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Improvements in the separation of polychlorinated biphenyl congeners by high-resolution gas chromatography

Application to the analysis of two mineral oils and powdered milk☆

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ABSTRACT

A comparative study of the separation of seven polychlorinated biphenyl (PCB) congeners (IUPAC Nos. 28, 52, 101, 118, 138, 153 and 180) and other important PCBs (31, 44, 61, 105, 128, 149, 156, 163, 170 and 186), selected on the basis of their toxicity and levels found in environmental and food samples, was performed using DB-5 and CP-Sil 8 CB (5% phenyl–95% methyl polysiloxane), DB-1701 (14% cyanopropylphenyl–86% methyl polysiloxane) and DB-17 (50% phenyl–50% methyl polysiloxane) fused-silica capillary columns in gas chromatography with electron-capture detection. The combination of DB-5 or CP-Sil 8 CB and DB-17 capillary columns allowed the separation and determination of PCB congeners 118–149, 138–163 and 153–105–132. Some of these congeners were determined in candidate reference materials, two waste mineral oils of different concentration levels and a milk powder, as part of an intercalibration exercise. The recoveries obtained for thirteen selected PCBs were >90% in the three different samples. The concentrations of PCB congeners determined in the samples ranged between 0.086 and 2.054 mg kg^{-1}, 0.758 and 66.720 mg kg^{-1} and 0.208 and 14.00 μg kg^{-1} for oil of low level, oil of high level and milk powder, respectively. The methods were validated by participation in several round-robin exercises and the results obtained were in good agreement (R.S.D. = 20–40%) for all participating laboratories (between 11 and 19).

INTRODUCTION

Residue levels of polychlorinated biphenyls (PCBs) have been found in aquatic biota, both continental and marine, as a result of their widespread distribution, environmental persistence and high lipophilicity [1–3]. Among the 209 possible PCB congeners, only around 150 have been reported in the total environment. Seven of them (IUPAC Nos. 28, 52, 101, 118, 138, 153 and 180) were selected as the most relevant because of their distribution throughout chromatograms, coverage of the chlorination range,

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use in technical mixtures, relative ease of analytical determination and proved toxicity. Consequently, they are commonly mentioned in environmental and food regulations [4].

Following the initial selection of these seven PCBs, considerable efforts have been made in the past to detect potential interferences and/or co-elutions of these congeners by capillary gas chromatography (GC). Initially a problem was encountered in the determination of PCB 138 [5] that later was attributed to the presence of PCB 163 [6]. The complete separation of the two congeners was possible only by using a polar SP-2330 (biscyanopropylphenyl polysiloxane) capillary GC column [6]. The co-elution problems between these two congeners, PCB 138 and 163, were found during a certification exercise in which most of the laboratories used DB-5-type columns and the congeners were unresolved. Hence it was impossible to certify the PCB 138 congener, and consequently, certification was indicated as the total amount of PCB 138 + 163 [4]. Recently, the separation of the two congeners was achieved using a polar FFAP (polyethylene glycol terephthalic acid ester) column [7].

When using the most common stationary phases, which usually contain 95% dimethyl–5% phenyl polysiloxane (SE-54, CP-Sil 8, DB-5), other co-elution problems have also been reported, *e.g.*, for PCBs 101–84–90, 123–149, 171–156–202 and 153–105 [8,9]. Such a co-elution problem can be solved either using multidimensional GC, with a non-polar column in combination with a more polar column by using the heart-cutting technique [8], a dual-column system (DB-5 and DB-1701) operated in parallel with a glass T-split [10] or using other columns of different polarity, *e.g.*, HP-5, CP-Sil 19 and CP-Sil 88. It is clear that many co-elution problems with PCBs have not been solved and it is necessary to find an appropriate column(s) that will solve specific problems [7,11].

