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# Gas chromatographic separation of semivolatile organohalogen compounds on the new stationary phase Optima $\delta$ -3

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## Abstract

The separation characteristics of the recently developed GC stationary phase on a methyl-phenyl-polysiloxane basis (Optima  $\delta$ -3) for the analysis of semivolatile organohalogen compounds are presented in this study. The stationary phase is characterised in its basic polarity by a sum of the Rohrschneider–McReynolds constants relative to squalane of 574 units. A complete determination of the elution order of all polychlorinated biphenyls (PCBs) is given in the form of temperature-programmed relative retention times,  $RRT = PCB_i / (PCB_{52} + PCB_{180})$ . A mixture of Aroclors 1242, 1254 and 1260 which contains 154 PCB congeners gives rise to 108 peaks on the Optima  $\delta$ -3 when using electron-capture detection. The gas chromatographic separation of chlorinated pesticides like hexachlorocyclohexanes, DDTs and cyclodiene insecticides, and other organohalogen compounds like polychlorinated terphenyls, polychlorinated alkanes, polychlorinated bornanes (toxaphenes), and polybrominated diphenyl ethers is also discussed. A real-world biological sample (Cod Liver Oil, NIST SRM 1588) is used to demonstrate the applicability of the Optima  $\delta$ -3 for the analysis of semivolatile organohalogen compounds in environmental samples. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Stationary phases, GC; PCB; Organohalogen compounds; Organochlorine compounds; Pesticides

## 1. Introduction

Optima  $\delta$ -3 is a new GC stationary phase consisting of methyl- and phenyl-polysiloxanes. The column was developed by Macherey-Nagel (Düren, Germany). The selectivity of the phase is different from other commercially available phases. Moreover, the high temperature limits (340/360°C) as well as the low bleeding make Optima  $\delta$ -3 capillaries ideal tools for electron-capture detection (ECD) or MS detection in environmental trace analysis [1]. Unfortunately the exact composition of the stationary

phase is not known to the authors. Congener specific analysis of polychlorinated biphenyls (PCBs) on different GC stationary phases has been performed by numerous researchers in the last two decades [2–14]. Although there are a lot of stationary phases available, there is still a great interest in new columns since no column is able to separate all 209 possible PCB congeners. Multidimensional gas chromatographic systems and column coupling have been used to improve the separation of the PCB congeners [15–17]. A collaborative study on the separation of PCBs on 27 different gas chromatographic systems was published recently [18,19].

In this paper we present the retention values of the

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209 PCB congeners, of the polychlorinated terphenyls (PCTs) and polychlorinated alkanes (chloroparaffins, CPs). Furthermore a number of organohalogen compounds like the DDT group, some cyclodiene insecticides, and other semivolatile compounds of interest in the field of environmental analysis are measured by high-resolution gas chromatography (HRGC)–ECD on the Optima  $\delta$ -3. To our knowledge this is the first comprehensive study on the separation characteristics of semivolatile organohalogen compounds on this new stationary phase.

## 2. Experimental

### 2.1. Gas chromatographic analysis

The determination of the Rohrschneider–McReynolds constants was performed on a HP 5890 gas chromatograph (Hewlett-Packard, Palo Alto, USA) with a split/splitless injector and a flame ionisation detector (FID). The oven temperature was kept at 120°C, injector and detector temperature were kept at 250°C and 300°C, respectively.

HRGC–ECD measurements were performed on a HP 6890 gas chromatograph equipped with an electron-capture detector ( $^{63}\text{Ni}$ - $\mu$ -ECD, Hewlett-Packard). Hydrogen was used as carrier gas, argon–methane (90:10, v/v) with a flow-rate of 60 ml/min was used as the ECD make-up gas. The injection (usually 2  $\mu\text{l}$ ) was done with the HP autosampler on-column at 80°C into a 2 m $\times$ 0.32 mm deactivated retention gap connected to each separation column.

HRGC–EI-MS (electron impact ionisation) measurements were performed on a HP 5890 gas chromatograph directly coupled to a HP 5970 quadrupole mass selective detector (Hewlett-Packard). Helium was used as carrier gas. Injections were performed manually on-column at 80°C into a 2 m $\times$ 0.32 mm retention gap. The chromatograms were recorded in the full-scan mode (50–650 u). Other chromatographic conditions are listed in Table 1.

Solutions of single compounds and the HRGC–EI-MS system were additionally used to confirm the peak identification (data not shown).

### 2.2. Reference compounds used for the selectivity studies

N-Alkanes from *n*-pentane to *n*-nonane and the five McReynolds test substances benzene, 1-butanol, 2-pentanone, 1-nitropropane and pyridine [20] were obtained from Fluka (Neu-Ulm, Germany).

Solutions of technical PCB mixtures Aroclor 1242, 1254, 1260 in isooctane, the technical PCT mixture Aroclor 5460 in isooctane, solutions of single PCB congeners, 1,2,3,4-tetrachloronaphthalene (TCN),  $\epsilon$ -hexachlorocyclohexane ( $\epsilon$ -HCH) and a toxaphene standard solution containing six toxaphene congeners (Parlar Nos. 26, 40, 41, 44, 50, 62) [21–24] were purchased from the Dr. Ehrenstorfer company (Augsburg, Germany). SRM 2261 (chlorinated pesticides in hexane), a supplementary pesticide calibration solution, and SRM 1588 (Organics in Cod Liver Oil) were obtained from NIST (Gaithersburg, USA). The multicongener PCB solutions according to Frame [18] were provided by Michele M. Schantz (NIST, Gaithersburg, USA), who obtained the solutions in an interlaboratory study [18,19]. Hordaflex LC60, a technical chloroparaffin mixture, was obtained from Hoechst (Frankfurt, Germany). The technical mixture of polybrominated diphenyl ethers (PBDEs), Bromkal 70-5 DE, widely used as flame retardants, was obtained from Chemische Fabrik Kalk (Köln, Germany).

Other organohalogen compounds and the high-purity solvents (acetone, cyclohexane, dichloromethane, isooctane, *n*-hexane) were purchased from Promochem (Wesel, Germany).

### 2.3. Characterisation of the stationary phase

A GC stationary phase can be characterised in its basic polarity by the Rohrschneider–McReynolds constants determined with benzene ( $x'$ ), 1-butanol ( $y'$ ), 2-pentanone ( $z'$ ), 1-nitropropane ( $u'$ ) and pyridine ( $s'$ ) relative to squalane as the stationary phase at 120°C [20,25]. The Kováts retention index values ( $I$ ) measured on squalane were taken from [20], the values for the five test substances are 653, 590, 627, 652 and 699, respectively.

