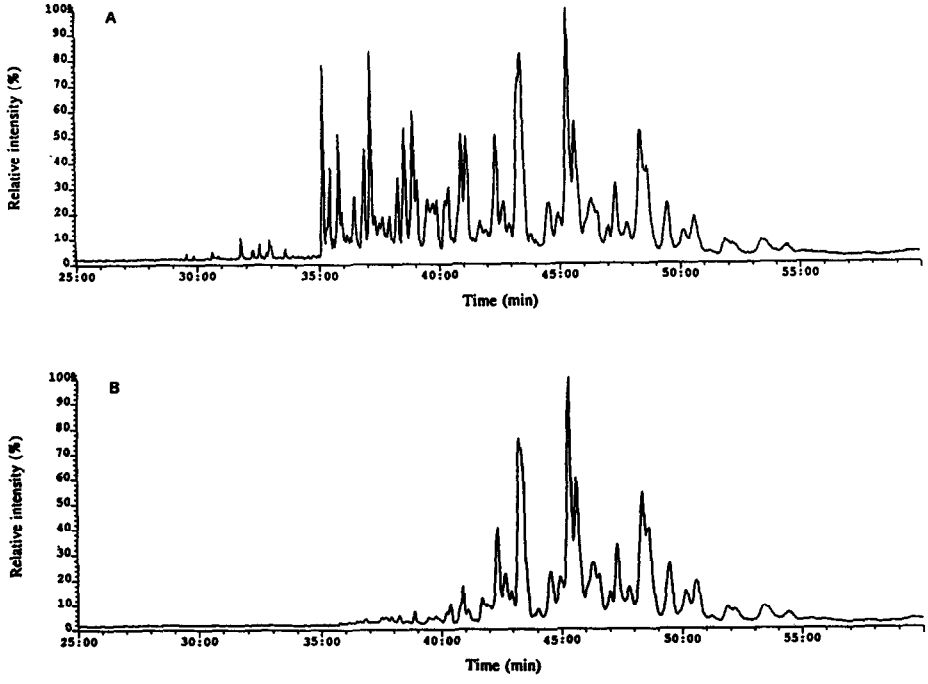

Fig. 3. Selected ion monitoring using LRMS for Aroclor 5460; (A) hepta-CTs, m/z 469.8; (B) nona-CTs, m/z 537.8.

Table 1
Calculated resolution and exact masses used for interfering and monitored ions

Homologue	Monitored m/z	Interfering m/z	Resolution[a]
Penta-CTs	401.9117	401.8931	21 600
	403.9088	403.8902	21 700
Hexa-CTs	435.8728	435.8542	23 400
	437.8698	437.8512	23 500
Hepta-CTs	469.8338	469.8152	25 300
	471.8308	471.8122	25 400
Octa-CTs	503.7948	503.7762	27 100
	505.7919	505.7733	27 200
Nona-CTs	537.7558	537.7372	28 900
	539.7529	539.7343	29 000
Deca-CTs	573.7139	573.6953	30 800
	575.7110	575.6924	31 000
Undeca-CTs	607.6750	607.6564	32 700
	609.6720	609.6534	32 800
Dodeca-CTs	641.6360	641.6174	34 500
	643.6330	643.6144	34 600

[a] Resolution calculated at 10% valley definition.

from $[M-2Cl]^+$. Fig. 5 shows the HRGC–LRMS-SIM profile for the hepta-CTs and the HRGC–HRMS-SIM profiles for the hepta- and nona-CTs. Co-elution of hepta- and nona-CTs between 35 and 40 min was observed. Integration of the HRMS-SIM profiles provided a quantitative determination for each chlorinated homologous family.

Table 2
Homologue distributions for Aroclor 5460 and Leromoll 141

Homologues	Percentage of homologues			
	Aroclor 5460		Leromoll 141	
	LRMS	HRMS	LRMS	HRMS
Penta-CTs	–[a]	–	14	12.0
Hexa-CTs	<1	0.9	28	30.2
Hepta-CTs	6	10.4	30	42.6
Octa-CTs	17	45.7	27	14.1
Nona-CTs	42	29.4	1	0.7
Deca-CTs	28	11.9	–	0.4
Undeca-CTs	6	1.2	–	–
Dodeca-CTs	–	<0.5	–	–

[a] – = Not detected.

The homologue distributions for Aroclor 5460 and Leromoll 141 calculated by HRMS are given in Table 2. These values indicated that Aroclor 5460 was mainly constituted by terphenyls with seven to ten chlorine atoms with a maximum of octa-CTs, and that Leromoll 141 was mainly composed of terphenyls with five to eight chlorine atoms with a maximum of hepta-CTs. A comparison between these percentages and those

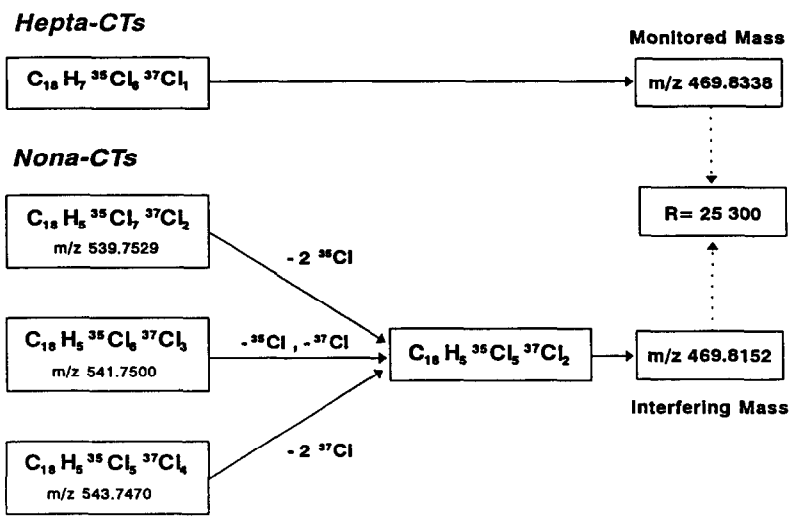

Fig. 4. Interferent mass of nona-CTs on the hepta-CTs monitored molecular mass for Aroclor 5460.

