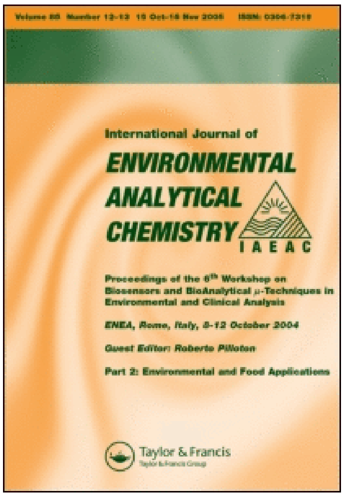

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INTERFERENCES IN THE DETERMINATION OF 2,4,5,2′,5′-PENTACHLOROBIPHENYL (CB 101) IN ENVIRONMENTAL AND TECHNICAL SAMPLES

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The gas chromatographic analysis of 2,4,5,2′,5′-pentachlorobiphenyl (CB 101) in environmental and technical samples may be biased by the presence of 2,3,6,2′,3′-pentachlorobiphenyl (CB 84) and 2,3,5,2′,4′-pentachlorobiphenyl (CB 90). These chlorobiphenyls both co-elute with CB 101 on a 95% dimethyl/5% phenyl polysiloxane (SE-54) column, which is often used for the analysis of chlorobiphenyls. This study describes how the chlorobiphenyls 84 and 90 can be properly identified and quantified by multidimensional gas chromatography (MDGC). It is shown that the concentration of CB 101 may be overestimated up to 35%, when analyzed on a SE-54 column.

KEY WORDS: Multi-dimensional gas chromatography, individual chlorobiphenyls, CB-101.

INTRODUCTION

In most laboratories, packed GC columns are replaced by capillary columns in the analysis of polychlorinated biphenyls in environmental samples. Instead of an estimation of a total PCB concentration, exact concentrations of individual CBs can now be determined. In the Netherlands and several other countries, tolerance levels for total PCB concentrations in food were changed into tolerance levels for a number of individual CBs. In 1984, in the Netherlands the CBs 28 (2,4,4′-trichlorobiphenyl), 52 (2,5,2′,5′-tetrachlorobiphenyl), 101 (2,4,5,2′,5′-pentachlorobiphenyl), 118 (2,4,5,3′,4′-pentachlorobiphenyl), 138 (2,3,4,2′,4′,5′-hexachlorobiphenyl), 153 (2,4,5,2′,4′,5′-hexachlorobiphenyl) and 180 (2,3,4,5,2′,4′,5′-heptachlorobiphenyl) were selected for this purpose.[1]

The same CBs were also used in the certification of two fish oils as reference materials for the CB analysis organized by the Community Bureau of Reference Materials, BCR,[2] in Brussels. Although this organization recommends the use of two different stationary phases for the confirmation of the various CB concentrations, in most laboratories it is common practice to use only one column for the routine analysis of individual CBs. The most used stationary phase for this purpose is a 95% dimethyl/5% phenyl polysiloxane phase (SE-54, CP-Sil 8). For this phase the chromatographic properties of all 209 CBs were described and it was claimed that, with the exception of 11 pairs of congeners, all CBs could be separated on a 50 m narrow-bore capillary column.[3]

The first experiments of Duinker *et al.*[4] with multi-dimensional GC in CB analysis suggested already that some interferences may co-elute with the various important CB peaks on a SE-54 column. However, these first results were of limited use, because the use of relatively wide-bore columns (i.d. 0.32 mm) and the restricted difference in polarity of the stationary phases SE-54 and OV-210. Due to the fact that PCB congeners have a relatively small range of polarity, only a marginal increase in separation is obtained on the second column.

Guenther *et al.*[5] introduced the use of a liquid crystalline stationary phase (SB-Smectic, Lee Scientific) in combination with a non-polar column, both narrow bore (i.d. 0.20–0.25 mm), for the analysis of CBs. The use of this liquid crystalline phase creates a completely different elution order of the CBs. The separation is influenced by the molecular shape rather than by the boiling point order, by which the CBs are separated on the non-polar column.