Therefore, to cope with the requirements of routine measurements of PCBs in food and environmental samples there is a need for the development of analytical methods for the confirmation of the different groups of PCBs, thus avoiding false-positive determination. Most of the PCBs can be easily separated using DB-5 or CP-Sil 8 CB apolar capillary columns. However, the complete separation of the whole group of PCBs is not possible even using these stationary phases in a 30- or 50-m column.

The purpose of this work was to carry out a comparative study of the separation of the seven common PCB congeners (28, 52, 101, 118, 138, 153 and 180) and a few other PCBs (31, 44, 61, 105, 128, 149, 156, 163, 170 and 187) selected on the basis of their proved toxicity and/or levels found in environmental and food samples [12], using DB-5 (60-m), CP-Sil 8 CB (50-m), DB-1701 (60-m) and DB-17 (30-m) capillary columns. These four columns were applied to the determination of some of the above PCB congeners in samples of two waste mineral oils and a milk powder, as a part of an intercalibration exercise of the BCR (Community Bureau of Reference) of the Commission of the European Communities (CEC). The results of the two laboratories were in good agreement in a round-robin exercise with the most probable values from different laboratories (total 22) with a relative standard deviation (R.S.D.) between 20 and 40%. By using the columns reported in this paper, an accurate assessment of the environmental levels of the different PCB congeners can be made, thus improving the quality assurance in the final analytical determination.

EXPERIMENTAL

Chemicals

The solvents *n*-hexane, acetone and dichloromethane of residue analysis grade were supplied by Merck (Darmstadt, Germany). The purity of the solvents was determined by concentration of a 150-ml volume to 0.5 ml and analysis by high-resolution GC with electron-capture detection (ECD). Isooctane of pesticide grade was obtained from Carlo Erba (Milan, Italy). Florisil (600–100 mesh), sulphuric acid (95%, G.R. grade) and anhydrous sodium sulphate for residue analysis were purchased form Merck. Florisil cartridges with 1 g of adsorbent were obtained from Analytichem (Varian, Palo Alto, CA, USA; purchased through Scharlau, Barcelona, Spain). Individual analytical-reagent grade PCBs were supplied from Promochem (Wesel, Germany) and 2,4-dichlorobenzylhexyl

ether (DCBE-C_6) and 2,4-dichlorobenzylhexadecyl ether (DCBE-C_{16}) (Dr. D. Wells, Aberdeen, U.K.) and 1,2,3,4-tetrachloronaphthalene (TCN) were used as internal standards. All glass materials were cleaned with AP-13 Extran alkaline soap (Merck) for 24 h, dried overnight at 180°C and rinsed with high-purity solvents immediately prior to use.

Sample treatment

Five replicates of 0.5 g of waste mineral oil of high and low PCB concentration levels were accurately weighed into a 25-ml volumetric flask and diluted to volume with *n*-hexane. An aliquot of diluted sample was removed for clean-up and analysis.

For the milk powder, five replicates of 5 g were placed in a mortar and then 15 ml of water, 12 g of Florisil (activated at 675°C for 2 h) and 130 g of anhydrous sodium sulphate were added. The mixture was mixed to yield a dry powder. This mixture was transfered into an extraction column (2 cm I.D.) previously filled with a small plug of glass-wool and eluted with 100 ml of *n*-hexane–acetone (2:1, v/v). The extract was concentrated to *ca.* 3 ml in a rotary evaporator.

Clean-up procedure

Laboratory 1. The oil extract was cleaned up by extensive shaking with 3×3 ml of sulphuric acid for about 3 min and, when a good phase separation had been obtained, the upper organic layer was removed and the extract was transfered into a Florisil cartridge that had previously been cleaned and activated with 20 ml of *n*-hexane. The PCB congeners were eluted with 10 ml of *n*-hexane. The organic fraction was evaporated and the final volume was adjusted to 0.5 ml, then being ready for injection into the GC–ECD system.