On the Optima  $\delta$ -3 capillary the retention times were measured using a mixture of *n*-alkanes from

Table 1  
GC parameters used for the different stationary phases and analytes

System (detection)	Analytes	Stationary phase	Column dimensions			Temperature program								Head pressure (kPa)	Flow velocity <sup>f</sup> (cm/s)	Detection temp. (°C)
						Initial temp.	Initial hold	Rate 1	1st break	Hold	Rate 2	Final temp.	Final hold			
			L (m)	d <sub>c</sub> (mm)	d <sub>f</sub> (µm)	(°C)	(min)	(°C/min)	(°C)	(min)	(°C/min)	(°C)	(min)			
1 (FID)	McReynolds test substances	Optima δ-3	60	0.25	0.25	120	5	–	–	–	–	–	–	100 (H <sub>2</sub> )	27.0	250
2 (ECD)	Column bleeding	Optima δ-3	60	0.25	0.25	80	3	20	280	0	2	350	5	180 (H <sub>2</sub> )	37.5	350
2 (MSD)	Column bleeding	Optima δ-3	60	0.25	0.25	80	3	20	280	0	2	350	5	140 (He)	19.1	350 <sup>g</sup>
3 (ECD)	Column bleeding	DB-5ms <sup>a</sup>	60	0.25	0.25	80	3	20	280	0	2	350	5	180 (H <sub>2</sub> )	37.5	350
3 (MSD)	Column bleeding	DB-5ms <sup>a</sup>	60	0.25	0.25	80	3	20	280	0	2	350	5	140 (He)	19.1	350 <sup>g</sup>
4 (ECD)	Pesticides, PCBs	Optima δ-3	60	0.25	0.25	80	3	20	200	0	1.5	290	5	180 (H <sub>2</sub> )	41.7	300
5 (ECD)	PCTs <sup>b</sup>	Optima δ-3	60	0.25	0.25	80	3	20	250	0	3	340	20	200 (H <sub>2</sub> )	43.0	350
6 (ECD)	CPs <sup>c</sup>	Optima δ-3	60	0.25	0.25	80	3	20	300	30	–	–	–	180 (H <sub>2</sub> )	36.6	300
7 (ECD)	Pesticides	SPB-Octyl <sup>d</sup>	90	0.32	0.1	80	3	20	170	0	1	250	5	150 (H <sub>2</sub> )	40.2	300
8 (ECD)	Pesticides	HP Ultra 2 <sup>e</sup>	45	0.25	0.33	80	3	20	170	7.5	3	300	7	130 (H <sub>2</sub> )	42.9	300
9 (ECD)	Pesticides	Optima 1701	50	0.32	0.1	80	3	20	170	0	2	280	5	90 (H <sub>2</sub> )	44.6	300

<sup>a</sup> J&W Scientific (Folsom, USA); <sup>b</sup> polychlorinated terphenyls; <sup>c</sup> chloroparaffins, polychlorinated alkanes; <sup>d</sup> Supelco (Bellefonte, USA); <sup>e</sup> Hewlett-Packard (Palo Alto, USA);

<sup>f</sup> calculated for the temperature of the first break using the Hewlett-Packard PC flow calculator; <sup>g</sup> temperature of transfer line.

*n*-pentane to *n*-nonane and two mixtures of the test substances to avoid coelutions. Approximately 4  $\mu$ l headspace of the *n*-alkane and the test substance solutions were injected manually. Hold-up time was calculated using the retention times of three subsequent *n*-alkane homologues as described in [25]. The retention indices determined on the Optima  $\delta$ -3 were 723, 698, 734, 814 and 826 for the five McReynolds test substances and the respective retention index differences ( $\Delta I$ ) between the Optima  $\delta$ -3 and the squalane stationary phase are 70, 108, 107, 162 and 127, the sum of the values ( $P=x'+y'+z'+u'+s'$ ) is 574. The basic polarity of the Optima  $\delta$ -3, therefore, corresponds closely to 20% phenyl–80% methylpolysiloxane. Values for other stationary phases with 20% phenyl–80% methylpolysiloxane are reported to range from 592 to 607 units [25].

#### 2.4. Determination of the column bleeding

There are no standardised methods to quantitate the bleeding of GC columns. Therefore, we compare the bleed of the Optima  $\delta$ -3 with the DB-5ms (5% phenyl-95% methyl polysiloxane, J&W Scientific, Folsom, USA), another commercially available low-bleed column. Measurements were performed using ECD and MS detection. Details of the chromatographic conditions are given in Table 1.

#### 2.5. Chlorinated pesticides and other organohalogen compounds

The standard solution containing 31 pesticide compounds was prepared by diluting NIST SRM 2261 (15 pesticides), a supplemental pesticide solution (nine pesticides), and stock solutions of seven additional compounds pentachlorobenzene (PCBz), pentachloroanisole (A19), 2,4,6-tribromo-anisole (A33), tetrachloro-1,4-dimethoxybenzene (TCDMB), TCN,  $\epsilon$ -HCH, PCB 103 to a concentration of about 150 pg/ $\mu$ l with iso-octane. The systematic numbering of halogenated anisoles (halogenated methyl-phenyl ethers) is given in [26]. The pesticide solution has also been analysed using three different stationary phases in addition to the Optima  $\delta$ -3: the nonpolar SPB-Octyl (50% *n*-octylmethylpolysiloxane,

Supelco, Bellefonte, PA, USA), the HP-2 (5% phenyl-substituted methylpolysiloxane, Hewlett-Packard) which corresponds to an Optima 5, SE-54 or a DB-5, and the semipolar Optima 1701 (14% cyanopropyl-phenyl-substituted methylpolysiloxane, Macherey-Nagel).

#### 2.6. Polychlorinated biphenyls (PCBs)

To determine the elution order of the PCBs on an Optima  $\delta$ -3 capillary, a set of nine multicongener solutions as proposed by Frame [18] was injected. Each solution also contained the tetrachlorobiphenyl PCB 52 and the heptachlorobiphenyl PCB 180 as retention time markers to calculate the relative retention times  $RRT=PCB_i/(PCB_{52}+PCB_{180})$  as suggested by Fischer and Ballschmiter [5]. This approach strongly increases the reproducibility of the temperature programmed RRTs and, furthermore, makes our data comparable to the systematic work in PCB separation of Frame [18,19]. A solution prepared of equal amounts of the technical PCB mixtures Aroclor 1242, 1254 and 1260 (1:1:1 solution) was also injected and the occurrence of detector signals was compared to the congener distributions published in [19]. The relative order of elution of the PCB congeners strictly follows the structural principles as given in [4].

#### 2.7. Polychlorinated terphenyls (PCTs)

Polychlorinated terphenyls have been identified in the environment for example in soil and sediment [27,28], water [29] and biota [30,31]. A standard solution of polychlorinated terphenyls (PCTs), an Aroclor 5460 as the most widely used technical mixture of PCTs [32] was injected. This mixture consists of isomers containing 7–11 chlorine atoms [32,33].

#### 2.8. Polychlorinated alkanes (chloroparaffins, CPs)

A solution of the technical chloroparaffin mixture Hordaflex LC 60 which consists of polychlorinated *n*-alkanes from *n*-decane ( $C_{10}$ ) to *n*-tridecane ( $C_{13}$ ) with 62% chlorine by mass was injected.

### 2.9. Cod liver oil as a real-world biological sample

A cod liver oil deriving from specimen caught in the North Atlantic in 1984 is available as the NIST standard reference material SRM 1588 (Organics in Cod Liver Oil). It was used as a typical multi-contaminant example of a 'real-world' sample. The sample clean-up was done as follows: the oil was spiked with TCN and  $\epsilon$ -HCH as recovery standards, lipid separation was performed with size exclusion chromatography on Bio-Beads S-X3 (Bio-Rad Labs., Hercules, CA, USA) using cyclohexane–acetone (3:1, v/v) as eluent. NP-HPLC group separation was performed on an aminopropyl–silica column (250 mm  $\times$  4 mm, Nucleosil-100 NH<sub>2</sub>, 10  $\mu$ m, Macherey-Nagel) using 10 ml *n*-hexane and 32 ml *n*-hexane–dichloromethane (90:10, v/v), respectively, as mobile phase for the first and second HPLC fraction. For both eluents the flow-rate was 1 ml/min. The

PCBs, HCB, 4,4'-DDE, Mirex, and the recovery standard TCN are quantitatively eluted in the first fraction. HCHs, DDDs, DDTs, and the chlordane compounds elute in the second fraction. PCB 103 was added as the quantification standard for the first fraction, TCN was added for the second fraction.

