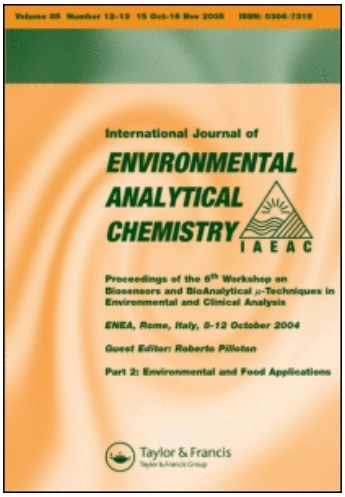

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

An International Study on Feasibility of Estimating Polychlorinated Biphenyls by Using Specific Polychlorinated Biphenyl Congeners

J. Mes[a]; H. B. S. Conacher[a]; S. Malcolm[a]
[a] Food Research Division, Bureau of Chemical Safety and Biostatistics and Computer Application Division, Food Directorate, Health Protection, Branch, Health and Welfare Canada, Ottawa, Canada

To cite this Article Mes, J. , Conacher, H. B. S. and Malcolm, S.(1993) 'An International Study on Feasibility of Estimating Polychlorinated Biphenyls by Using Specific Polychlorinated Biphenyl Congeners', International Journal of Environmental Analytical Chemistry, 50: 4, 285 — 297
To link to this Article: DOI: 10.1080/03067319308027604
URL: http://dx.doi.org/10.1080/03067319308027604

Intern. J. Environ. Anal. Chem., Vol. 50, pp. 285-297
Reprints available directly from the publisher
Photocopying permitted by license only

AN INTERNATIONAL STUDY ON FEASIBILITY OF ESTIMATING POLYCHLORINATED BIPHENYLS BY USING SPECIFIC POLYCHLORINATED BIPHENYL CONGENERS

J. MES, H. B. S. CONACHER and S. MALCOLM

Food Research Division, Bureau of Chemical Safety and Biostatistics and Computer Application Division, Food Directorate, Health Protection, Branch, Health and Welfare Canada, Tunney's Pasture, Ottawa, Canada, K1A OL2

(Received, 24 November 1992)

The feasibility of using specific PCB congeners was studied in two parts: a questionnaire to obtain information on the methodology used in various countries for quantification of PCBs and an international check sample program to evaluate the accuracy of the specific PCB congener approach. Information from the questionnaires indicated the use of a wide variety of PCB quantification procedures and considerable interest in using specific PCB congeners. In the check sample program, participants were requested to analyze two mixtures of Aroclor 1242 and 1254 in different proportions, and a human milk extract. The results indicated that when individual congeners were present at less than approximately 5 pg/μl per injection, the coefficients of variation for reproducibility were unsatisfactory for many congeners, some of which could not be detected by the participants. Interlaboratory coefficients of variation were generally acceptable (<20%) for many congeners at concentrations >5 pg/μl with the exception of congener No. 28, which is known to co-elute with PCB congener No. 31 and thus affect its estimation.

KEY WORDS: PCB, congener, quantitation, check sample.

INTRODUCTION

Until comparatively recently attempts to quantitate polychlorinated biphenyls (PCBs) involved their separation by gas chromatography (GC) on packed columns, using commercial PCB mixtures, such as the Aroclor series, as standards[1-3]. However, the GC elution pattern of PCBs observed in biological samples, such as for example breast milk, blood and adipose tissue, seldom exactly resembled that of any particular Aroclor, probably due to the various metabolic changes taking place during transition from one animal species to another in the ecological food chain. This led to concerns as to the accuracy of PCB quantification and although many attempts were made to improve on the accuracy, none was considered fully satisfactory[4-6].

In the last decade or so, this situation changed considerably with the firm establishment

of capillary column GC and the commercial availability of many individual PCB congeners of high purity. Mullin *et al.*[7] not only synthesized all 209 possible congeners, but successfully separated 187 of them on a 50 m SE-54 capillary column. More recently Guenther *et al.*[8] used a multidimensional capillary column technique to further improve the separation of those congeners which here to fore were not readily resolved. All this work paved the way for reassessment of PCB quantitation based on specific PCB congener analysis. Somewhat earlier Tuinstra *et al.*[9] published a method for the identification and quantification of several PCB congeners in milkfat and subsequently successfully conducted an interlaboratory study on six major congeners to demonstrate its application[10].

In 1985 the International Union of Pure and Applied Chemistry (IUPAC) through its Food Chemistry Commission Working Group on Halogenated Hydrocarbon Environmental Contaminants initiated a project to further examine the feasibility of estimating PCBs by measuring individual congeners. The project (No. 33/85) was conducted in two parts: compilation and distribution of a questionnaire to obtain information on the methodology used for PCB quantitation by the international scientific community and an international check sample program to evaluate the accuracy of the specific PCB congener approach. The experimental outline of this project and the results obtained are described in this paper.

EXPERIMENTAL

The questionnaire

A questionnaire on PCB quantitation was developed and disseminated by members of the Working Group to scientists in their respective countries. The questions were phrased such that answers would give an insight into approaches used for PCB quantification within the various participating laboratories and at the same time give an indication as to the preferences regarding PCB estimation using specific congeners.

The check sample program

Each participant received 4 glass ampules, 1 containing a known (qualitative and quantitative) mixture of 12 PCB congeners and the other ampules containing a mixture of Aroclors 1242/1254 (30:70), Aroclors 1242/1254 (80:20), and a cleaned-up human milk extract, respectively. All samples were provided dissolved in 2 ml isooctane (2,2,4-trimethylpentane), except for the human milk extract, which was dissolved in 1 ml isoctane.

Individual PCB congeners were 90–99% pure and were obtained from a variety of sources (gifts from Dr. Safe, Texas A&M University; Wellington Consultants, Guelph, Canada; and Ultra Scientific Co., Northwest Kingston, Rhode Island, USA). The OCS was 99% pure and a gift from Dr. Newsome (Health Protection Branch, Ottawa), while the Aroclors 1242 and 1254 were of a technical grade and gifts from the US Environmental Protection Agency (Cincinnati, Ohio).

Table 1 Concentrations of PCB congeners in standard mixture.