In this study we describe the results of a multi-dimensional gas chromatographic (MDGC) technique using a non-polar column (HP-1, methyl polysiloxane) in combination with a SB-Smectic column for the determination of CB 101 in environmental and technical samples. Instead of a flame ionisation detector and a mass-selective detector, which were used by Guenther *et al.*,[5] we used two independent electron-capture detectors. In an earlier stage problems encountered in the analysis of CB 138 were already published by Roos *et al.*[6] and Larsen and Riego.[7]

EXPERIMENTAL

The gas chromatograph was a Siemens Sichromat 2–8, equipped with two independently controllable ovens. The following conditions were used:

Parameter	*First oven*	*Second oven*
Column type	HP-1	SB-Smectic
Length	25 m	25 m
Internal diameter	0.20 mm	0.20 mm
Film thickness	0.50 μm	0.15 μm
Carrier gas	helium	helium
Linear gas velocity	45 cm/s	51 cm/s
Detector	ECD, 370 MBq	ECD, 370 MBq
Make-up gas	nitrogen	nitrogen
Injection type	splitless	—
Splitter time	2 min	—
Detector temperature	300 °C	300 °C
Injector temperature	270 °C	—
Initial oven temperature	90 °C	140 °C
Temperature programme	3 min 90 °C	40 min 140 °C[a]
	30 °C/min–215 °C	2 °C/min–180 °C
	30 min 215 °C	5 min 180 °C
	5 °C/min–270 °C	3 °C/min–215 °C
	20 min 270 °C	4 min 215 °C

[a] 25 min 140 °C for mineral waste oil (Figure 3d).

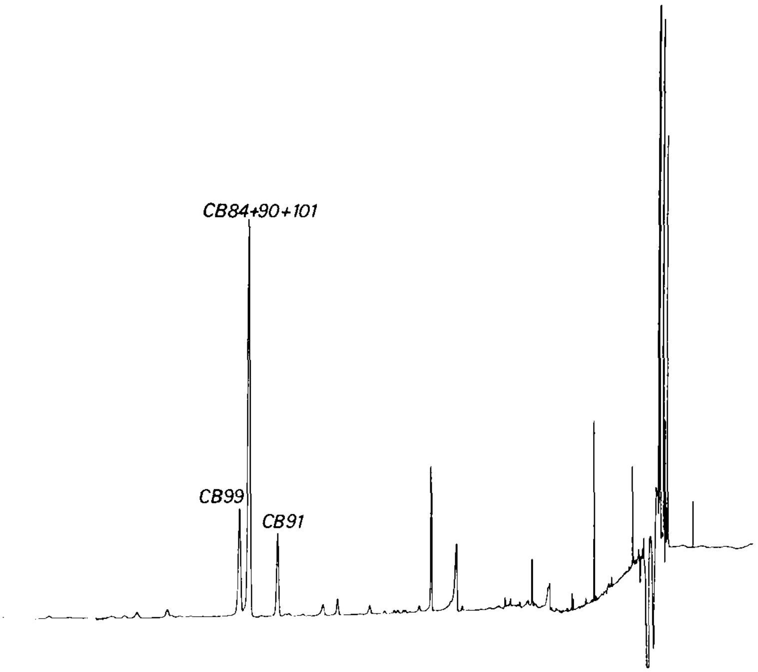

Figure 1 Co-elution of the CBs 84, 90 and 101 on a 50 m CP-Sil 8 CB column (i.d.: 0.15 mm, film thickness 0.2 μm[9]).

By means of the live *T*-piece installed in the first oven, very accurate heart-cuts from the first chromatogram could be made, which were analysed again on the second column. Data were acquired and processed on a Maxima workstation. Glassware, solvents and chemicals were pesticide grade or cleaned as usual for this type of trace analysis. The CB 101 standard was a certified standard, obtained from BCR. The CB 84 standard was obtained from Promochem (Wesel, FRG).