## 3. Results and discussion

### 3.1. Determination of the column bleeding

The ECD and MS chromatograms recorded under the same conditions on the Optima  $\delta$ -3 and the DB-5ms are depicted in Fig. 1. The bars in the chromatograms indicate the peak heights corresponding to an absolute amount of 1 pg and 750 pg of PCB 209, respectively. It can be clearly seen from both the ECD and the MS chromatograms that the bleeding of the Optima  $\delta$ -3 is almost as low as the

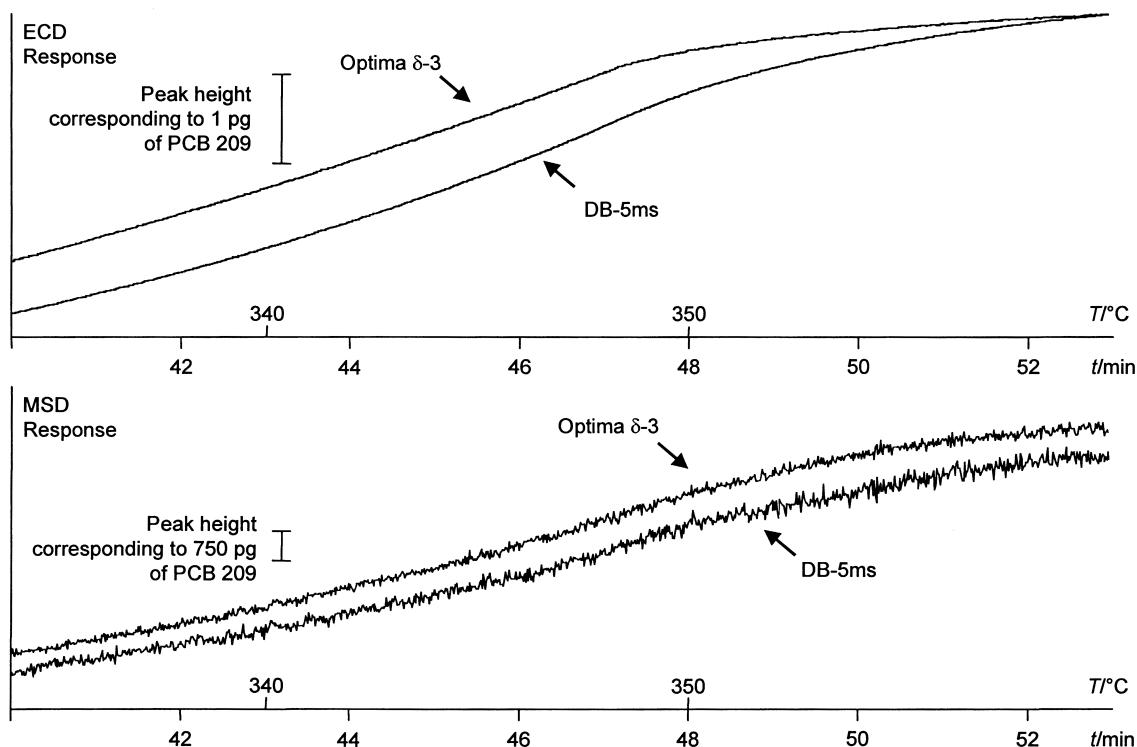


Fig. 1. HRGC–ECD (top) and HRGC–MS full-scan 50–650 u (bottom) chromatograms showing the column bleeding of the Optima  $\delta$ -3 in comparison to a DB-5ms, another commercially available low-bleed capillary column. The bars indicate the peak heights corresponding to an absolute amount of 1 pg (ECD) and 750 pg (MS) of PCB 209.

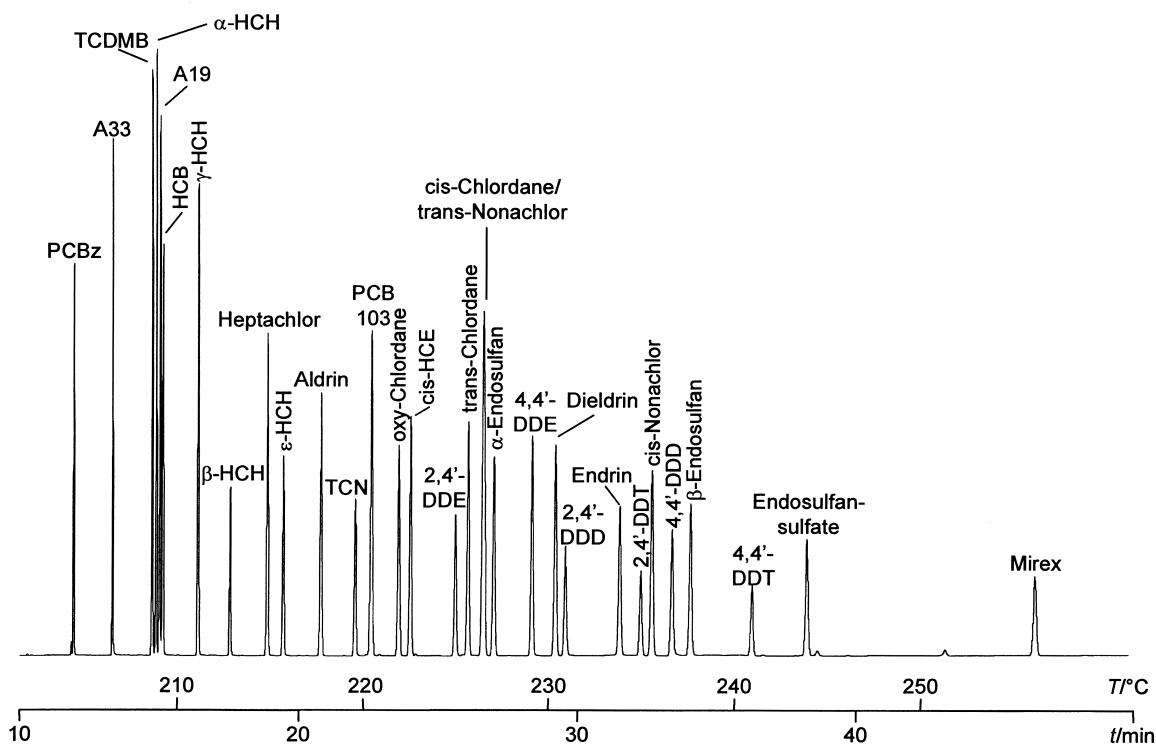


Fig. 2. HRGC–ECD chromatogram of pesticide standard solution (150 pg/μl of each compound) on the Optima δ-3. For chromatographic conditions see Table 1. Abbreviations are explained in Table 2.

bleeding of the DB-5ms. At the end temperature of the chromatogram the ECD signal is equal for both capillaries. The use of the mass selective detector reveals an even lower baseline noise for the Optima δ-3 resulting in a better signal to noise ratio for the detection of low amounts of analytes.