PCB congener No.[a]	*Chlorine substitution pattern*	*Concentration (ng/μl)*
18	2,5,2′	2.192
28	2,4,4′	1.944
52	2,5,2′,5′	2.230
74	2,4,5,4′	1.546
101	2,4,5,2′,5′	1.302
138	2,3,4,2′,4′,5′	0.934
153	2,4,5,2′,4′,5′	0.688
156	2,3,4,5,3′,4′	0.785
180	2,3,4,5,2′,4′,5′	0.640
189	2,3,4,5,3′,4′,5′	0.448
194	2,3,4,5,2′,3′,4′,5′	0.858
206	2,3,4,5,6,2′,3′,4′,5′	0.598

[a] Numbering system according to Ballschmiter and Zell[12]

The identity and concentration of each congener in the standard mixture (sample No. 1) are given in Table 1. Concentrations in the Aroclor mixtures were 0.846 and 1.955 ng/μl of Aroclor 1242 and 1254 (sample No. 2) and 3.805 and 0.977 ng/μl (sample No. 3) respectively. The human milk extract (sample No. 4) was obtained by pooling 60 PCB fractions of breast milk extracts. These fractions were prepared as described previously[11].

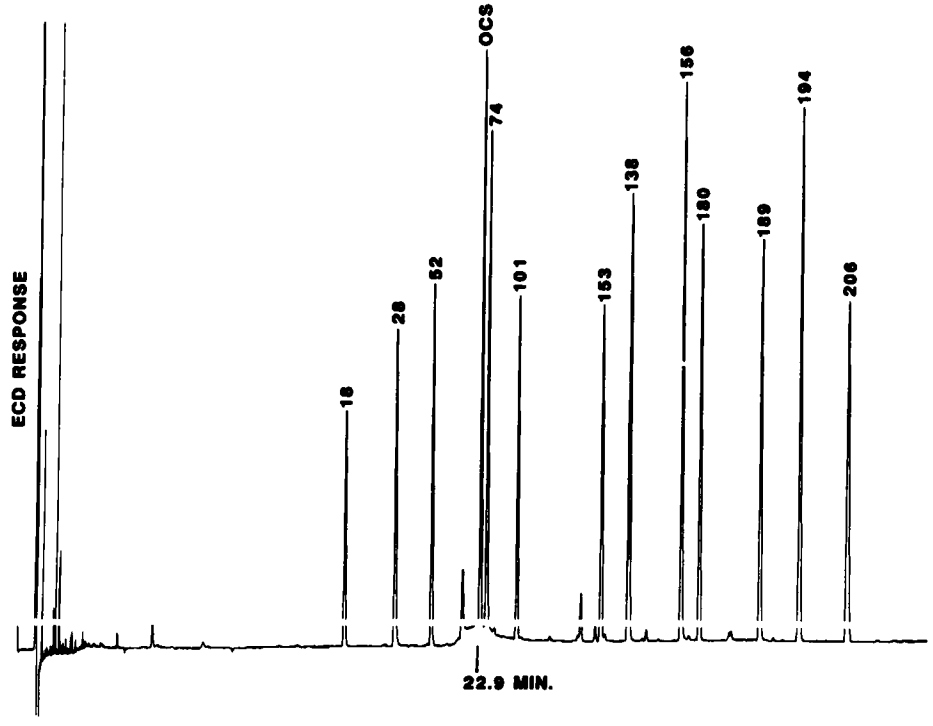

Figure 1 GC elution pattern of standard PCB congener mixture (sample No. 1).

Table 2 Chromatographic conditions used in the originating laboratory for the analysis of 12 PCB congeners in check samples.

GC components	*Type*	*Parameters*
Oven and accessories	Varian 3500 Series	
Injector	On-column	Programmed from 90° (0.5 min) to 240° C at 160° C/min. One microliter injected.
Column	30 m × 0.24 mm (i.d.) fused silica capillary, coated with 0.25 μm of DB-5 (J&W Scientific Inc., Folsom, CA, USA)	Initial temperature of 90 (1 min) increased to 130 at 30°/min and held for 7 min, then further programmed to 190° and 230° C at 4 and 3°/min respectively and held at 230° for the duration of the GC run.
Detector.	Election capture (ECD)	300°C
Carrier gas flow system	Helium	Linear velocity of 20cm/sec
Make-up gas flow system	Nitrogen	30 ml/min

In addition to these 4 samples, each participant received instructions for dilution, a short questionnaire on their GC conditions, and a chromatogram of the standard PCB congener mixture (Figure 1) together with the details of the chromatographic conditions used in the originating laboratory. These conditions along with typical chromatograms obtained from the other samples are given in Table 2 and Figures 2–4, respectively.

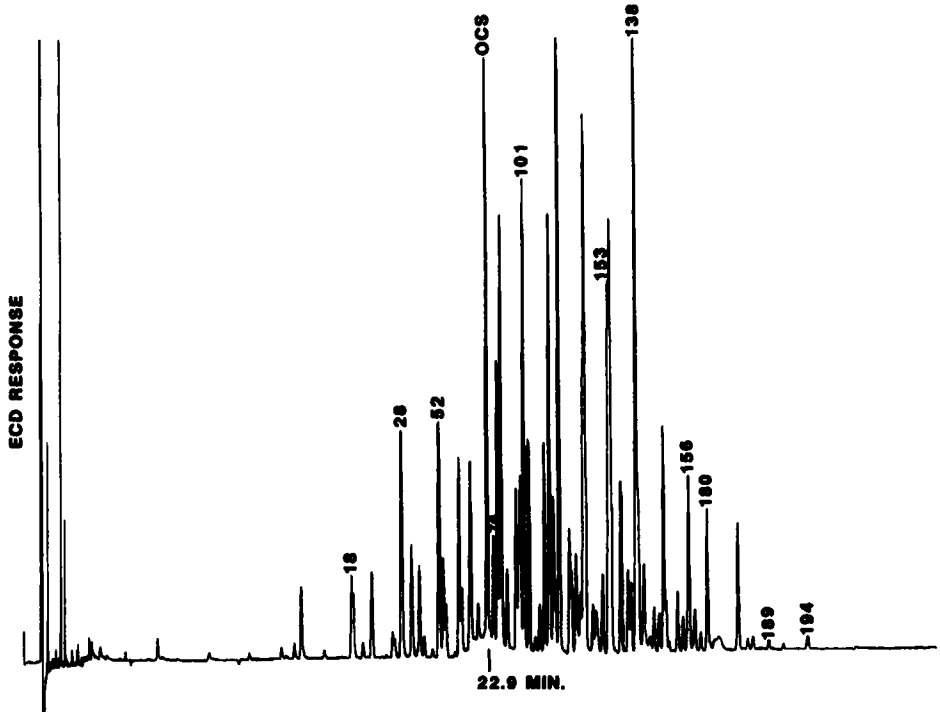

Figure 2 GC elution pattern of a mixture of Aroclor 1242 and 1254 (30:70) (sample No. 2).