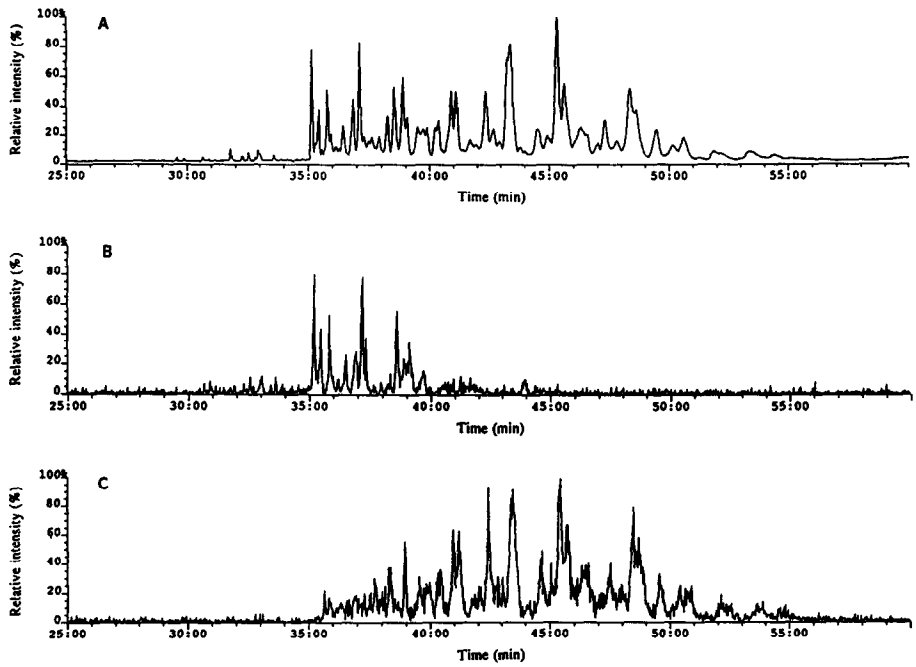

Fig. 5. Selected ion monitoring using (A) LRMS for hepta-CTs, m/z 469.8, and HRMS for (B) hepta-CTs, m/z 469.8338 and (C) nona-CTs after loss of two chlorine atoms, m/z 469.8152.

calculated previously using LRMS showed differences in the data for the octa-, nona-, deca- and undeca-CTs for Aroclor 5460 and hepta- and octa-CTs for Leromoll 141. These differences were due to the simultaneous co-elution of some iomers with different degrees of chlorination.

PCTs were found in samples of shellfish from the Ebro Delta (Catalonia, Spain) collected in

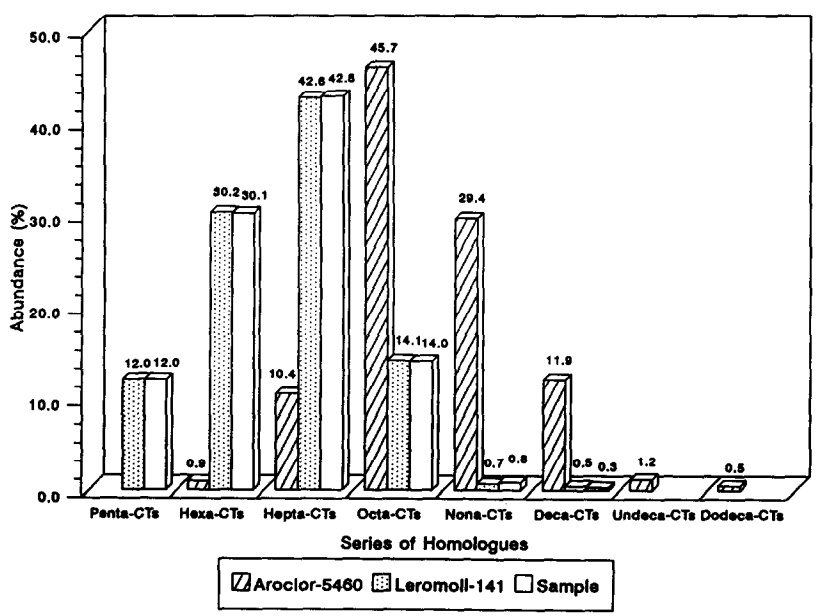

Fig. 6. Homologue distributions for Aroclor 5460, Leromoll 141 and a sample of shellfish.

1989 [11]. For identification purposes, HRGC–HRMS-SIM was applied to samples with high levels of PCTs. The homologue distributions obtained for Aroclor 5460, Leromoll 141 and the shellfish samples are given in Fig. 6. Identical compositions in the last two were observed, so the terphenyls detected in the shellfish samples are due to Leromoll 141 formulations or similar.

4. Conclusions

The homologue distribution of PCTs in the commercial mixtures Aroclor 5460 and Leromoll 141 calculated using HRGC–HRMS-SIM was proposed. HRMS with a resolving power between 30 000 and 35 000 was needed. Previously, the correct homologue compositions of Aroclor 5460 and Leromoll 141 had not been reported in the literature data. These homologue distributions would allow the source of PCTs in real samples to be determined and could be considered as reference values for the determination of the degree of chlorination of each PCT in commercial formulations and environmental samples.

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