### 3.2. Separation of chlorinated pesticides and other organohalogen compounds

Fig. 2 shows a chromatogram of the pesticide standard solution on the Optima δ-3. The elution order of the 31 organohalogen compounds on the four GC columns used, together with the relative retention times calculated relative to TCN are given in Table 2. The selectivity of the Optima δ-3 differs from all the other stationary phases investigated here. There is only one coelution (*cis*-chlordane and *trans*-nonachlor) on Optima δ-3, but these compounds can be distinguished by using a mass selective detector. On the Optima δ-3 the elution order of the com-

pounds A33 (tribromoanisole), TCDMB, α-HCH, A19 (pentachloroanisole), HCB, γ-HCH and β-HCH is the same as on the nonpolar SPB-Octyl. However, the pairs *cis*-heptachlorepoxide/oxy-chlordane and 2,4'-DDE/*trans*-chlordane, respectively, change their sequence as compared to SPB-Octyl and elute in the same order as on the more polar Optima 1701 (Table 2).

### 3.3. Separation of polychlorinated biphenyls (PCBs)

Table 3 summarises the elution order and the relative retention times (RRT) of all 209 polychlorinated biphenyl congeners (PCBs). The PCBs are numbered according to Ballschmiter and Zell [2] as finally revised in [34]. The separation takes place within a retention time window of 50 min under the conditions used here. Fig. 3 depicts the chromatogram of the Aroclor 1:1:1 mixture. Coelutions observed for this mixture are marked in Fig. 3.

Table 2

Comparison of the elution order of chlorinated pesticides and other organohalogen compounds on four different stationary phases

SPB-Octyl (50% <i>n</i> -Octyl, 50% methyl siloxane)		HP Ultra 2 (5% Phenyl, 95% methyl siloxane)		Optima δ-3		Optima 1701 (14% Cyanopropyl- phenyl, 86% methyl siloxane)	
Compound	RRT <sup>h</sup>	Compound	RRT	Compound	RRT	Compound	RRT
PCBz <sup>a</sup>	0.4897	PCBz	0.5308	PCBz	0.5395	PCBz	0.5107
A33 <sup>b</sup>	0.5494	A33	0.6244	A33	0.6029	A33	0.5925
TCDMB <sup>c</sup>	0.5982	α-HCH	0.7093	TCDMB	0.6679	HCB	0.6592
α-HCH	0.6027	<b>HCB</b>	<b>0.7295</b>	α-HCH	0.6746	A19	0.6899
A19 <sup>d</sup>	0.6279	<b>TCDMB</b>	<b>0.7295</b>	A19	0.6805	TCDMB	0.7016
HCB	0.6470	A19	0.7364	HCB	0.6853	α-HCH	0.7466
γ-HCH	0.6680	β-HCH	0.7630	γ-HCH	0.7435	γ-HCH	0.8448
β-HCH	0.7043	γ-HCH	0.7777	β-HCH	0.7967	Heptachlor	0.9030
ε-HCH	0.7548	ε-HCH	0.8481	Heptachlor	0.8577	Aldrin	0.9778
Heptachlor	0.7925	Heptachlor	0.9299	ε-HCH	0.8837	TCN	1.0000
Aldrin	0.9043	TCN	1.0000	Aldrin	0.9445	β-HCH	1.0646
TCN <sup>e</sup>	1.0000	Aldrin	1.0038	TCN	1.0000	PCB 103	1.0757
<i>cis</i> -HCE <sup>f</sup>	1.0141	PCB 103	1.0513	PCB 103	1.0263	ε-HCH	1.0861
Oxy-chlordane	1.0299	<b>Oxy-chlordane</b>	<b>1.0848</b>	Oxy-chlordane	1.0713	Oxy-chlordane	1.1510
PCB 103	1.0368	<i>cis</i> -HCE	<b>1.0848</b>	<i>cis</i> -HCE	1.0905	<i>cis</i> -HCE	1.1987
<i>trans</i> -Chlordane	1.1259	<i>trans</i> -Chlordane	1.1330	2,4'-DDE	1.1642	2,4'-DDE	1.2593
2,4'-DDE	1.1598	2,4'-DDE	1.1391	<i>trans</i> -Chlordane	1.1851	α-Endosulfan	1.2864
α-Endosulfan	1.1758	α-Endosulfan	1.1597	<i>cis</i> -Chlordane	<b>1.2101</b>	<i>trans</i> -Chlordane	1.3106
<i>cis</i> -Chlordane	1.1981	<i>cis</i> -Chlordane	1.1637	<i>trans</i> -Nonachlor	<b>1.2101</b>	<i>cis</i> -Chlordane	1.3395
<i>trans</i> -Nonachlor	1.2232	<i>trans</i> -Nonachlor	1.1734	α-Endosulfan	1.2274	<i>trans</i> -Nonachlor	1.3526
Dieldrin	1.2722	4,4'-DDE	1.2011	4,4'-DDE	1.2900	4,4'-DDE	1.3790
4,4'-DDE	1.3422	Dieldrin	1.2122	Dieldrin	1.3280	Dieldrin	1.4187
2,4'-DDD	1.3675	2,4'-DDD	1.2194	2,4'-DDD	1.3442	<b>2,4'-DDD</b>	<b>1.4924</b>
Endrin	1.4049	Endrin	1.2568	Endrin	1.4323	<b>Endrin</b>	<b>1.4924</b>
β-Endosulfan	1.4396	β-Endosulfan	1.2740	2,4'-DDT	1.4667	2,4'-DDT	1.5473
<i>cis</i> -Nonachlor	1.5396	<i>cis</i> -Nonachlor	1.2845	<i>cis</i> -Nonachlor	1.4846	<b>β-Endosulfan</b>	<b>1.6765</b>
2,4'-DDT	1.5515	2,4'-DDT	1.2930	4,4'-DDD	1.5170	<b>4,4'-DDD</b>	<b>1.6765</b>
4,4'-DDD	1.5759	4,4'-DDD	1.2984	β-Endosulfan	1.5476	<i>cis</i> -Nonachlor	1.6982
ES-sulfate <sup>g</sup>	1.5906	<b>4,4'-DDT</b>	<b>1.3573</b>	4,4'-DDT	1.6488	4,4'-DDT	1.7419
4,4'-DDT	1.7862	<b>ES-sulfate</b>	<b>1.3573</b>	ES-sulfate	1.7387	Mirex	1.9052
Mirex	2.3242	Mirex	1.5615	Mirex	2.1104	ES-sulfate	1.9670

<sup>a</sup> pentachlorobenzene; <sup>b</sup> 2,4,6-tribromo-anisole, for systematic numbering of the halogenated anisoles see [26]; <sup>c</sup> tetrachloro-1,4-dimethoxybenzene; <sup>d</sup> pentachloro-anisole; <sup>e</sup> 1,2,3,4-tetrachloronaphthalene; <sup>f</sup> heptachlor epoxide; <sup>g</sup> endosulfan sulfate; <sup>h</sup> relative retention time calculated relative to TCN;

The coeluting compounds are shown in bold.

Coeluting non-Aroclor compounds are not marked in Table 3. The 154 PCB congeners that are present in the three Aroclor mixtures [19] give rise to a total of 108 peaks using ECD detection. Mass spectrometric detection leads to 126 identifiable peaks. The presence or absence of single congeners as analysed here are consistent with the Aroclor congener distributions given in [19]. On other phenyl-methyl-poly-siloxane stationary phases the same PCB mixture results in 112 peaks (5% phenyl), 127 peaks (13%

phenyl), 110 peaks (20% phenyl), 108 peaks (35% phenyl), 120 peaks (35% phenyl) and 112 peaks (50% phenyl), respectively (values adopted from [18]).