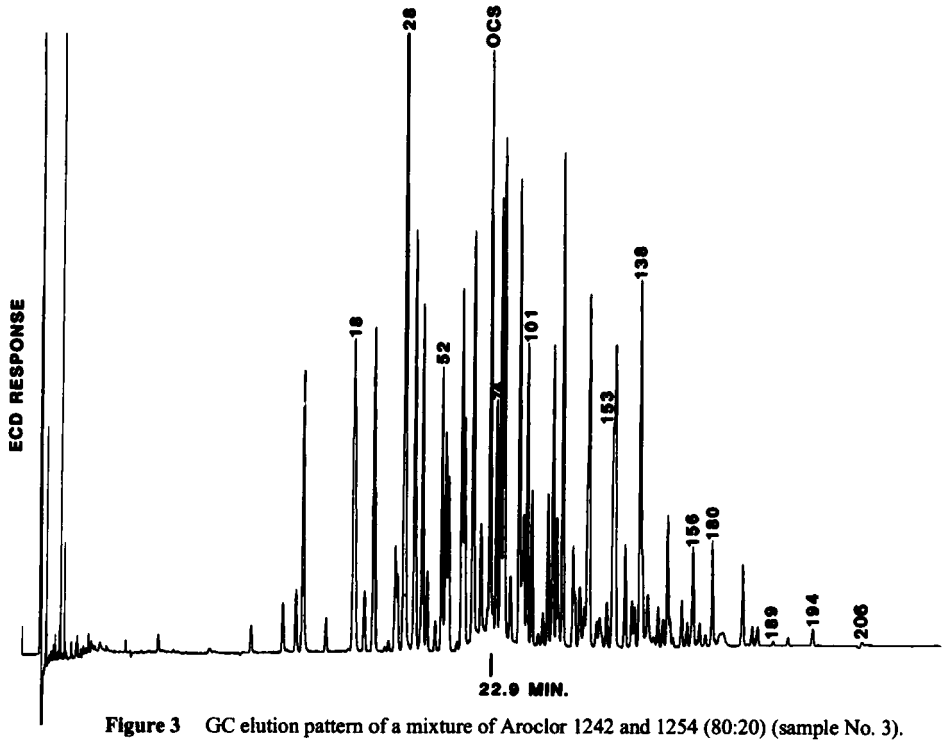

Figure 3 GC elution pattern of a mixture of Aroclor 1242 and 1254 (80:20) (sample No. 3).

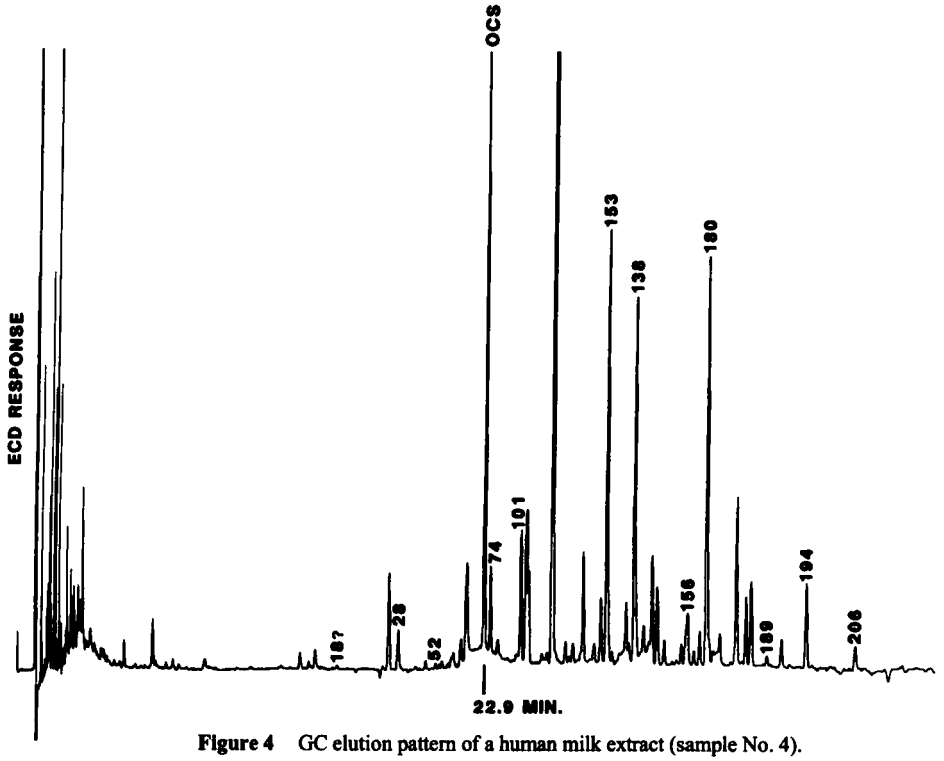

Figure 4 GC elution pattern of a human milk extract (sample No. 4).

The presence of the selected 12 PCB congeners in the Aroclor mixtures and human milk extract was quantitatively confirmed by GC-mass spectrometry (MS), using a Varian 6000 series GC with a DB-5 capillary column as in table 2 and a VG Analytical Model 7070 EQ hybrid MS. The ion source temperature was 250° C, the electron energy 70 eV, the resolution 1000, and the dwell time 50 msec. The tri-to nonachlorobiphenyl congeners were monitored with least interference, using the following ions (m/z): 258, 292, 328, 360, 396, 428 and 462.