Laboratory 2. The clean-up column (1 cm I.D.) was prepared using 8 g of Florisil activated at 675°C for at least 2h, and stored at 150°C before use. At the two ends of the column an anhydrous sodium sulphate layer *ca.* 2 cm high was applied. Subsequently, the column was eluted with 50 ml of *n*-hexane to clean the absorbent. The oil extract (1 ml) was transfered quantitatively to a Florisil column and was eluted with 50 ml of *n*-hexane at a flow-rate of 1 ml min^{-1}.

A 1-ml volume of the hexane–acetone extract obtained for the milk sample as described previously was mixed with 5 ml of 95% sulphuric acid and after 3 h the organic phase was removed and quantitatively transferred to a Florisil column. The clean-up procedure for the milk was the same as that used for the waste mineral oil extracts. The overall procedures for the different samples are outlined in Fig. 1.

Chromatographic conditions

Purified extracts were analysed on a Hewlett-Packard (Palo Alto, CA, USA) Model 5890 capillary gas chromatograph with an HP 7673A autosampler and equipped with a ^{63}Ni electron-capture detector (laboratory 1) and on a Carlo Erba (Milan, Italy) 5300 Mega Series chromatograph equipped with a ^{63}Ni electron-capture detector (laboratory 2). Fused-silica capillary

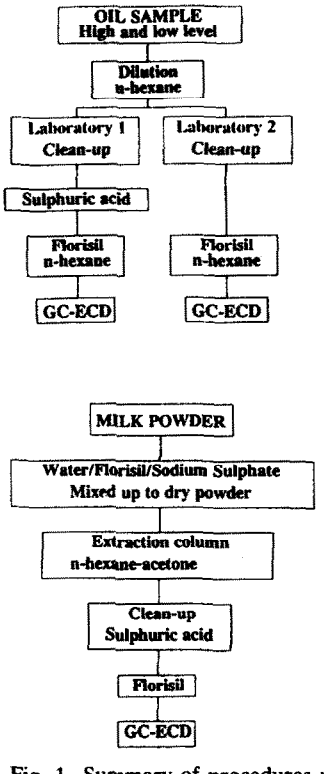

Fig. 1. Summary of procedures used for the separation and determination of PCBs in high- and low-level mineral oils and powdered milk. Solvent ratio in extraction column: *n*-hexane–acetone (2:1, v/v).

columns of DB-5 (J&W Scientific, Folsom, CA, USA) and CP-Sil 8 CB (Chrompack, Middelburg, Netherlands), both containing 5% phenyl–95% methyl polysiloxane, DB-1701 (J&W Scientific), containing 14% cyanopropylphenyl–86% methyl polysiloxane, and DB-17 (J&W Scientific), containing 50% phenyl–50% methyl polysiloxane, were used. The characteristics of the columns and the chromatographic conditions are given in Table I. The chromatographic data were recorded on an HP 59970C GC workstation data system and a Merck–Hitachi (Darmstadt, Germany) Model D-2000 integrator in laboratories 1 and 2, respectively.

The linearity of the ECD response for each congener was determined by plotting calibration graphs of peak height/mass injected *versus* mass injected. The linear range for the PCB congeners was between 10 and 300 $\mu g\ l^{-1}$. The reproducibility of the peak heights calculated from ten replicate analyses of a standard mixture of the PCB congeners was between 4.1 and 6.7%. Quantitative analysis was carried out using external calibration with an internal standard. Standard solutions containing 20–300 pg μl^{-1} in isooctane of the mixed PCB congeners and the internal standard were prepared and injected with the automatic sampler into the GC–ECD system.