Among the seven indicator congeners (PCB 28, 52, 101, 118, 138, 153, 180), only PCB 153 and PCB 180 can be separated without coelutions. PCB 28 and PCB 31 coelute like on many other stationary phases routinely used for PCB analysis (DB-5, Optima 1701), but can be well separated on methyl-

Table 3

Elution order of PCBs and relative retention time (RRT)  $PCB_i/(PCB_{52}+PCB_{180})$  (PCB numbers as given by Ballschmiter and Zell [2] and revised in [34])

PCB	RRT	PCB	RRT	PCB	RRT	PCB	RRT	PCB	RRT	PCB	RRT	PCB	RRT	PCB	RRT	PCB	RRT	PCB	RRT	PCB	RRT	PCB	RRT
1	0.1788	24	0.2628	<b>45</b>	<b>0.3108</b>	35	0.3479	<i>121</i>	<i>0.3826</i>	60	0.4181	<b>87</b>	<b>0.4534</b>	<b>109</b>	<b>0.4998</b>	<b>105</b>	<b>0.5498</b>	<i>159</i>	<i>0.6070</i>	<u>180</u>	<u>0.6785</u>		
2	<i>0.1954</i>	15	0.2646	<i>73</i>	<i>0.3151</i>	72	<i>0.3512</i>	<b>93</b>	<b>0.3845</b>	99	0.4206	<b>115</b>	<b>0.4542</b>	<b>123</b>	<b>0.4999</b>	<b>141</b>	<b>0.5502</b>	<i>126</i>	<i>0.6084</i>	<b>200</b>	<b>0.6786</b>		
3	0.1982	<b>32</b>	<b>0.2691</b>	36	0.3152	71	0.3518	<b>74</b>	<b>0.3851</b>	<i>150</i>	<i>0.4235</i>	<b>136</b>	<b>0.4571</b>	<i>188</i>	<i>0.5028</i>	176	0.5521	162	0.6146	<b>193</b>	<b>0.6807</b>		
<b>10</b>	<b>0.2053</b>	<b>16</b>	<b>0.2693</b>	<i>69</i>	<i>0.3159</i>	<i>68</i>	<i>0.3551</i>	<b>76</b>	<b>0.3856</b>	119	0.4287	<b>85</b>	<b>0.4581</b>	134	0.5064	<i>127</i>	<i>0.5532</i>	185	0.6176	191	0.6884		
<b>4</b>	<b>0.2056</b>	34	0.2730	46	0.3178	41	0.3556	95	0.3880	<i>152</i>	<i>0.4324</i>	<i>120</i>	<i>0.4583</i>	<i>106</i>	<i>0.5065</i>	137	0.5579	128	0.6202	198	0.7233		
<b>9</b>	<b>0.2182</b>	23	0.2747	<b>43</b>	<b>0.3209</b>	<i>103</i>	<i>0.3568</i>	<i>88</i>	<i>0.3891</i>	<b>112</b>	<b>0.4337</b>	110	0.4663	<b>133</b>	<b>0.5080</b>	<i>186</i>	<i>0.5634</i>	<b>202</b>	<b>0.6238</b>	199	0.7261		
<b>7</b>	<b>0.2183</b>	29	0.2780	<u>52</u>	<u>0.3214</u>	<b>64</b>	<b>0.3579</b>	70	0.3906	<b>83</b>	<b>0.4344</b>	<i>81</i>	<i>0.4669</i>	<u>118</u>	<u>0.5081</u>	130	0.5636	<b>174</b>	<b>0.6248</b>	170	0.7284		
6	0.2243	54	0.2806	<b>49</b>	<b>0.3249</b>	<b>37</b>	<b>0.3586</b>	<i>155</i>	<i>0.3920</i>	<i>108</i>	<i>0.4369</i>	151	0.4744	131	0.5133	164	0.5688	<b>167</b>	<b>0.6254</b>	<b>190</b>	<b>0.7362</b>		
<b>8</b>	<b>0.2289</b>	26	0.2844	<b>39</b>	<b>0.3259</b>	<i>96</i>	<i>0.3592</i>	66	0.3936	<i>79</i>	<i>0.4376</i>	135	0.4778	<i>142</i>	<i>0.5134</i>	178	0.5716	<i>181</i>	<i>0.6302</i>	<b>196</b>	<b>0.7372</b>		
<b>5</b>	<b>0.2289</b>	25	0.2858	<b>48</b>	<b>0.3260</b>	<i>100</i>	<i>0.3635</i>	<i>80</i>	<i>0.3940</i>	125	0.4396	<b>144</b>	<b>0.4815</b>	<i>184</i>	<i>0.5146</i>	<b>163</b>	<b>0.5739</b>	177	0.6363	<i>169</i>	<i>0.7384</i>		
<i>14</i>	<i>0.2369</i>	50	0.2860	<b>47</b>	<b>0.3275</b>	<b>40</b>	<b>0.3656</b>	91	0.3955	<i>148</i>	<i>0.4410</i>	<b>82</b>	<b>0.4821</b>	<i>165</i>	<i>0.5151</i>	<u>138</u>	<u>0.5739</u>	201	0.6387	203	0.7402		
19	0.2406	<b>31</b>	<b>0.2931</b>	<b>75</b>	<b>0.3277</b>	<b>57</b>	<b>0.3664</b>	55	0.4056	<b>86</b>	<b>0.4413</b>	<b>77</b>	<b>0.4830</b>	146	0.5186	<i>160</i>	<i>0.5786</i>	<i>204</i>	<i>0.6413</i>	208	0.7689		
30	0.2426	<u>28</u>	<u>0.2939</u>	<i>65</i>	<i>0.3302</i>	94	0.3703	92	0.4073	<b>145</b>	<b>0.4413</b>	<b>147</b>	<b>0.4845</b>	<i>161</i>	<i>0.5205</i>	158	0.5790	171	0.6451	207	0.7856		
<i>11</i>	<i>0.2526</i>	53	0.2977	<i>62</i>	<i>0.3317</i>	67	0.3721	90	0.4129	<b>97</b>	<b>0.4423</b>	<b>149</b>	<b>0.4905</b>	<b>122</b>	<b>0.5236</b>	175	0.5810	<b>197</b>	<b>0.6528</b>	189	0.7895		
18	0.2540	<b>33</b>	<b>0.3005</b>	<i>104</i>	<i>0.3317</i>	<i>58</i>	<i>0.3739</i>	<b>56</b>	<b>0.4147</b>	<i>111</i>	<i>0.4505</i>	<b>139</b>	<b>0.4912</b>	<b>114</b>	<b>0.5245</b>	<i>182</i>	<i>0.5829</i>	<b>173</b>	<b>0.6540</b>	195	0.7936		
17	0.2554	<i>21</i>	<b>0.3006</b>	<i>38</i>	<i>0.3331</i>	<b>63</b>	<b>0.3796</b>	<b>84</b>	<b>0.4152</b>	<i>116</i>	<i>0.4505</i>	<b>124</b>	<b>0.4940</b>	<i>168</i>	<i>0.5271</i>	129	0.5832	<b>172</b>	<b>0.6654</b>	194	0.8339		
12	0.2570	<b>20</b>	<b>0.3015</b>	44	0.3426	<b>102</b>	<b>0.3798</b>	<u>101</u>	<u>0.4156</u>	<i>78</i>	<i>0.4506</i>	<b>140</b>	<b>0.4950</b>	<u>153</u>	<u>0.5292</u>	187	0.5869	<b>156</b>	<b>0.6661</b>	205	0.8464		
13	0.2587	<b>51</b>	<b>0.3022</b>	<b>59</b>	<b>0.3448</b>	<i>98</i>	<i>0.3814</i>	<b>89</b>	<b>0.4160</b>	117	0.4516	<i>107</i>	<i>0.4980</i>	132	0.5350	183	0.5962	<i>192</i>	<i>0.6704</i>	206	0.8835		
27	0.2610	<b>22</b>	<b>0.3101</b>	<b>42</b>	<b>0.3459</b>	<i>61</i>	<i>0.3817</i>	<i>113</i>	<i>0.4166</i>	<b>154</b>	<b>0.4531</b>	<i>143</i>	<i>0.488</i>	179	0.5396	166	0.6008	157	0.6728	209	0.9175		

Retention times were 21.3 min for PCB 52 and 44.9 min for PCB 180.