Statistical procedure

Statistical analyses were conducted separately for each sample and congener. Duplicate results for each sample and congener were reported by all but one of the laboratories; all data from that laboratory were deleted. Duplicate values were deleted prior to statistical analyses if either of the duplicates were reported as '<' a given value or as 'not detected'. The remaining data were tested for homogeneity of between duplicate variances using Cochran's test[13] and for outlying mean laboratory values, using Grubbs' test[14]. These tests were not carried out with data from five or fewer laboratories, and deletions were not executed where there would be more than one in five rejections. Summary statistics, including means, and repeatability and reproducibility relative standard deviations, were calculated with or without data identified using these screening tests.

RESULTS AND DISCUSSION

The questionnaire

Thirty-three scientists from Europe, North America and Asia responded to the questionnaire. Of these 60% were affiliated with the government and 40% with university, industry and private laboratories. The majority of participants were engaged in research with, and/or the monitoring of, PCBs; 50% of them had more than 10 years experience in PCB analysis.

A summary of the responses to the questionnaire is given in Table 3. It is interesting to note that, although ~ 60% of respondents still used packed column GC for their analysis, 75% of this particular group also used capillary column GC. Thus, 85% of participants used capillary column GC to some extent. The most widely used capillary columns were 25 or 30 m long with inner diameters ranging from 0.20–0.32 mm and most common film thickness of 0.25 μm. Practically all capillary column GC (96%) was carried out using temperature programming with helium and hydrogen as the preferred carrier gases.

To quantitate PCBs, 66% of the respondents used commercial Aroclor(s) as standard. The choice of Aroclor was based predominantly on visual inspection of all or part of the chromatographic elution pattern and comparison of retention times of peaks in standard and sample. The number of peaks selected for quantitation varied greatly, but the majority (73%) of the participants used the sum of peak heights (areas) for PCB quantitation.

With regard to the use of individual PCB congeners for quantitation, only 17% of all laboratories were using this approach. However, most were interested in assessing it.

Table 3 Summary of PCB quantitation methodology used by respondents to the questionnaire.

Characteristics of PCB quantitation methodology	*Qualitative and quantitative resume of respondent's answers to questionnaire*
Always used same method:	35% of respondents.
Changed methods over the years:	65% of respondents.
Used method from the literature:	62% of respondents.
Criteria for choice of method:	Based mainly on greatest resolution and minimal interference.
Types of samples used in order of frequency:	Tissues > water > soil > sediment > body fluids > food/beverages > air.
Used packed GC columns:	60% of respondents.
Used packed and capillary GC columns:	75% of respondents using packed GC columns.
Solid support used for packed columns:	50% of respondents used Chromosorb W, while other frequently used Supelcoport HP or Gas Chrom. Q.
Mixed stationary phase used:	50% of respondents used one of the following phases: SE-30 + OV-210, QF-1 + SF-96, SP-2401 + SP2250.
Single stationary phase used:	While most respondents used OV-101, some used SE-30, OV-210 or SP-2100.
Capillary column dimensions:	25–30 m × 0.20–0.32 mm preferred by most respondents.
Stationary phase and film thickness for capillary columns:	52% of respondents used DB-5 and most used μm (range 0.10–0.44) coating.
Carrier gas for capillary GC:	56% of respondents used helium; 30% used hydrogen; some used nitrogen.
Programmed capillary column temperature:	96% of respondents.
Injection mode used in order of frequency:	Splitless > on-column > split
GC standard used:	66% of respondents used one or more Aroclors.
Use of specific PCB congeners:	17% of respondents.
Criteria for standard selection:	Visual inspection of GC pattern and comparison of retention times in standard and sample.
Number of peaks used in standard Aroclor:	47% of respondents used 1–10 peaks, others up to 20 or more.
Method of calculation:	73% of respondents summed peak heights.
Confirmation:	GC-MS or two different GC columns.
Number of congeners preferred for PCB quantitation:	55% of respondents preferred a selected number of congeners, while 45% wanted to use all identifiable congeners.
Basis for congener selection:	Frequency of occurrence, toxicity and magnitude.
Use of "surrogate" Aroclor[a]:	77% of respondents in favour.

[a] A "Surrogate" Aroclor is an Aroclor of known PCB congener composition.

Fifty-five percent of respondents preferred to use selected PCB congeners for quantitation, while the remainder would use all identified congeners in a sample, if given the choice. Those respondents preferring certain congeners only, would base their selection more on frequency of occurrence and toxicity rather than on the magnitude of congener levels in the sample. Nevertheless most participants (77%) favoured the use of a "surrogate" Aroclor of known PCB congener composition as standard for quantitation of PCBs, regardless of the fact that they had access to some of the most frequently encountered PCB congeners, such as Nos. 28, 52, 101, 138, 153, 180, 194 and 206. The results of the questionnaire indicated a definite trend towards the use of specific PCB congeners in the quantitation of PCBs in the environment and the food supply.

The check sample program

Eighteen laboratories participated in the check sample program. Duplicate analyses of the check samples were carried out by all laboratories, except No. 7. Therefore the results of laboratory No. 7 were not included in the statistical evaluation of the data. In addition, all laboratories reported details of their GC conditions. The most predominant stationary phase used was 5% phenyl, 95% methyl silicone, while the remainder of the participating laboratories used methyl silicone rubbers of varying percentages of phenyl substitution. Stationary film thickness, injection models and carrier gases used were essentially as given in Table 3. Laboratory No. 12 submitted two sets of data obtained on capillary columns with different stationary phases, namely DB-5 and DB-17. Only data from the DB-5 column were considered, as this represented the most common phase in the study. Most laboratories used 25–50 m capillary columns for the PCB congener analysis, except laboratories 9, 10 and 18, which used 15–18 m long columns. Preliminary statistical analysis indicated that laboratories 4, 9, 10 and 18 generally had more outliers than other laboratories. In addition, laboratories 9 and 10 were the only two participating laboratories, which failed to report levels for congeners 156 and 180 in samples 2 and 3. Since the use of shorter GC columns by laboratories 9, 10 and 18 may have contributed to the large number of outliers, they were not included in the final statistical analysis. All outliers for laboratory No. 4 were due to large differences between duplicate results.

Data from the remaining laboratories are shown in Tables 4–6. Summary statistics are shown in the same tables and were calculated using all data (indicated by A) and after deletion of outliers (indicated by B). Where one or both values of a duplicate determination was reported as '<' a given value or as 'not detected', both values were deleted prior to any calculations.