Recovery

The recoveries of the PCBs were calculated by spiking the samples by careful mixing of standard solutions. Different amounts of each congener were used in order to obtain concentrations

TABLE I

EXPERIMENTAL CHROMATOGRAPHIC CONDITIONS

Parameter	Column					
	DB-5[a]		CPSil-8[c]	DB-1701[a]	DB-17[c]	DB-17[a]
	A[b]	B[b]				
Injector splitless	Yes	Yes	Yes	Yes	Yes	Yes
Splitter time (min)	50	60	35	60	35	60
Injection volume (μl)	1	1	2	1	2	1
Injector temperature (°C)	270	270	270	270	270	270
Carrier gas	He	He	He	He	He	He
Linear carrier gas velocity (cm^{-1} s)	25	28	26	26	25	27
Make-up gas	N_2	N_2	N_2	N_2	N_2	N_2
Make-up gas flow-rate (ml min^{-1})	35	31	60	32	58	32
Column length (m)	60	60	50	60	30	30
Column I.D. (mm)	0.25	0.25	0.25	0.25	0.25	0.25
Film thickness (μm)	0.25	0.25	0.25	0.25	0.25	0.25
Initial oven temperature (°C)	90	90	80	90	80	90
Initial isothermal period (min)	3	3	2	3	2	2
Initial programming rate (°C min^{-1})	20	2.5	6	3	6	20
Second isothermal temperature (°C)	150	–	–	–	–	150
Second isothermal period (min)	1	–	–	–	–	1
Second programming rate (°C min^{-1})	3	–	–	–	–	3
Final isothermal temperature (°C)	280	290	280	280	290	280
Final isothermal period (min)	20	30	15	30	10	30
Detection	ECD	ECD	ECD	ECD	ECD	ECD
Detector temperature (°C)	310	330	310	330	310	330

[a] Laboratory 2.
[b] (A) Conditions for low-level oil; (B) conditions for high-level oil.
[c] Laboratory 1.

TABLE II

RECOVERIES OF PCB CONGENERS IN MINERAL OIL AND MILK POWDER SAMPLES

PCB	Recovery (%)					
	Low-level oil		High-level oil		Milk powder	
	Mean	S.D.	Mean	S.D.	Mean	S.D.
28	80.1	6.5	91.6	7.2	98.2	6.2
52	81.4	6.9	96.7	8.1	95.7	5.1
101	90.0	8.1	103.0	9.4	98.6	5.2
105	–	–	90.8	7.6	97.3	5.7
118	97.6	7.3	99.3	4.8	99.2	4.2
128	–	–	97.9	4.9	93.7	6.9
138	92.3	5.7	100.2	5.3	96.4	6.3
149	–	–	92.5	5.6	97.2	5.1
153	87.7	6.5	94.6	4.2	98.7	4.0
156	–	–	83.8	7.5	92.1	5.8
163	–	–	85.7	5.6	98.7	6.4
180	105.1	5.1	97.2	4.6	97.9	6.3
170	–	–	93.4	6.7	95.4	5.9

around 50, 100, 150 and 200% ($n = 3$) of the actual concentration in the real samples.

The efficiency was evaluated by studying the recovery of PCBs from samples of spiked oils and milk. The analytical recoveries observed for the thirteen congeners from the two oil samples and milk powder were calculated as described under Experimental and were >90% for all the compounds studied in the three different samples (see Table II).

RESULTS AND DISCUSSION

Chromatographic separation

Data in the literature shown that not all the PCBs can be separated in the columns usually used. The pairs 28–31, 118–149, 138–163 and 153–105 showed inadequate separation with a DB-5-type column and hence there is a need to use other GC columns. The columns studied in this work were DB-5, DB-1701, DB-17 and CP-Sil 8 CB. The retentions time of the PCB congeners 28, 31, 44, 52, 61, 101, 105, 118, 128, 138, 149, 153, 156, 163, 170, 180 and 186, relative to PCB 153, obtained using these columns are given in Table III. These PCB congeners are recommended by the BCR to be determined in milk powder and mineral oil, and are representative of the level of chlorination. Chromatograms of the mineral oils and milk powder using the DB-5 column are shown in Fig. 2 and a chromatogram of high-level mineral oil on the DB-17 column is shown in Fig. 3. It should be noted that all the studies reported in this paper on the separation of the different PCB congeners were performed with real samples of oils and milk.