The indicator congeners are shown underlined; the congeners not present in the technical mixtures are shown in italics; the coeluting congeners in the technical Aroclor mixtures are shown in bold.



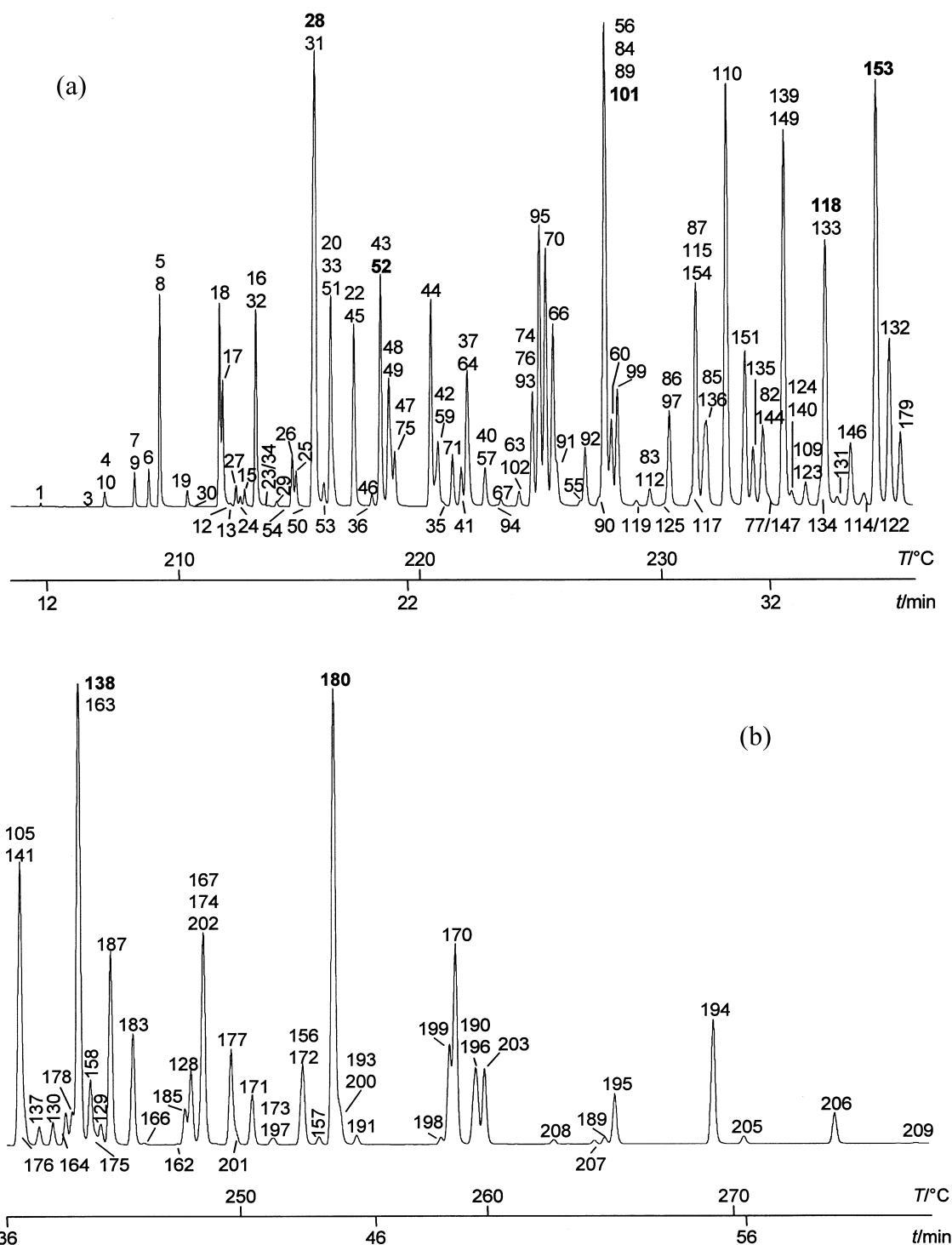


Fig. 3. HRGC-ECD chromatogram of the technical PCB mixtures Aroclor 1242, 1254, 1260 (1:1:1 solution) (5 ng/μl each) on the Optima δ-3 [retention time window: (a) 11–36 min; (b) 36–61 min]. PCB indicator congeners are shown in bold. For chromatographic conditions see Table 1.

octyl- [5] or methyl–octadecyl-polysiloxanes [9] among other stationary phases [13,14,18]. The coelutions of the pairs PCB 52/PCB 43 and PCB 118/PCB 133 are not of major relevance because PCB 43 and PCB 133 are only minor congeners in the technical mixtures. PCB 90 cannot be completely separated from PCB 101 but the chromatogram reveals the low concentration of PCB 90 in the technical mixture. Unfortunately the more abundant PCB 84 coelutes with PCB 101. PCB 164 can be separated from the coeluting pair PCB 138/PCB 163. Experiments in column coupling to reduce some major coelutions of PCBs are under investigation.

#### 3.4. Separation of polychlorinated terphenyls (PCTs)

Fig. 4 depicts the chromatogram of the PCT standard mixture Aroclor 5460. The high number of homologues and congeners gives a complex mixture of peaks for which no complete separation can be obtained. The separation could be improved by the use of a mass selective detector that is able to

distinguish between the different degrees of chlorination of the PCTs. Even during the isothermal end temperature of 340°C only low column bleeding is observed and so the coupling of the Optima  $\delta$ -3 with MS to resolve the complexity of the PCTs is possible without problems. Due to the lack of commercially available single PCT reference compounds which are proved to be environmentally relevant, quantitation of PCTs in environmental samples can only be done semiquantitatively with technical PCT mixtures as standards [30]. Attempts to overcome this problem by using single congeners [35] and more advanced mass spectrometric techniques [33,36] have been made recently.