The technical Aroclor 1254 PCB mixture was obtained from Monsanto Industrial Chemicals (St. Louis, USA). A mixture of the CBs 90, 91 and 99 was kindly supplied by Ir. L.G.M.T. Tuinstra of the State Institute for Quality Control of Agricultural Products (Wageningen, The Netherlands).

The samples of cod liver oil, mackerel oil, sewage sludge and waste oil were certified reference materials or materials under certification of the BCR. The method of extraction and clean-up over alumina and silica columns, used for the samples cod liver oil, mackerel oil, waste oil and eel was described earlier.[8] The sewage sludge sample was cold extracted with a hexane/acetone mixture, saponified and cleaned in the same way over alumina and silica columns.

RESULTS AND DISCUSSION

According to Mullin's list,[3] the following CBs possibly can interfere with CB 101

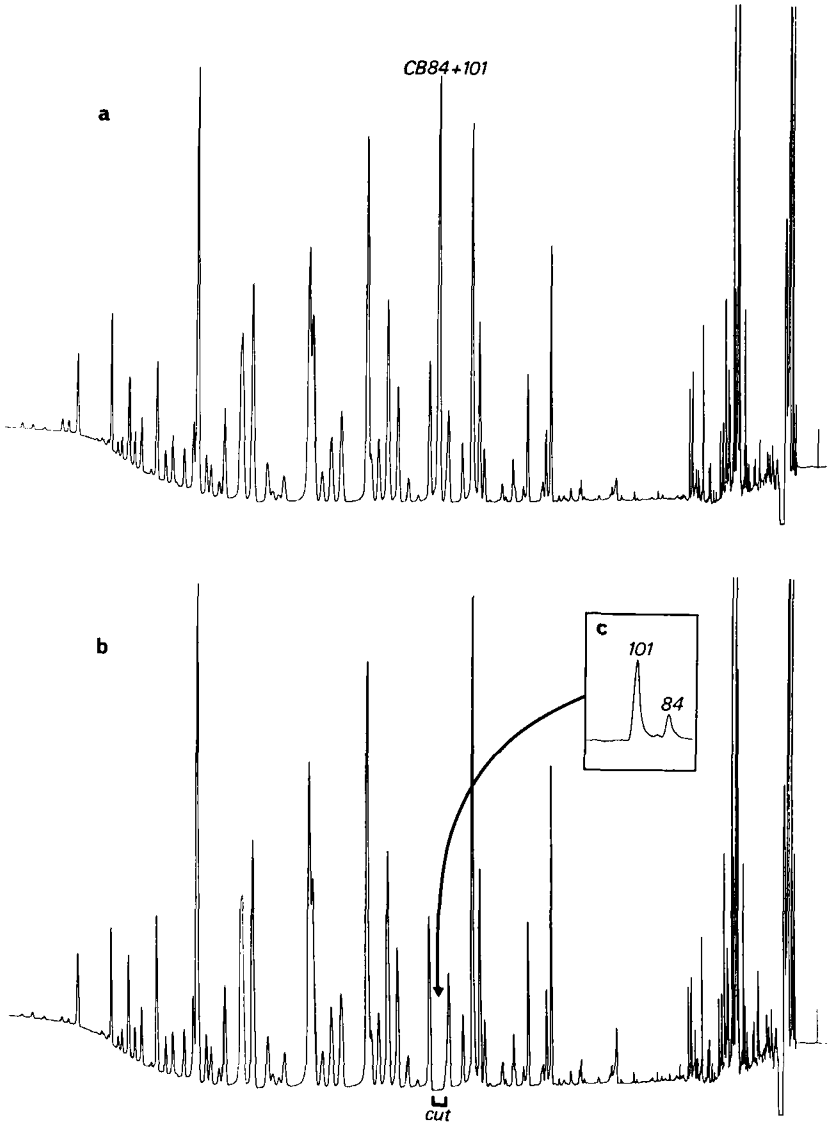

Figure 2 (a) Chromatogram of an Aroclor 1254 mixture from the first column (HP-1) of the multi-dimensional GC system. (b) Idem, after heart cutting of the CB 101/84 peak. (c) Heart-cut of the CB 101/84 peak on the SB-Smectic column.