Chlorobiphenyls 31 and 28. This pair of congeners can be separated using columns of CP-Sil 8 CB or DB-5 of sufficient length, 50 m or more, as can be seen in Table III. Adequate resolution, with a 75% of separation, between the two congeners can be obtained using helium as carrier gas. This separation of PCBs 28 and 31 is better than that using more polar stationary phases such as DB-1701 and DB-17. These results are in agreement with the literature data, showing that it is possible to separate these congeners on a routine basis by using DB-5-type columns of 50 m × 0.22 mm I.D. and a film thickness of 0.2 μm or more [13]. Narrow-bore columns of 0.15 mm I.D. give a much improved

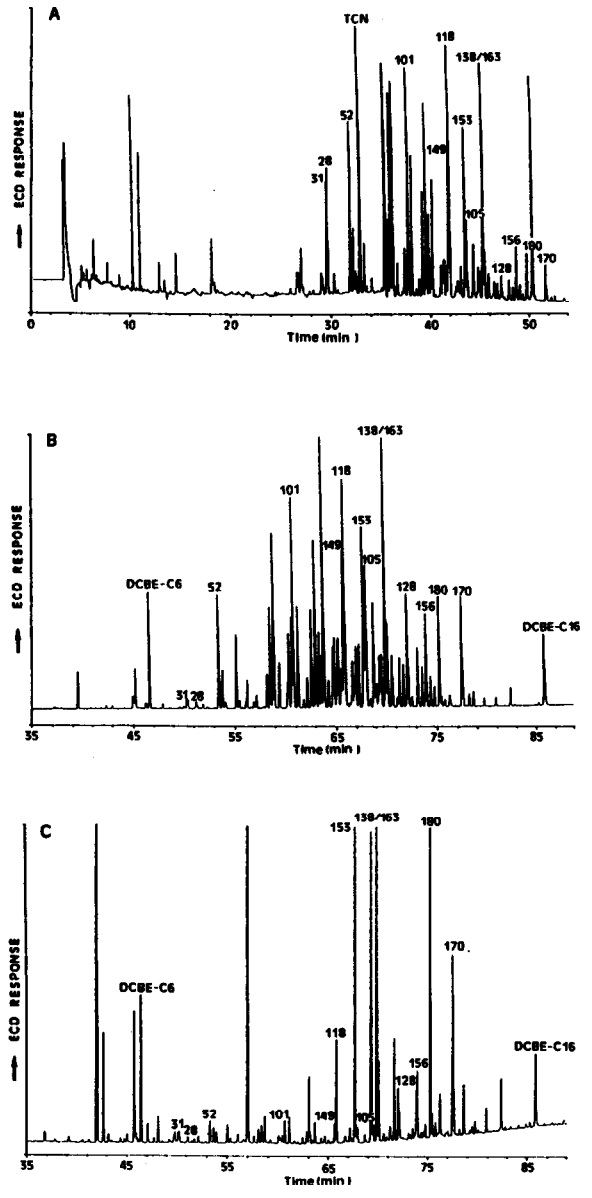

Fig. 2. GC–ECD using a DB-5 column (60 m × 0.25 mm I.D., 0.25 μm film thickness): (A) low-level waste mineral oil (TCN as internal standard); (B) high-level waste mineral oil; (C) powdered milk (DCBE-C_6 and DCBE-C_{16} as internal standards). The chromatographic conditions are given in Table I.

separation [14] so these congeners can then be resolved even with a 25-m column, but the increased pressure required to maintain the optimum linear velocity requires close attention

