Determination of the Total Content of Polychlorinated Biphenyls Using Multiple Linear Regression

M.Ambos, H.Lehmann

Deutsche Shell AG, PAE-Labor , Hohe-Schaar-Str. 36, 2102 Hamburg 93

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Multiple linear regression can be used as a versatile tool for the determination of the total content of traces of polychlorinated biphenyls (PCBs) as shown by Burkhard and Weiningers COMSTAR program[1]. However, because it was not possible to obtain the COMSTAR program, an appropriate computer program was developed at Deutsche Shell AG PAE-Laboratory comprising all the functions for succesfull regression. This enables the analyst to distinguish the compounds of technical PCB mixtures from other compounds occurring in the gas chromatogram and to distinguish between the different PCB mixtures. The method is applicable on used mineral oils e.g. used transformer oils giving an instrument for the detection of peaks not belonging to a PCB. Peaks of other compounds than polychlorinated biphenyls can thus be detected and eliminated.

Polychlorinated biphenyls (PCBs) constitute a group with 209 theoretically possible congeners. PCBs had been manufactured as commercial mixtures: [Aroclors (USA), Clophens (Germany) and Kanochlor (Japan)]. Traces of those mixtures may occur in used oils. The determination of the total concentration of those traces in a routine scale is nearly impossible because of the great number of congeners of which many are not commercially available. The main difficulty therefore is the point that not all congeners can be identified and the response factors of those congeners cannot be determined.

Clean up Procedure

Any clean up procedure eliminating interferring compounds can be applied. The GC-Analysis has to be done by using capillary columns to get the highest resolution as possible and by applying the ECD as a specific and sensitive detector. PAE-Laboratory employed the clean up procedure and GC column described in DIN 51 527 P 1. Decachlorbiphenyl was used as internal standard.

Principle of Multiple Linear Regression

The principle is, that the regression function expressed as:

$$C_i = C_A \times f_{iA} + C_B \times f_{iB} + C_C \times f_{iC} + C_D \times f_{iD} \qquad (1)$$

is applied on each PCB congener. In this equation (1) C_i is the concentration of each congener occurring in the chromatogram of the sample. C_A, C_B, C_C and C_D are the concentrations of the technical PCB Mixtures A, B, C and D by which the sample can be contaminated, e.g. the clophens A30, A40 A50 and A60. In the set of data of one analysis they are the unknown coefficients of the multiple regression which are to be determined; f_{iA}, f_{iB}, f_{iC} and f_{iD} being the independent variables in the regression, are the weight fractions of the congener i in the technical PCB mixtures A, B, C and D. They have to be determined once and can be used as constants in the appropiate computer program of the multiple regression. The only values which have to be fed, are the concentrations of each congener, C_i (Cm. values in the tables 1 to 3). The total PCB content of the sample is given by the sum of

1) L.P.Burkhard, D.Weininger; Anal. Chem. 1987, 59, 1187-1190

C_A, C_B, C_C, and C_D, beeing calculated by the regression:

$$\Sigma PCB = C_A + C_B + C_C + C_D \qquad (2)$$

Using these concentrations and the weight fractions of the congeners in the Clophenes the concentration of each congener is calculated (Cc. values in tables 1 to 3).

Peak Selection

Contrary to normal GC-analysis, where only compounds of the sample are taken into account, in the computer program a fixed set of the most significant congeners of the possible technical PCB mixtures has to be installed. Although even the small number of six congeners as determined according to DIN 51 527 P 1 is sufficient to run the regression, the number of peaks should be considerably higher in order to increase the precision and accuracy. On the other hand only those peaks can be used, which are corresponding to only one congener and this congener must be commercially available to determine the response factor. We selected a set up of 15 peaks each being well separated in the gas chromatogram.

Adaption of the Regression/Detection and Elimination of Outliers

When carrying out the regression negative coefficients, i.e. negative concentrations for clophen mixtures may occur. As negative concentrations cannot exist those mixtures must be excluded from the regression. The regression has to be rerun with less coefficients e.g. three instead of four.

The detection of peaks which are not members of one of the Clophen mixtures used in the regression can easily be achieved by comparing the measured concentrations of the congeners with the calculated ones. If the measured concentration is significantly higher than the calculated concentration, this peak may belong to an other type of halogenated compounds e.g. Ugilecs. After elimination of such peaks the regression is rerun and the value of r^2 will increase.