#### 3.5. Separation of polychlorinated alkanes (chloroparaffins, CPs)

Due to their high number of isomeric compounds, the technical mixture of polychlorinated alkanes (chloroparaffins, CPs) cannot be separated even by high-resolution gas chromatography. Analysis of CPs is normally performed on short (10–15 m) capillaries

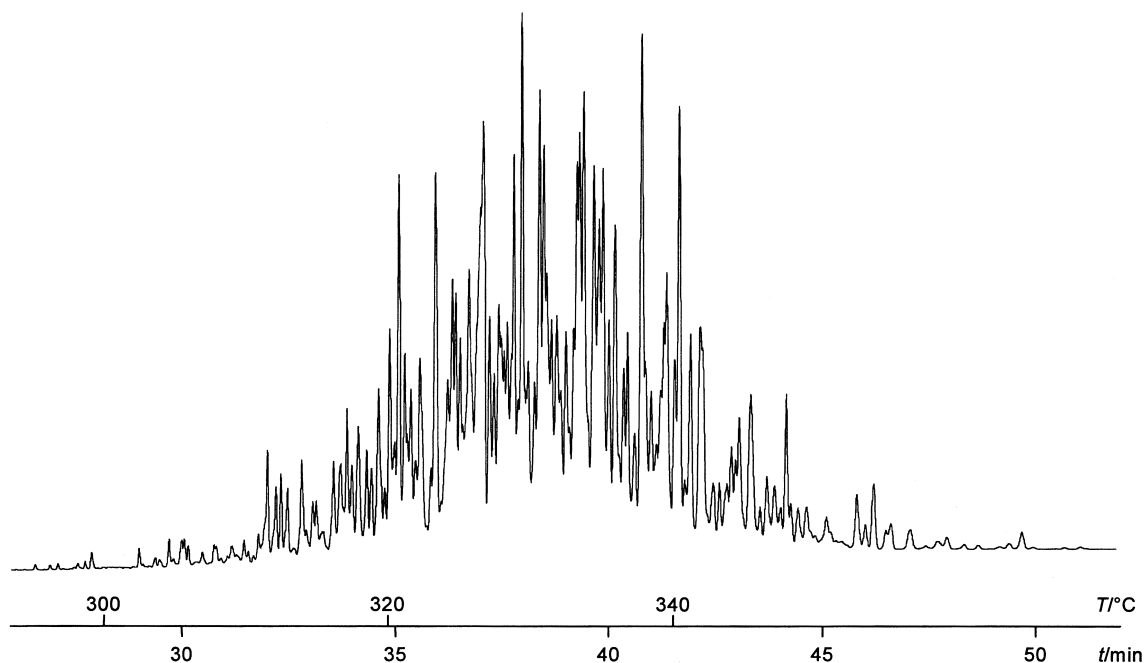


Fig. 4. HRGC–ECD chromatogram of the technical PCT mixture Aroclor 5460 (10 ng/ $\mu$ l) on the Optima  $\delta$ -3. For chromatographic conditions see Table 1.

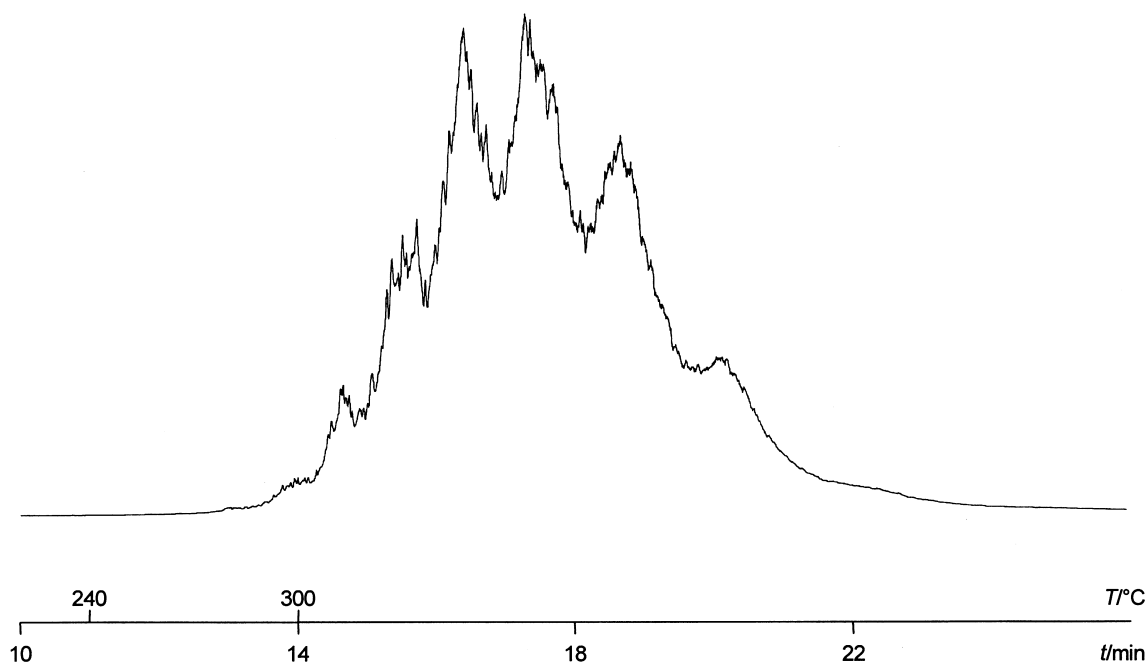


Fig. 5. HRGC-ECD chromatogram of the technical chloroparaffin mixture Hordaflex LC60 ( $C_{10}$ - $C_{13}$ , 62% Cl by mass) (100 ng/ $\mu$ l) on the Optima  $\delta$ -3. For chromatographic conditions see Table 1.

[37–39]. A fast heating leads to a narrower detector signal and thus to better signal to noise ratio for the otherwise very broad detector signals of the CPs. Fig. 5 depicts the typically structured, still broad signals of the technical CP mixture Hordaflex LC 60 on the Optima  $\delta$ -3. The separation of the CPs takes place within about 12 min with a total run duration of less than 25 min so the same capillary could be used for the determination of a broad spectrum of organohalogen compounds, for example in multi-residue methods like those proposed by Jansson et al. [40]. The low bleeding of the stationary phase recommends the Optima  $\delta$ -3 for the use with a mass selective detector preferably with negative ion chemical ionisation (GC-NCI-MS) for a more selective determination of the CPs [39,41].

### 3.6. Halogenated compounds in cod liver oil from the North Atlantic

The well-characterised NIST reference material SRM 1588 [42–44], a cod liver oil from the North Atlantic, was used to investigate the applicability of

the Optima  $\delta$ -3 for the analysis of semivolatile organohalogen compounds in a biological matrix. Figs. 6 and 7 depict the chromatograms of the first and second NP-HPLC fraction of the extract obtained after the clean-up procedure. The PCBs and other compounds with a low polarity occur in the first NP-HPLC fraction. Compounds with a higher polarity, for example most pesticides elute in the second fraction, can be seen in the corresponding chromatogram. The non-optimal peak shape of some PCBs is due to coelution with compounds of the insecticide toxaphene (polychlorinated bornanes) which are also ubiquitous environmental contaminants. Some components of the complex toxaphene mixture elute together with the PCBs in the HPLC group separation. The presence of toxaphene compounds in SRM 1588 was investigated in [45,46]. Six of the most abundant congeners as proposed in [24] are marked in Figs. 6 and 7.