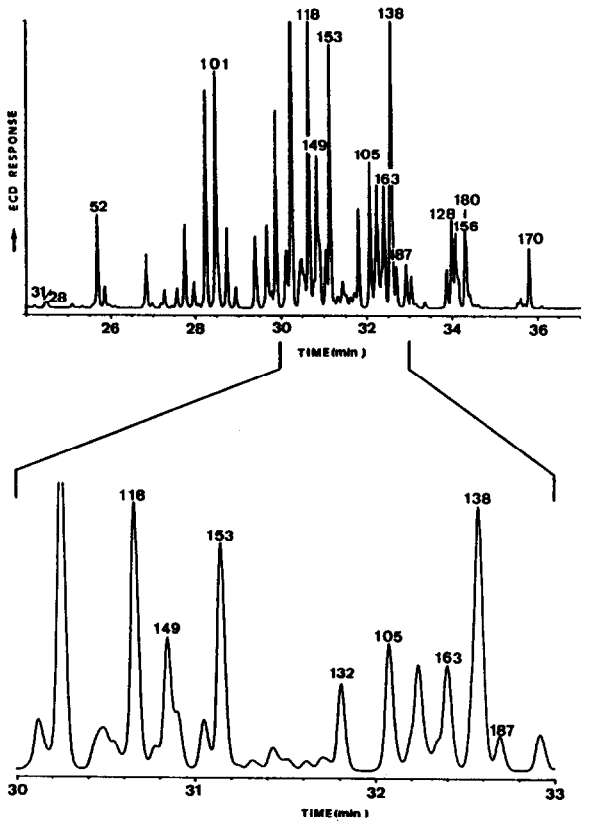

Fig. 3. GC–ECD using a DB-17 column (30 m × 0.25 mm I.D., 0.25 μm film thickness) for extract of high-level waste mineral oil. The chromatographic conditions are given in Table I.

to the possibility of leaks at the front end of the column.

Chlorobiphenyls 118 and 149. It is difficult to force a baseline separation of the pair of PCBs 118 and 149 on a DB-5-type column, as can be seen in Fig. 2, but their separation is excellent on the two polar columns, DB-1701 and DB-17 (see Fig. 3), and the use of polar columns allows the baseline separation of this two congeners. Other workers have obtained similar separations using other polar stationary phases, such as CP-Sil 19 CB (7% phenyl–85% methyl–7% cyanopropyl–1% vinyl polysiloxane) [8,15]. The separation of the other problematic pairs of congeners with this last column is similar to that with the DB-1701 and poorer than that with the DB-17 column.

Chlorobiphenyls 138 and 163. This pair of

TABLE III

RETENTION TIMES AND RELATIVE RETENTION TIMES OF PCB CONGENERS

PCB	Column							
	CPSil-8		DB-5[a]		DB-1701		DB-17[b]	
	t_R (min)	RRT[c]	t_R (min)	RRT[c]	t_R (min)	RRT[c]	t_R (min)	RRT[c]
31	29.84	0.801	49.93	0.741	51.26	0.778	25.98	0.663
28	29.91	0.802	50.04	0.743	51.31	0.779	25.98	0.663
52	31.15	0.836	53.08	0.788	53.88	0.818	28.21	0.720
44	31.94	0.857	54.94	0.815	56.15	0.853	30.52	0.779
61	33.31	0.894	57.86	0.859	58.75	0.892	32.82	0.838
101	34.30	0.920	60.44	0.897	60.01	0.911	33.74	0.861
149	36.46	0.925	65.40	0.971	64.37	0.977	38.46	0.982
118	35.52	0.980	65.53	0.958	64.86	0.985	38.10	0.973
153	37.27	1.000	67.37	1.000	65.86	1.000	39.17	1.000
105	37.48	1.006	67.65	1.004	67.26	1.021	41.02	1.047
138	38.30	1.028	69.56	1.033	68.34	1.038	42.09	1.075
163	38.30	1.028	69.56	1.033	68.34	1.038	41.73	1.065
187	38.91	1.044	70.98	1.054	69.16	1.050	44.87	1.146
128	39.36	1.056	71.70	1.064	71.06	1.079	45.01	1.149
156	40.26	1.080	73.57	1.092	72.78	1.105	45.17	1.153
180	40.89	1.097	74.89	1.112	73.50	1.116	45.68	1.166
170	42.20	1.132	77.16	1.145	76.93	1.168	48.77	1.245