Therefore, both possibilities were installed in the computer program: elimination of coefficient and peaks.

It should be mentioned that the elimination of peaks should not be done on a pure mathematical or statistical basis. In each case there should be an analytical justification. Such reasons may be:

1.) overlaying peaks of other halogen containing substances, e.g. UGILECs (polychlorinated benzyltoluenes),

2.) wrong integration of too small or badly resolved peaks.

It has been found that in most cases it is not necessary to eliminate peaks.

Results and Discussion

The analysis of a test mixture, containing equal amounts of A30, A40 and A60 with a total PCB concentration of 24 µg/g is shown in Table 1. As expected, the agreement between the measured and calculated concentrations of the different congeners is exellent. The relative differences are below 10 %. After elimination of the slightly negative concentration of A50 (see Table 1b) the agreement of the concentrations of the Clophen mixtures and the total PCBs with the nominal concentrations cannot be better. Accordingly the value of r^2 is above 0.99.

The results of the analysis of a tranformer oil containing the same amount and type of PCB is summerized in Table 2. Again a negative concentration of A50 occurs which has to be eliminated. The comparision of both tables shows that the weight fractions of the congeners in the Clophens are different. The reason is that for analyzing real samples, these weight fractions should be determined not in the pure Clophens but in oils doped with the Clophen and beeing run through the total clean up procedure.

Table 3 shows the analysis of a used oil contaminated with PCBs and with UGILEC. As can be seen from Table 3a, peak no 12 is enhanced and might be overlapped by an UGILEC compound. Eliminating this peak increases r^2 but now peak no 11 seems to be enhanced. The elimination of this peak leads to Table 3c . Now r^2 is nearly 1.00 showing that the fit is sufficient. Further peak eliminations (e.g. of the peaks 13 and 14) would give no improvement; on the contrary, in this case the value of r^2 would be reduced to 0.989 while the total PCB concentration is nearly uneffected (2023 µg/g instead of 2024).

The conformity of the measured concentrations of the 15 congeners with the calculated ones is surprising because there will be

differences in the compositions of the different chlophen mixtures having contaminated the oil and those used here as standards (vide [2), 3), 4)]. Even the restriction to the six congeners which are to be determined according to DIN 51 527 P.1 can lead to acceptable results, as has been found when applying this regression method on the results of a round robin test of transformer oils. The differences of the measured total PCB contents from the real ones were below ten percent.

The computer program can be run on every IBM computer. The additional time required for the input of the GC result into the computer and running the regression is below 4 minutes if the data set of the concentrations of the Clophenes has already been loaded (this set can still remain in the computer and be used again). Loading this set will need about 15 minutes.

As this regression program is based on the accuracy of the concentrations determined by the GC-method it can only be applied at concentrations well above the detection limits.

2)Verband Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten: Rahmenkonzept für die Routineanalytik von Polychlorierten Biphenylen, VDLUFA-Schriftenreihe, Heft 12 (1985)
3)E.Schulte, R.Malisch: Z. Anal. Chem. 314 (1983) 545
4)J.C.Duinker, D.E.Schulz, G.Petrick: Anal. Chem. Vol.60 (1988) 478

Table 1a: test mixture of A30/ A40/ A 60/ (1:1:1) equivalent to a concentration of 24 µg/g total PCB

Peak-no.	Ball. no.	technical clophen mixtures content in massquotient A 30 fiA	A 40 fiB	A 50 fiC	A 60 fiD	Conc. µg/g (meas.) Cm.	Conc. µg/g (calc.) Cc.	Difference of conc. Cm.-Cc.	relative difference (%) (Cm-Cc)*100/Cc
1	8	0,0836	0,0025	0,0042		0,647	0,684	-0,037	-5
2	16	0,0336	0,0089	0,0018		0,320	0,340	-0,020	-6
3	20	0,0982	0,0416	0,0073		1,169	1,120	0,050	4
4	52	0,0264	0,0701	0,0589	0,0081	0,830	0,841	-0,011	-1
5	44	0,0247	0,0572	0,0279	0,0011	0,650	0,669	-0,019	-3
6	42	0,0243	0,0246	0,0034		0,380	0,394	-0,014	-4
7	70	0,0272	0,0717	0,0409	0,0016	0,810	0,810	0,000	0
8	101	0,0022	0,0213	0,0772	0,0505	0,603	0,593	0,010	2
9	81	0,0039	0,0339	0,0934	0,0231	0,488	0,484	0,004	1
10	77	0,0086	0,0603	0,2056	0,0633	1,048	1,050	-0,002	0
11	153		0,0034	0,0303	0,0787	0,658	0,664	-0,007	-1
12	105	0,0028	0,0206	0,0818	0,0636	0,699	0,698	0,001	0
13	183		0,00086	0,0033	0,0225	0,187	0,190	-0,003	-2
14	181		0,00089	0,0029	0,0199	0,170	0,169	0,001	1
15	170		0,0046	0,0120	0,0664	0,576	0,577	-0,001	0