Fig. 6 also reveals the occurrence of very low but detectable amounts of polybrominated diphenyl ethers (PBDEs) in the cod liver oil. On the Optima  $\delta$ -3 no coelution and therefore no interference of the

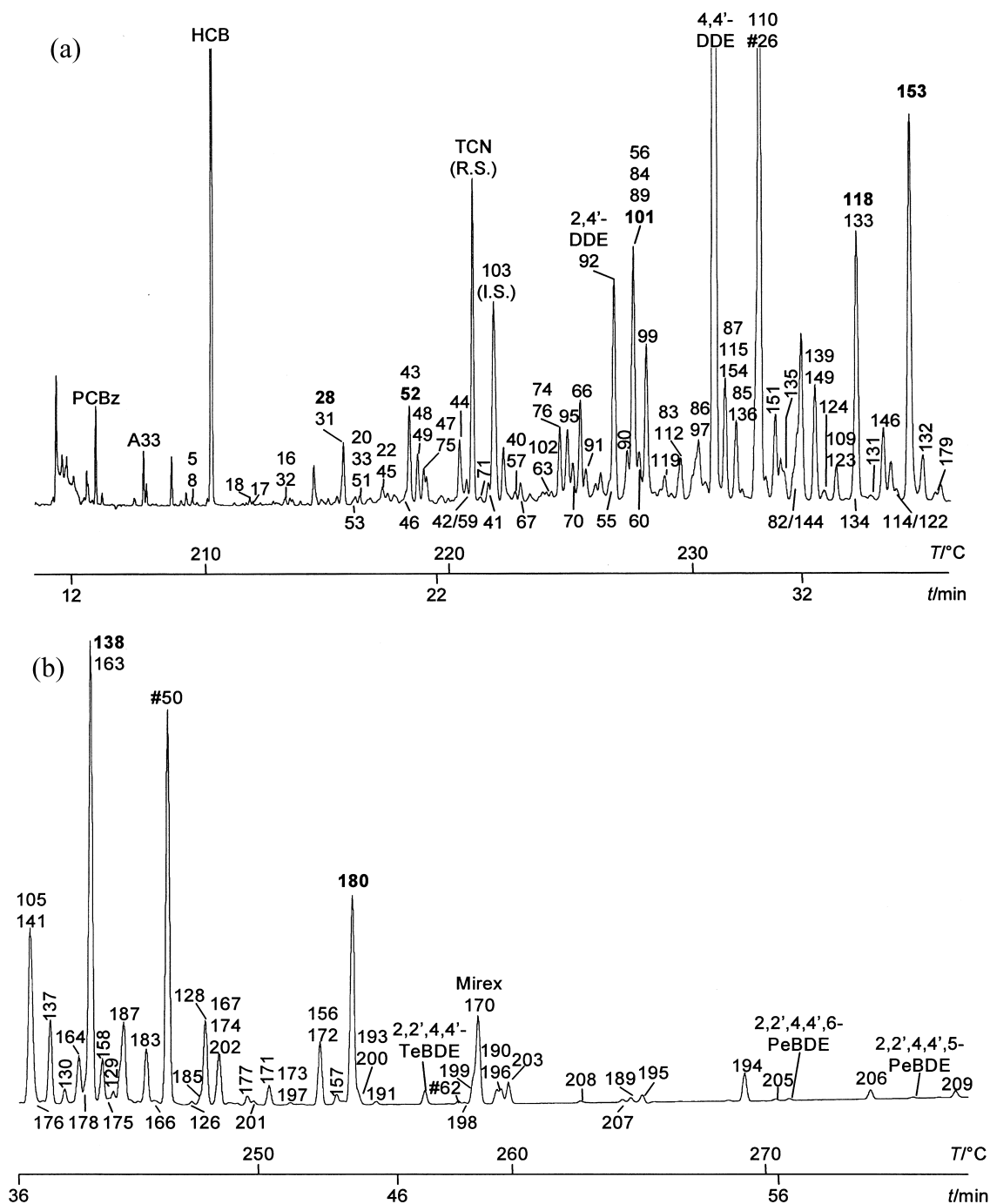


Fig. 6. HRGC-ECD chromatogram of the PCB fraction (fraction 1) isolated from NIST SRM 1588 (Organics in Cod Liver Oil) on the Optima  $\delta$ -3 [retention time window: (a) 11–36 min; (b) 36–61 min]. (R.S.: recovery standard; I.S.: internal standard; PCB indicator congeners are shown in bold; TeBDE: tetrabromo-diphenylether; PeBDE: pentabromo-diphenylether; Nos. 26, 50, 62: toxaphene congeners [21].) For chromatographic conditions see Table 1.

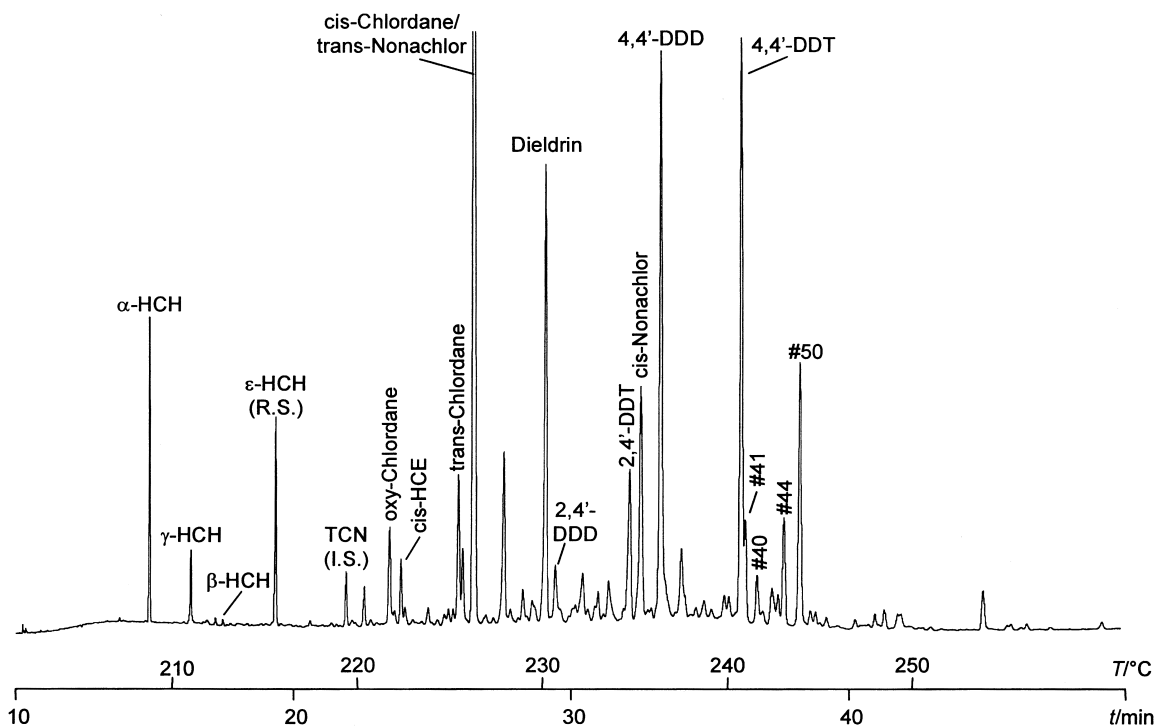


Fig. 7. HRGC–ECD chromatogram of the pesticide fraction (fraction 2) isolated from NIST SRM 1588 (Organics in Cod Liver Oil) on the Optima  $\delta$ -3. (R.S.: recovery standard; I.S.: internal standard; Nos. 40, 41, 44, 50: toxaphene congeners [21].) For chromatographic conditions see Table 1.

detection of the PBDEs (e.g. technical mixture Bromkal 70-5DE) used as flame retardants [47–50], by the ubiquitous PCBs and vice versa, is observed.

#### 4. Conclusion

The selectivity of the new thermally very stable stationary phase differs from other commonly used GC capillaries. It makes the Optima  $\delta$ -3 a suitable capillary column for the analysis of chlorinated pesticides and as reference column for the congener specific analysis of PCBs in spite of some coelutions in this case. The high temperature stability makes it possible to use the same capillary for the analysis of polychlorinated biphenyls and the even lower volatile polychlorinated terphenyls, polychlorinated alkanes, and polybrominated diphenyl ethers as well.

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