on a SE-54 column: CB 92 (2,3,5,2′,5′-pentachlorobiphenyl) t_r rel. to octachloronaphthalene (OCN): 0.5742; CB 84 (2,3,6,2′,3′-pentachlorobiphenyl) t_r rel. to OCN: 0.5744; CB 89 (2,3,4,2′,6′-pentachlorobiphenyl) t_r rel. to OCN: 0.5779; and CB 90 (2,3,5,2′,4′-pentachlorobiphenyl) t_r rel. to OCN: 0.5814. Although Mullin suggests that, theoretically, a separation of these CBs from CB 101 is possible (t_r rel. to OCN: 0.5816), in practice it appears to be very difficult to obtain a separation.

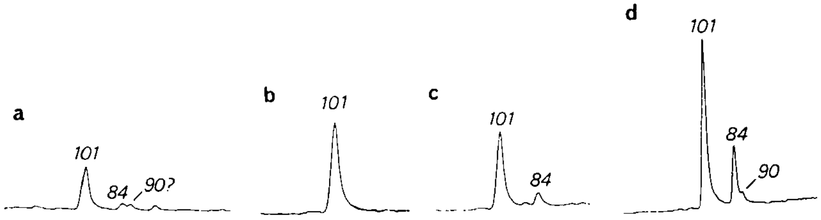

Figure 3 Heart cuts of the CB 101/84/90 peak on the SB-Smectic column. (a) Eel, River Roer; (b) Cod liver oil; (c) Sewage sludge; (d) Mineral waste oil.

Table 1 Concentrations of CBs 84 and 101 in different samples, analyzed by multi-dimensional GC (expressed in $\mu g/kg$ on a product base, for Aroclor 1254 in g/kg)

Sample	*CB 84*	*CB 101*		*% Difference CP-Sil 8 MDGC*	*Certified value*
		MDGC	*CP-Sil 8*		
Eel, River Roer	<4	270	270	0	—
Cod liver oil	<2	380	385	1	372±17
Mackerel oil	<2	170	174	2	165±9
Sewage sludge[a]	50	150	177	18	132±22
Mineral waste oil	610	1470	1990	35	—
Aroclor 1254	30	70	88	25	—

[a] Freeze-dried material.

Even with a 50 m × 0.15 mm i.d. SE-54 column,[9] we were not able to separate CB 84 from CB 101 (Figure 1). With our multi-dimensional GC system we could prove that the CB 101 peak in Aroclor 1254 on a SE-54 column consisted of different congeners, viz. CB 101 and CB 84 (Figure 2).

The identity of CB 84 was confirmed by spiking experiments. Figure 3 shows the heart-cut of several environmental samples and of a mineral waste oil. In this oil the presence of CB 90 could also be identified. This shows that CB 90 was present in technical PCB mixtures, with which the mineral waste oil was contaminated. The identification of CB 90 was performed by spiking with a mixture of the congeners 90, 91 and 99 (a pure CB 90 standard was not available). CB 90 could also be detected in minor quantity in an eel sample from the River Roer. The absence of CB 89 is explained by the unfavourable 2,6 substitution in one phenyl ring. A CB 92 standard was not available, so the presence of CB 92 cannot be excluded completely.

Table 1 shows the concentrations of the CBs 84 and 101 in the various samples. Also an estimation is made of the error in the calculation of CB 101 when analysed on a CP-Sil 8 CB column.