The overall performance is best evaluated by examining means and both the repeatability [RSD(r)] and reproducibility [RSD(R)] coefficients of variation. Generally the effect of outliers on the computation of the means was minimal in all check samples.

In the case of the two Aroclor mixtures in Tables 4 and 5, approximately one third of the participants failed to estimate the levels of congeners 189 and 194. In addition the data that were reported for these two congeners displayed considerably higher coefficients of variation of repeatability and reproducibility than for other congeners. Furthermore, almost half the participants failed to report the presence of congener 206. In sample No. 3 (Table 5), this congener had the highest coefficient of variation of repeatability and reproducibility of

Table 4 Interlaboratory comparison of the content of selected PCB congeners in a mixture of 30% Aroclor 1242 (Sample No. 2).

Number		*pg/µl*											
Lab[a]	*Rep*[b]	*PCB congener number*											
		18	*28*	*52*	*74*	*101*	*138*	*153*	*156*	*180*	*189*	*194*	*206*
1	1	67.4	109.0	140.0	28.6	174.0	121.0	69.5	21.1	18.4	ND[k]	ND	ND
	2	68.8	110.0	142.0	29.4	175.0	121.0	70.4	22.2	19.0	ND	ND	ND
2	1	107.0	130.0	144.0	27.0	198.0	198.0[g]	68.0	21.0	18.0	<1.0	<1.0	<1.1
	2	110.0	128.0	160.0	30.0	213.0	213.0[g]	69.0	24.0	19.0	<1.0	<1.0	<1.1
3	1	60.0	116.0	186.0[g]	23.0	165.0	128.0	66.0	15.0	12.0	<1.0	2.0	1.0
	2	73.0	127.0	184.0[g]	25.0	155.0	123.0	67.0	17.0	12.0	<1.0	1.0	<1.1
4	1	69.0[c]	180.0[c]	140.0	32.0	220.0[c]	170.0[c]	60.0	26.0	18.0	4.0	8.0	4.0
	2	110.0[c]	150.0[c]	140.0	29.0	160.0[c]	110.0[c]	66.0	25.0	19.0	5.0	7.0	5.0
5	1	79.0	107.0	148.5	29.0	183.5	140.0	71.0	25.0	21.0	1.0	2.0	1.5
	2	82.5	103.0	143.0	29.0	177.5	131.0	69.5	22.5	19.0	1.0	1.5	1.5
6	1	77.0	162.0	147.0	48.0[g]	197.0	145.0	86.0	32.0	25.0	3.0	6.3	0.7
	2	76.0	170.0	145.0	48.0[g]	197.0	143.0	87.0	33.0	26.0	3.1	7.5	1.0
8	1	52.4	45.5	149.7	28.1	245.1	143.8	73.1	24.4	18.4	NR[l]	NR	NR
	2	53.4	40.2	150.3	28.2	246.9	145.0	74.0	24.6	18.8	NR	NR	NR
11	1	71.0	123.0	141.0	30.0	180.0	136.0	82.0	22.0	20.0	<5.0	<5.0	<5.0
	2	81.0	123.0	151.0	34.0	183.0	137.0	86.0	24.0	22.0	<5.0	<5.0	<5.0
12	1	100.9	157.3	116.8[g]	22.7	190.4	138.8	85.2	19.4	16.8	1.5	1.7	ND
	2	101.7	155.0	105.6[g]	21.5	194.5	153.2	94.9	17.8	15.5	1.7	1.2	ND
13	1	78.5	142.5	293.5[g]	33.0	176.5	136.0	77.0	25.5	21.5	1.0	2.0	NR
	2	78.0	143.0	296.0[g]	33.0	179.0	137.5	77.0	25.0	22.0	1.0	2.0	NR
14	1	68.0	104.0	152.0	88.0[g]	222.0	98.0[g]	92.0	18.0	22.0	28.0[c]	ND	ND
	2	70.0	111.0	147.0	90.0[g]	223.0	104.0[g]	96.0	21.0	18.0	10.0[c]	ND	ND
15	1	68.0	98.0	127.0	29.0	177.0	148.0	67.0	21.0	18.0	<1.0	1.4	<1.0
	2	66.0	98.0	124.0	28.0	176.0	147.0	68.0	21.0	18.0	<1.0	1.3	<1.0
16	1	70.0	111.0	142.0	34.0	223.0	143.0	66.0	30.0	20.0	<2.0	<2.0	<2.0
	2	71.0	111.0	142.0	33.0	223.0	142.0	65.0	28.0	20.0	<2.0	<2.0	<2.0
17	1	119.0	173.0	154.0	31.0	169.0	157.0	86.0	27.8	20.0	<4.0	6.2	4.5
	2	121.0	173.0	153.0	30.8	169.0	155.0	83.4	25.7	19.3	<4.0	5.1	<4.0
No. of labs (A)		14	14	14	14	14	14	14	14	14	6	8	3
Mean[d] based on A[e]		80.3	125.0	155.9	34.7	192.6	141.6	75.8	23.5	19.2	5.0	3.5	2.3
No. of labs (B)		13	13	11	12	13	11	14	14	14	5	8	3
Mean based on B[f]		79.6	121.9	144.7	29.1	192.8	139.6	75.8	23.5	19.2	2.2	3.5	2.3
RSD(r[h]) based on A		10.5	5.2	2.9	3.7	6.2	8.6	3.3	5.5	5.4	103.6	16.2	18.7
RSD(r) based on B		4.3	2.7	3.1	4.5	2.0	2.8	3.3	5.5	5.4	14.5	16.2	18.7
RSD(R[i]) based on A		24.1	27.9	27.7	48.2	13.3	17.2	13.6	18.6	16.0	157.0	77.2	86.3
RSD[j](R) based on B		24.1	27.9	5.8	12.0	13.1	7.4	13.6	18.6	16.0	69.0	77.2	86.3

[a] Participating laboratories. [b] Replicates. [c] Outliers according to Cochran[14]. [d] Arithmetic mean. [e] A = mean of all data. [f] B = mean of data after deletions of outliers. [g] Outliers according to Grubbs[15]. [h] Repeatability. [i] Reproducibility. [j] Relative standard deviation. [k] ND = not detected. [l] NR = not reported.