Result of the regression:

Regr. no.	elim. Ball. no.	technical clophen mixtures µg/g A 30 A	µg/g A 40 B	µg/g A 50 C	µg/g A 60 D	Σ PCB µg/g (meas.) Cm.	r^2
1		7,95	8,17	-0,13	8,14	24,13	0,996

Table 1b: test mixture of A30/ A40/ A 60/ (1:1:1) equivalent to a concentration of 24 µg/g total PCB after elimination of A50 as coefficient

Peak-no.	Ball. no.	technical clophen mixtures content in massquotient A 30 fiA	A 40 fiB	A 50 fiC	A 60 fiD	Conc. µg/g (meas.) Cm.	Conc. µg/g (calc.) Cc.	Difference of conc. Cm.-Cc.	relative difference (%) (Cm-Cc)*100/Cc
1	8	0,0836	0,0025	0,0042		0,647	0,684	-0,037	-5
2	16	0,0336	0,0089	0,0018		0,320	0,340	-0,020	-6
3	20	0,0982	0,0416	0,0073		1,169	1,120	0,050	4
4	52	0,0264	0,0701	0,0589	0,0081	0,830	0,841	-0,011	-1
5	44	0,0247	0,0572	0,0279	0,0011	0,650	0,669	-0,019	-3
6	42	0,0243	0,0246	0,0034		0,380	0,394	-0,014	-4
7	70	0,0272	0,0717	0,0409	0,0016	0,810	0,810	0,000	0
8	101	0,0022	0,0213	0,0772	0,0505	0,603	0,593	0,010	2
9	81	0,0039	0,0339	0,0934	0,0231	0,488	0,484	0,004	1
10	77	0,0086	0,0603	0,2056	0,0633	1,048	1,050	-0,002	0
11	153		0,0034	0,0303	0,0787	0,658	0,664	-0,007	-1
12	105	0,0028	0,0206	0,0818	0,0636	0,699	0,698	0,001	0
13	183		0,00086	0,0033	0,0225	0,187	0,190	-0,003	-2
14	181		0,00089	0,0029	0,0199	0,170	0,169	0,001	1
15	170		0,0046	0,0120	0,0664	0,576	0,577	-0,001	0

Result of the regression:

Regr. no.	elim. Ball. no.	technical clophen mixtures µg/g A 30 A	µg/g A 40 B	µg/g A 50 C	µg/g A 60 D	Σ PCB µg/g (meas.) Cm.	r^2
2		8,00	8,01	0	8,03	24,04	0,995

Table 2a: tranformer oil containing 24 µg/g PCB (A30/ A40/ A 60 = 1:1:1)

Peak-no.	Ball. no.	technical clophen mixtures content in massquotient A 30 fiA	A 40 fiB	A 50 fiC	A 60 fiD	Conc. µg/g (meas.) Cm.	Conc. µg/g (calc.) Cc.	Difference of conc. Cm.-Cc.	relative difference (%) (Cm-Cc)*100/Cc
1	8	0,0668		0,0035		0,628	0,501	0,127	25
2	16	0,0323	0,0070	0,0011		0,287	0,304	-0,017	-6
3	20	0,0751	0,0308	0,0048		0,819	0,834	-0,015	-2
4	52	0,0173	0,0552	0,0440	0,0056	0,640	0,645	-0,005	-1
5	44	0,0194	0,0476	0,0194		0,626	0,556	0,070	13
6	42	0,0212	0,0211	0,0022		0,419	0,344	0,075	22
7	70	0,0229	0,0649	0,0357	0,0013	0,699	0,739	-0,040	-5
8	101		0,0058	0,0597	0,0359	0,452	0,337	0,115	34
9	81	0,0035	0,0273	0,0753	0,0174	0,340	0,383	-0,043	-11
10	77	0,0095	0,0529	0,1730	0,0487	0,855	0,881	-0,026	-3
11	153		0,0027	0,0266	0,0643	0,555	0,575	-0,020	-4
12	105	0,0034	0,0200	0,0688	0,0494	0,632	0,602	0,030	5
13	183		0,00075	0,0032	0,0176	0,153	0,160	-0,007	-4
14	181		0,00110	0,0026	0,0161	0,134	0,150	-0,016	-11
15	170		0,0055	0,0150	0,0648	0,581	0,610	-0,029	-5