[a] Obtained with DB-5 (B) (laboratory 2) conditions (see Table I).
[b] Obtained with DB-17 (laboratory 1) conditions (see Table I).
[c] RRT = Retention time relative to PCB 153.

congeners is well separated using the most polar stationary phase studied, DB-17, and have similar retention times on CP-Sil 8 CB, DB-5 and DB-1701 phases. Most earlier workers considered that the PCB 163 was unlikely to exist to any extent in technical mixtures [16], but Larsen and Reigo [6] synthesized this compound and confirmed its presence in a large number of environmental matrices. The separation of PCBs 163 and 138 is important because they have relatively high toxicity. Until now, this separation was only possible with the very polar SP-2330 (biscyanopropylphenyl polysiloxane) [6], which shows interferences for the congeners 101, 153 and 180, or with the FFAP (polyethylene glycol terephthalic acid ester) that gives very long retention times for the PCBs 169, 170 and 206 [7]. One drawback with the DB-17 phase is the loss of resolution between the congeners 128 and 156, but these two compounds are not among the seven legislated for in EEC countries [4,17,18]. In addition, the DB-17 column is only 25 m long and the analysis time is shorter than with the FFAP column (see Fig. 3).

Chlorobiphenyls 153 and 105. It is possible to separate PCB 153 from 105 on a CP-Sil 8 CB column (see Table III), but it is more difficult to resolve PCB 132 from 105, which elutes immediately after the PCB 153. When using CP-Sil 19 and CP-Sil 88 columns a good separation between PCB congeners 153, 105 and 132 was obtained [11], although other problems occurred, *e.g.*, 105 now co-eluted with 141 and 176, and 132 with 179 (CP-Sil 19), and 105 co-eluted with 129 (CB-Sil 88). The separation of these congeners by multi-dimensional GC using a smectic phase as second column has been described [15], but this requires the use of more expensive equipment. A much simpler approach would be to use a 25-m DB-17 column, which

TABLE IV

RESULTS FOR PCB CONGENERS IN LOW-LEVEL WASTE MINERAL OIL ($n = 5$)

PCB	Concentration (mg kg^{-1})						
	Laboratory 1		Laboratory 2		Interlaboratory		
	Mean	S.D.	Mean	S.D.	No. of results	Mean	S.D.
28	0.615	0.075	N.D.[a]	N.D.	19	0.601	0.175
52	1.441	0.096	1.308	0.209	18	1.202	0.204
101	2.054	0.186	1.722	0.134	19	1.739	0.363
118	1.578	0.215	1.644	0.083	18	1.908	0.423
138 + 163	1.140	0.127	1.668	0.061	19	1.406	0.208
153	0.623	0.062	0.738	0.072	19	0.887	0.144
180	0.094	0.010	0.086	0.006	19	0.179	0.046

[a] ND = Not determined.

separate the PCBs congeners 153, 105 and 132 (see Fig. 3).

Validation of results

In order to validate the performance of the analytical methods used, we have participated in three interlaboratory round-robin exercises organized by the BCR. Tables IV, V and VI show the results obtained for low- and high-level waste mineral oils and milk powder, respectively. Our results are compared with the mean values obtained in several European laboratories. From the results for the low-level mineral oil, several comments can be made. First, PCBs 138 and 163 were quantified together because most of the laboratories involved in the round-robin test

TABLE V

RESULTS FOR PCB CONGENERS IN HIGH-LEVEL WASTE MINERAL OIL ($n = 5$)