Table 5 Interlaboratory comparison of the content of selected PCB congeners in a mixture of 80% Aroclor 1242 and 20% Aroclor 1254 (Sample No. 3).

Number		*pg/μl*											
Lab[a]	*Rep*[b]	*PCB congener number*											
		18	*28*	*52*	*74*	*101*	*138*	*153*	*156*	*180*	*189*	*194*	*206*
1	1	282.0	397.0	176.0	68.0	114.0	70.0	31.6	9.6	12.7	ND[k]	ND	ND
	2	279.0	396.0	176.0	70.0	115.0	70.0	37.1	9.5	13.0	ND	ND	ND
2	1	460.0[g]	528.0	184.0	66.0	120.0	68.0[c]	38.0	11.0	12.0	<1.0	<1.0	<1.1
	2	461.0[g]	526.0	199.0	70.0	138.0	51.0[c]	40.0	10.0	13.0	<1.0	<1.0	<1.1
3	1	262.0	288.0	200.0	83.0	120.0	84.0	42.0	9.0	10.0	<1.0	2.0	<1.0
	2	263.0	292.0	201.0	81.0	118.0	87.0	42.0	8.0	9.0	<1.0	2.0	<1.0
4	1	280.0[c]	660.0	180.0	76.0[c]	160.0[c]	100.0[c]	37.0	26.0[c]	21.0[c]	10.0	19.0[c]	13.0
	2	380.0[c]	520.0	180.0	54.0[c]	94.0[c]	57.0[c]	34.0	13.0[c]	11.0[c]	4.0	4.0[c]	3.0
5	1	291.5	441.0	180.5	76.0	119.5	76.5	42.5	13.0	14.5	1.5	2.5	0.5
	2	287.5	437.0	178.0	73.5	117.5	76.5	42.5	13.0	15.5	0.5	1.5	0.5
6	1	300.0	666.0	175.0	85.0	120.0	88.0	49.0	21.0	17.0	2.8	6.3	0.7
	2	293.0	666.0	175.0	88.0	123.0	83.0	49.0	24.0	18.0	2.9	6.6	0.9
8	1	211.7	189.6	176.1	67.3	156.7	75.5	41.3	13.0	13.3	NR[l]	NR	NR
	2	213.7	185.3	176.9	67.1	156.3	74.7	41.2	13.0	13.6	NR	NR	NR
11	1	285.0	520.0	172.0	70.0	112.0	72.0	45.0	12.0	14.0	<5.0	<5.0	<5.0
	2	297.0	478.0	183.0	75.0	118.0	77.0	49.0	12.0	16.0	<5.0	<5.0	<5.0
12	1	409.1[g]	780.1	143.2	54.1	124.9	65.9	46.6	9.8	12.3	1.1	1.5	ND
	2	427.3[g]	893.7	129.9	49.5	113.8	64.3	48.2	9.0	11.6	ND	1.3	ND
13	1	298.0	552.5	357.0[g]	73.5	114.0	77.0	46.0	14.5	16.5	0.5	2.5	1.0
	2	285.5	536.0	346.5[g]	71.0	112.5	77.0	46.0	14.0	15.5	0.5	2.5	1.0
14	1	262.0	447.0	270.0[c]	148.0[g]	159.0	60.0	55.0	12.0	19.0	27.0	ND	ND
	2	255.0	421.0	175.0[c]	141.0[g]	159.0	58.0	56.0	12.0	15.0	11.0	ND	ND
15	1	321.0	466.0	179.0	66.0	120.0	81.0	37.0	10.0	13.0	<1.0	1.8	<1.0
	2	320.0	456.0	174.0	64.0	116.0	79.0	35.0	10.0	13.0	<1.0	1.8	<1.0
16	1	246.0	368.0	165.0	72.0	150.0	82.0	38.0	17.0	15.0	<2.0	<2.0	<2.0
	2	245.0	367.0	165.0	71.0	149.0	81.0	38.0	16.0	14.0	<2.0	<2.0	<2.0
17	1	285.0	640.0	166.0	71.8	108.0	89.5	50.6	20.4	18.0	4.2	7.8	5.7
	2	298.0	663.0	169.0	70.2	106.0	86.7	47.3	16.6	15.2	<4.0	5.5	<4.0
No. of labs (A)		14	14	14	14	14	14	14	14	14	5	8	4
Mean[d] based on A[e]		303.5	492.2	191.1	75.8	126.2	75.4	43.0	13.5	14.3	6.1	4.3	2.6
No. of labs (B)		11	14	12	12	13	12	14	13	13	5	7	4
Mean based on B[f]		276.4	492.2	175.2	71.0	126.2	76.5	43.0	13.1	14.2	6.1	3.3	2.6
RSD(r[h]) based on A		6.5	7.3	9.7	6.3	10.5	11.8	3.9	19.6	15.3	89.2	88.7	137.3
RSD(r) based on B		1.9	7.3	2.8	2.9	3.6	2.4	3.9	7.9	8.1	89.2	20.8	137.3
RSD(R[i]) based on A		22.0	33.9	27.0	28.5	15.1	14.8	14.6	34.4	19.1	141.2	104.7	170.9
RSD[j](R) based on B		10.8	33.9	9.0	12.3	13.9	11.4	14.6	31.5	17.1	141.2	71.3	170.9

[a] Participating laboratories. [b] Replicates. [c] Outliers according to Cochran[14]. [d] Arithmetic mean. [e] A = mean of all data. [f] B = mean of data after deletions of outliers. [g] Outliers according to Grubbs[15]. [h] Repeatability. [i] Reproducibility. [j] Relative standard deviation. [k] ND = not detected. [l] NR = not reported.

Table 6 Interlaboratory comparison of the content of selected PCB congeners in human milk (Sample No. 4).