Table 1 shows that CB 84 is below the detection limit in the analyzed fishery products. In the sewage sludge a CB 84 concentration of 50 $\mu g/kg$ was measured. The quantification was performed by means of spiking experiments. The certified values of CB 101 in cod liver oil and mackerel oil are therefore not influenced by

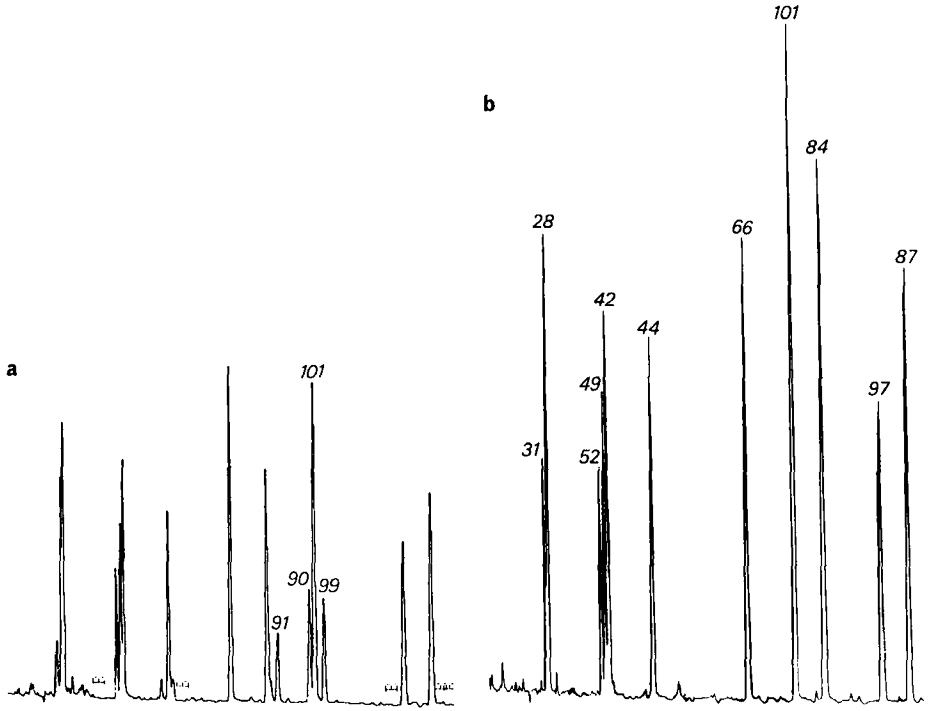

Figure 4 (a) Separation of CB 101 from CB 90. (b) Separation of CB 101 from CB 84. Experimental: 60 m CP-Sil 19 CB column; i.d.: 0.15 mm, film thickness 0.2 μm[9].

the co-elution of CB 84 and CB 101. The certified value of CB 101 in sewage sludge (132 ± 22 μg/kg) is lower than we calculated for CB 101 in sewage sludge after MDGC analysis. Apparently the difference in the CB 101 concentration in sewage sludge caused by the presence of CB 84 is smaller than the analytical error made in the certification of CB 101. However, for the mineral waste oil sample there are consequences. For the certification of this sample all CB 101 results obtained only on SE-54 columns have been rejected.

The consequences for analyses in relation with PCB tolerance levels in fishery products seem to be of minor importance, because of the absence of CB 84 in the analyzed fishery products. However, it will be necessary to analyse more samples of different fish species to confirm this result. Further research is also needed to evaluate the consequences in relation to the established tolerance level for CB 101 of the observed co-elution of the CBs 84 and 101 for other food products.

Figure 4 shows that on a 60 m narrow bore CP-Sil 19 CB column, CB 101 is separated from the CBs 90 and 84. For a reliable quantitative analysis of CB 101 this column is recommended. Table 1 shows that the use of CP-Sil 8 CB columns can lead to an over-estimation of the CB 101 concentration of up to 35%.

CONCLUSIONS

The use of multi-dimensional gas chromatography with narrow-bore GC columns appears to be a valuable tool in the analysis of chlorobiphenyls to separate possible co-eluting peaks. The use of stationary phases with a very different character, like the combination of a non-polar column with a SB-Smectic column, makes it highly unlikely that two polychlorinated biphenyls will co-elute on both columns.

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