

UNAMBIGUOUS DETERMINATION OF REGULATION-
RELEVANT AND TOXIC PCB CONGENERS BESIDES
CHLORINATED PESTICIDES IN SEAFOOD
BY APPLICATION OF DUAL-COLUMN HRGC

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Many countries have established maximum residue limits (MRL) for organochlorines in food, and special regulations exist for tolerable concentrations of chlorinated pesticides as well as for chlorobiphenyl congeners (PCBs) in fish and shellfish¹.

The nontoxic PCB congeners (IUPAC²) Nos. 28, 52, 101, 138, 153, 180 claim particular attention³.

The application of two capillary columns with SE-54 and OV-1701 like stationary phases for the exact quantification of these regulation-relevant PCBs was proposed.⁴ Their analysis is, however, still hindered by the insufficient separation of some PCB congeners on these standard capillary columns.⁵

Recently, the contamination of biological materials with non-ortho and mono-ortho congeners has obtained increasing attention due to their toxicity⁶.

Investigations carried out with multidimensional GC and mass spectrometry showed that both, the regulation-relevant and the toxic chlorobiphenyls may be interfered by other PCB congeners on an SE-54 column^{7,8}.

Therefore, the use of a second column coated with a very polar stationary phase based on bis-cyanopropylphenyl polysiloxane in addition to the SE-54 column was proposed⁹.

Vetter et al.¹⁰ succeeded in separating the PCB Nos. 153, 132, 105 by application of an OV-225 column, and Larsen et al.⁹ demonstrated the separation of the PCB Nos. 138 and 163 on an SP-2330 column. However, the complete separation of the congeners which co-elute with PCB No. 138 on an SE-54 column, i.e. PCB Nos. 163, 164, 158, 186, 160¹¹, was not achieved with the bis-cyanopropylphenyl polysiloxane phase, although certain problems associated with co-eluting congeners could be solved by use of such a strongly polar column.

Difficulties mainly arise by routine determination of the regulation-relevant PCB Nos. 28, 101, 138, 153¹¹ and the toxic PCB congeners 77, 105, 118, 126, 156, 157¹² on an SE-54 column. Therefore, the SE-54 phase was modified by incorporating 10% methyl-C18¹³ (CP SIL-8 plus 10% C-18; Chrompack International, Middelburg, Netherlands).

By parallel application of an SE-54/C18 column and a polar dioxin column (SP-2331, Supelco Inc., Bellefonte, PA, USA) the simultaneous quantification of the otherwise interfering PCB congeners could be achieved (Fig. 1).

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This dual-column HRGC allows the unambiguous determination of regulation-relevant and toxic PCB congeners besides chlorinated pesticides (Tab. 1).

Therefore, the proposed approach represents an effective alternative to the standard column combination SE-54 and OV-1701 with the additional advantage that changes of the chromatographic conditions¹⁴ are not required.

Chromatographic conditions

Gas chromatograph: HP 5890 (Hewlett Packard)

Injector: 220 °C (splitless) with fixed inlet splitter for capillary columns

Detector: 300 °C (ECD)

Temperature program: start: 180 °C, 4 min
rate 1: 180 °C-210 °C, 6 °C/min
hold 1: 210 °C, 4 min
rate 2: 210 °C-270 °C, 4 °C/min
hold 2: 270 °C, 25 min

capillary columns: 1) CP SIL-8/10% C18 (50 m, ID: 0,25 mm, Chrompack International, Middelburg, NL)
2) SP-2331 (60 m, ID: 0,25 mm, Supelco Inc., Bellefonte, PA, USA)

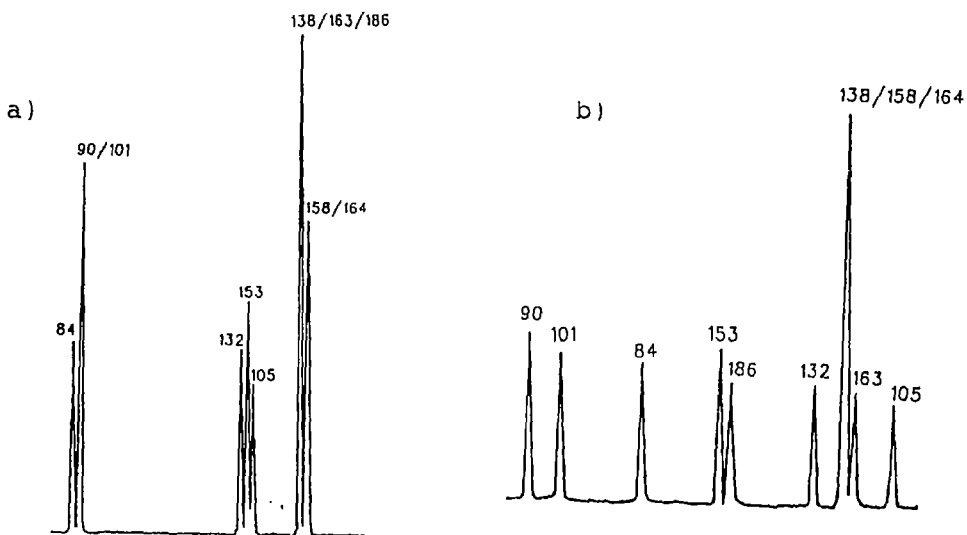


Fig. 1: Separation of regulation-relevant PCB congeners by combination of SE-54/C18 (a) and SP-2331 (b) columns.

Tab. 1: Retention times (R_t) of PCB congeners (co-eluting on an SE-54 column) obtained by parallel application of SE-54/C18 and SP-2331 capillary columns (chromatographic conditions see ref. 14).

PCB No.	SE-54/C18 R_t (min)	SP-2331 R_t (min)
<u>28</u>	22.57	28.06
31	22.38	28.23
<u>52</u>	24.23	29.08
77 ^x	30.62	39.55
110	31.15	36.20
<u>101</u>	29.17	33.08
90	29.19	32.07
84	28.82	34.49
118 ^x	33.26	37.16
123	33.06	36.39
149	32.71	35.27
<u>153</u>	34.76	36.16
132	34.45	38.18
105 ^x	34.98	40.06
<u>138</u>	36.66	39.10
163	36.59	39.40
164	36.80	39.00
158	36.79	39.10
186	36.65	36.38
126 ^x	37.70	44.18
129	37.03	39.89
178	37.21	36.95
156 ^x	41.24	43.47
171	40.61	40.50
202	40.45	36.74
<u>180</u>	42.86	41.78

underlined = regulation-relevant PCBs
x = toxic PCB congeners

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