Number		*pg/μl*											
Lab[a]	*Rep*[b]	*PCB congener number*											
		18	*28*	*52*	*74*	*101*	*138*	*153*	*156*	*180*	*189*	*194*	*206*
1	1	ND[i]	3.3	ND	5.1	4.1	15.5	19.8	1.0	12.8	ND[k]	2.2	0.6
	2	ND	3.1	ND	4.7	3.6	15.4	19.1	0.9	13.0	0.2	2.2	0.6
2	1	<5.0	<3.2	<4.2	4.0	<2.5	15.0	19.0	<1.0	13.0	<1.0	<1.0	<1.1
	2	<5.0	<3.2	<4.2	4.0	<2.5	14.0	20.0	<1.0	13.0	<1.0	<1.0	<1.1
3	1	<1.0	3.2	<2.0	3.9	0.9	15.3	15.8	0.9	11.9	0.2	1.3	0.5
	2	<1.0	2.7	<2.0	3.6	0.9	15.2	16.0	0.8	12.1	0.2	1.2	0.5
4	1	N.D	4.0	2.0	5.0	2.0	16.0[c]	18.0	3.0	12.0	1.0	4.0	2.0[c]
	2	2.0	ND	1.0	4.0	4.0	13.0[c]	17.0	3.0	10.0	3.0	2.0	1.0[c]
5	1	1.6	4.1	1.6	5.4	1.6	14.5	17.9	2.3[c]	12.1	0.9	2.7	1.1
	2	1.6	2.5	0.5	4.5	0.8	14.9	18.4	1.7[c]	12.5	0.2	2.2	0.9
6	1	NR[j]	8.5	2.7	8.1[g]	1.6	15.0	19.0	3.8	13.0	0.6	2.6	0.9
	2	NR	8.5	2.7	7.8[g]	1.6	14.0	19.0	3.8	12.0	0.6	2.5	0.7
8	1	NR	2.6	6.3	4.3	NR	16.3	20.9	1.7	12.3	NR[l]	2.0	0.8
	2	NR	2.7	6.5	4.3	NR	16.0	20.4	1.7	11.9	NR	1.8	0.8
11	1	<5.0	<5.0	<5.0	4.5	<5.0	14.0	18.0	<5.0	12.0	<5.0	2.0	<5.0
	2	<5.0	<5.0	<5.0	5.0	<5.0	15.0	20.0	<5.0	14.0	<5.0	2.0	<5.0
12	1	ND	2.2	2.0	4.6	2.8	11.0[g]	23.8[g]	ND	13.1	ND	1.4	0.8
	2	ND	1.8	1.8	4.0	2.5	10.3[g]	24.9[g]	ND	12.8	ND	1.3	0.6
13	1	0.8	4.9	1.3	5.0	9.5[g]	14.8	17.2	1.4	12.7	0.2	2.8	0.9
	2	0.6	4.8	1.2	5.2	9.3[g]	14.5	17.1	1.5	12.3	0.3	2.7	0.8
14	1	ND	13.0	ND	10.0[g]	1.0	12.0[g]	26.0[g]	2.0	15.0	9.0	3.0	ND
	2	ND	12.0	ND	8.0[g]	1.0	12.0[g]	26.0[g]	2.0	15.0	3.0	2.0	1.0
15	1	<1.0	2.4	<1.0	3.7	<1.0	14.0	18.0	<1.0	12.0	<1.0	1.7	<1.0
	2	<1.0	2.4	<1.0	3.9	<1.0	14.0	18.0	<1.0	12.0	<1.0	1.8	<1.0
16	1	<2.0	5.0	<2.0	6.0	<2.0	16.0	17.0	3.0	14.0	<2.0	2.0	<2.0
	2	<2.0	5.0	<2.0	6.0	<2.0	16.0	18.0	3.0	15.0	<2.0	3.0	<2.0
17	1	<0.5	6.0	<0.5	4.9	1.0[c]	14.8	18.7	2.9[c]	12.1	0.7	2.7	1.4
	2	<0.5	5.5	<0.5	4.9	5.6[c]	15.3	19.6	1.4[c]	13.1	0.5	3.0	1.4
No. of labs (A)		2	11	6	14	9	14	14	10	14	7	13	9
Mean[d] based on A[e]		1.2	4.8	2.5	5.2	3.0	14.4	19.4	2.1	12.7	1.5	2.2	0.9
No. of labs (B)		2	11	6	12	7	11	12	8	14	7	13	8
Mean based on B[f]		1.2	4.8	2.5	4.6	2.0	15.0	18.4	2.1	12.7	1.5	2.2	0.8
RSD(r[h]) based on A		8.7	9.2	17.8	9.6	40.4	4.7	3.1	17.4	5.1	116.8	22.3	27.8
RSD(r) based on B		8.7	9.2	17.8	7.4	29.4	2.7	3.3	2.6	5.1	116.8	22.3	10.9
RSD(R[i]) based on A		55.7	66.1	82.2	30.6	92.7	10.7	14.3	46.8	8.7	165.6	29.4	43.0
RSD[j](R) based on B		55.7	66.1	82.2	14.7	59.9	4.9	7.4	51.1	8.7	165.6	29.4	34.7

[a] Participating laboratories. [b] Replicates. [c] Outliers according to Cochran[14]. [d] Arithmetic mean. [e] A = mean of all data. [f] B = mean of data after deletions of outliers. [g] Outliers according to Grubbs[15]. [h] Repeatability. [i] Reproducibility. [j] Relative standard deviation. [k] ND = not detected. [l] NR = not reported.

all congeners. These above observations can probably be attributed to the fact that these congeners (189, 194 and 206) were present at concentrations approaching the detection limit, as suggested by the reported values of < 1 to < 5 pg/μl. The other nine congeners (Nos. 18–180) could be measured with much better precision and most displayed reproducibilities of 1 20% or less after removal of outliers, with coefficients of variation for repeatability of ~ 10% or less. The relatively high coefficient of variation for the reproducibility of congener 28 is probably due to interference from congener 31. The performance of most other congeners within this group of nine, with relatively high coefficients of variation (24–48%) for reproducibility, such as congeners 18, 52 and 74, improved after removal of outliers. Participating laboratories also experienced some difficulty with congener 156 in sample 3 [RSD(R) = ~ 30%]. With the human milk extract (Table 6), the same three congeners (189, 194 and 206), together with additional congeners Nos. 18, 28, 52, 74, 101 and 156, were all present at levels approaching the limit of detection, as suggested by the reported values of < 1 to < 5 pg/μl. All nine congeners showed high coefficients of variation for reproducibility, with the exception of congener 74, and were either not detected, not reported or reported as '<' by many of the participating laboratories. Good precision was generally observed with the remaining three congeners (Nos. 138, 153 and 180), present at levels of $^{15\ pg/\mu l}$ or above. A comparison of the data obtained in the interlaboratory study with that by a GC-MS determination "in house", is given in Table 7. There appears agreement between the data sets, except for the congeners present at low concentrations (< 5 pg/μl). The relatively large discrepancies observed for congener No. 28 provide some confirmation of the co-eluting congener referred to earlier.