PCB	Concentration (mg kg^{-1})						
	Laboratory 1		Laboratory 2		Interlaboratory		
	Mean	S.D.	Mean	S.D.	No. of results	Mean	S.D.
28	1.760[a]	0.055	0.758	0.026	13	0.769	0.116
52	32.640	2.535	29.076	1.593	21	31.523	3.936
101	66.720	3.255	56.526	2.612	22	60.662	7.358
105	16.160	0.241	17.254	0.745	18	18.581	2.699
118	42.660	0.483	39.918	3.877	21	47.756	6.630
128	16.420	0.973	12.178	0.666	19	11.998	2.288
138	58.240	0.695	42.526	5.049	22	53.226	7.938
149	22.280	1.217	30.986	0.934	14	34.308	3.090
153	38.260	2.390	32.738	4.451	21	39.547	4.911
156	4.540	0.385	9.137	0.320	16	7.033	0.825
163	12.30	0.500	10.508	0.303	11	11.505	4.706
180	10.020	0.882	11.256	0.419	20	10.525	0.831
170	7.320	0.606	11.326	0.466	19	6.970	1.462

[a] Sum of congeners 28 and 31.

TABLE VI

RESULTS FOR PCB CONGENERS IN DRIED MILK POWDER ($n = 5$)

PCB	Concentration ($\mu g\ kg^{-1}$)				
	Laboratory 2		Interlaboratory		
	Mean	S.D.	No. of results	Mean	S.D.
28	0.208	0.015	12	0.442	0.204
52	0.722	0.074	15	1.089	0.349
101	0.431	0.049	11	0.599	0.300
105	0.289	0.017	15	0.428	0.193
118	2.70	0.23	15	3.29	0.58
128	1.68	0.25	15	1.42	0.23
138	14.00	1.55	15	15.25	1.89
149	0.401	0.057	13	0.468	0.169
153	17.01	1.53	15	18.95	1.75
156	1.19	0.15	17	1.67	0.57
163	1.90	0.09	8	2.36	1.29
180	9.00	0.88	17	11.09	2.34
170	4.20	0.40	17	5.76	1.76

were unable to separate this mixture because they used DB-5 columns. The second point is that most of our results agreed with the mean values obtained in the different laboratories, with the exception of PCBs 153 and 180. In both of our laboratories these values were much lower than the mean values. We attribute this difference to the use of relatively "older" standard solutions, so a slight evaporation of this solution might have taken place, thus concentrating to some extent the more volatile PCBs. This would lead to lower values for PCBs 153 and 180 in comparison with other PCBs when using the external standard method. Another effect to consider was the recoveries of these congeners achieved using these standard solutions, which will affect the attainment of correct final values.

The problem of the determination of these two congeners was overcome when analysing the high-level waste mineral oil (see Table V). Here fresh solutions were prepared for the external standard determination (laboratory 1) and at the same time an internal standard (laboratory 2) was used for determination. A problem was noticed in the separation of PCBs 28 and 31 in laboratory 1, and this was attributed to the ageing of the GC column used. In Table V the problems encountered with the complete separation of PCBs 138 and 163 can still be noticed, as only eleven laboratories were able to give an acceptable mean value for such congeners. For analysis of milk powder only laboratory 2 was involved, as laboratory 1 only participated with the environmental samples. The first point to consider is the problem of determining PCB 163 in the different laboratories, for the same reasons as mentioned above. The second point to consider in the analysis of milk powder is the higher standard deviation obtained for the mean interlaboratory values compared with waste mineral oil. This could be attributed to the difficulties in performing the determination of PCB congeners in milk powder, which was also observed in the method of calculating recoveries. The extraction of fat from milk was a critical step in the analytical procedure because the PCB congeners are absorbed in the globules of fat and their reproducible extraction was time consuming and laborious.

CONCLUSIONS

The use of GC columns of different polarity was tested for the complete separation of thirteen PCB congeners found in waste mineral oils of low and high concentration levels and in milk

powder. The separation of congeners 118–149, 138–163 and 105–153 was achieved using a DB-17 capillary column much more effectively than using the conventional DB-5-type columns.

The performance of the different analytical methodologies was validated by participation in three interlaboratory exercises, showing that the different extraction and clean-up methods and also the chromatographic separation were adequate for such analyses. The proposed methodology can be easily implemented in routine determinations of PCBs in the two matrices described.

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