The results of the present study indicate that the individual congener approach for the quantitation of PCBs could constitute a practical alternative to the use of commercial PCB mixtures, provided the congener concentrations are > 5 pg/μl injection, at which concentration acceptable coefficients of variation for repeatability and reproducibility were obtained.

Table 7 A comparison between gas chromatographic and mass spectrometric determination of selected PCB congeners in mixtures of Aroclors and human milk.

PCB Congener No.	*pg/μl*					
	Aroclor mixtures				*Human milk*	
	1242:1254 (3:7, w/w)		*1242:1254 (8:2, w/w)*			
	GC-ECD	*GC-MS*	*GC-ECD*	*GC-MS*	*GC-ECD*	*GC-MS*
18	80.3	62.2	303.5	319.2	1.2	0.1
28	125.0	91.3	492.2	462.6	4.8	3.2
52	155.9	133.2	191.1	182.3	2.5	0.4
74	34.7	25.4	75.8	67.6	5.2	4.1
101	192.6	190.0	126.2	120.0	3.0	0.5
138	141.6	154.0	75.4	82.5	14.4	15.8
153	75.8	75.4	43.0	41.4	19.4	21.6
156	23.5	19.2	13.5	9.0	2.1	0.7
180	19.2	15.8	14.3	12.5	12.7	13.5
189	5.0	0.4	6.1	0.2	1.5	0.1
194	3.5	0.7	4.3	1.0	2.2	1.4
206	2.3	0.2	2.6	0.3	0.9	0.4

Buchholz *et al.*[15] not only found the specific congener approach applicable, but also superior to the PCB pattern recognition, for many of the same congeners as used in the present study. However the possibility of interferences from co-eluting congeners remains a problem for such congeners as 28, 52, 101, 138 and 153[16].

Acknowledgements

The authors wish to thank Mrs. L. Marchand for technical assistance, Dr. P. Y. Lau for the GC-MS analysis and the following laboratories for their participation in this study: Acurex Corporation, Mountain View, CA, USA; Canadian Wildlife Service, Ottawa, ON, Canada; Daiichi College of Pharmaceutical Sciences, Minami-ku, Fukuoka, Japan; Department of Fisheries and Oceans, Burlington, ON, Canada; Department of Health and Human Services, Atlanta, GA, USA; Dr. F. Messier, Laval, PQ, Canada; Michigan Department of Natural Resources, Lansing, MI, USA; Michigan Department of Public Health, Lansing, MI, USA; Ministry of Agriculture, Fisheries and Food, Norwich, United Kingdom; Ministry of Environment, S;toborg, Denmark; National Fisheries Contamination Research Center, Columbia, MO, USA; National Health and Welfare Canada, Ottawa, ON, Canada; National Institute for Public Health and Environmental Protection, Bilthoven, The Netherlands; Netherlands Organization for Applied Scientific Research, Zeist, The Netherlands; Ontario Ministry of Agriculture and Food, Guelph, ON, Canada; Patuxent Wildlife Research Centre, Laurel, MD, USA; Royal Veterinary and Agricultural University, Copenhagen, Denmark; State Institute for Quality Control of Agricultural Products, Wageningen, The Netherlands; Swedish National Food Administration, Uppsala, Sweden; Technical Research Centre of Finland, Espoo, Finland; The Norwegian College of Veterinary Medicine, Oslo, Norway; University of Wisconsin, Madison, WI, USA; US Department of the Interior, Ann Arbor, MI, USA; US Environmental Protection Agency, Grosse Ile, MI, Chicago, IL; and Cincinnati, OH, USA; US Food and Drug Administration, Detroit, MI, USA.

References

1. J. Mes, D. L. Arnold, F. Bryce, D. J. Davies and K. Karpinski, *Arch. Environ. Contam. Toxicol.*, **18**, 858–865 (1989).
2. M. Ando, H. Saito and I. Wakisaka, *Arch. Environ. Contam. Toxicol.*, **14**, 51–57 (1985).
3. C. V. Rao and S. A. Banerji, *Toxicol. Environ. Chem.*, **17**, 313–317 (1988).
4. L. D. Sawyer, *J. Assoc. Off. Anal. Chem.*, **61**, 272–281 (1978).
5. R. G. Webb and A. C. McCall, *J. Chromatogr. Sci.*, **11**, 366–373 (1973).
6. T. R. Schwartz, D. L. Stalling and C. L. Rice, *Environ. Sci. Technol.*, **21**, 72–76 (1987).
7. M. D. Mullin, C. M. Pochini, S. McCrindle, M. Romkes, S. H. Safe and L. M. Safe, *Environ. Sci. Technol.*, **18**, 468–476 (1984).
8. F. R. Guenther, S. N. Chesler and R. E. Rebbert, *J. High Resolut. Chromatogr.*, **12**, 821–824 (1989).
9. L. G. M. Th. Tuinstra, W. A. Traag and H. J. Keukens, *J. Assoc. Off. Anal. Chem.*, **63**, 952–958 (1980).
10. L. G. M. Th. Tuinstra, A. H. Roos and G. A. Werdnuller, *J. Assoc. Off. Anal. Chem.*, **68**, 756–759 (1985).
11. J. Mes, D. J. Davies, D. Turton and W.-F. Sun, *Food Addit. Contam.*, **3**, 313–322 (1986).
12. K. Ballschmiter and M. Zell, *Fresenius' Z. Anal. Chem.*, **320**, 20–31 (1980).
13. H. Solomon and M. A. Stephens, *J. Quality Technol.*, **22**, 46–56 (1990).
14. F. E. Grubbs, *Technometrics*, **11**, 1–21 (1969).
15. H. Buchholz, M. Carl, H. Beck and L. G. M. Th. Tuinstra, *Landwirtsch. Forsch.*, **39**, 104–108 (1986).
16. J. C. Duinker, D. E. Schultz and G. Petrick, *Mar. Pollut. Bull.*, **19**, 19–25 (1988).