Result of regression:

Regr. no.	elim. Ball. no.	technical clophen mixtures µg/g A 30 A	µg/g A 40 B	µg/g A 50 C	µg/g A 60 D	Σ PCB µg/g (meas.) Cm.	r^2
1		7,52	8,82	-0,49	8,78	24,63	0,954

Table 2b: tranformer oil containing 24 µg/g PCB (A30/ A40/ A 60 = 1:1:1) after elimination of A50 as coefficient

Peak-no.	Ball. no.	technical clophen mixtures content in massquotient A 30 fiA	A 40 fiB	A 50 fiC	A 60 fiD	Conc. µg/g (meas.) Cm.	Conc. µg/g (calc.) Cc.	Difference of conc. Cm.-Cc.	relative difference (%) (Cm-Cc)*100/Cc
1	8	0,0668		0,0035		0,628	0,501	0,127	25
2	16	0,0323	0,0070	0,0011		0,287	0,304	-0,017	-6
3	20	0,0751	0,0308	0,0048		0,819	0,834	-0,015	-2
4	52	0,0173	0,0552	0,0440	0,0056	0,640	0,645	-0,005	-1
5	44	0,0194	0,0476	0,0194		0,626	0,556	0,070	13
6	42	0,0212	0,0211	0,0022		0,419	0,344	0,075	22
7	70	0,0229	0,0649	0,0357	0,0013	0,699	0,739	-0,040	-5
8	101		0,0058	0,0597	0,0359	0,452	0,337	0,115	34
9	81	0,0035	0,0273	0,0753	0,0174	0,340	0,383	-0,043	-11
10	77	0,0095	0,0529	0,1730	0,0487	0,855	0,881	-0,026	-3
11	153		0,0027	0,0266	0,0643	0,555	0,575	-0,020	-4
12	105	0,0034	0,0200	0,0688	0,0494	0,632	0,602	0,030	5
13	183		0,00075	0,0032	0,0176	0,153	0,160	-0,007	-4
14	181		0,00110	0,0026	0,0161	0,134	0,150	-0,016	-11
15	170		0,0055	0,0150	0,0648	0,581	0,610	-0,029	-5

Result of regression:

Regr. no.	elim. Ball. no.	technical clophen mixtures µg/g A 30 A	µg/g A 40 B	µg/g A 50 C	µg/g A 60 D	Σ PCB µg/g (meas.) Cm.	r^2
2		8,56	7,82	0	8,48	24,86	0,941

Table 3: unknown used oil contaminated with PCBs and UGILEC

Table 3a: Regression with all peaks

Peak-no.	Ball. no.	technical clophen mixtures content in massquotient A 30 fiA	A 40 fiB	A 50 fiC	A 60 fiD	Conc. µg/g (meas.) Cm.	Conc. µg/g (calc.) Cc.	Difference of conc. Cm.-Cc.	relative difference (%) (Cm-Cc)*100/Cc
1	8	0,0668		0,0035		107,30	111,650	-4,350	-4
2	16	0,0323	0,0070	0,0011		50,50	55,297	-4,797	-9
3	20	0,0751	0,0308	0,0048		138,50	131,753	6,747	5
4	52	0,0173	0,0552	0,0440	0,0056	46,60	46,827	-0,227	0
5	44	0,0194	0,0476	0,0194		46,00	44,339	1,661	4
6	42	0,0212	0,0211	0,0022		37,50	39,769	-2,269	-6
7	70	0,0229	0,0649	0,0357	0,0013	52,50	56,057	-3,557	-6
8	101		0,0058	0,0597	0,0359	10,88	16,703	-5,823	-35
9	81	0,0035	0,0273	0,0753	0,0174	14,56	24,996	-10,436	-42
10	77	0,0095	0,0529	0,1730	0,0487	55,00	59,740	-4,740	-8
11	153		0,0027	0,0266	0,0643	16,72	17,625	-0,905	-5
12	105	0,0034	0,0200	0,0688	0,0494	62,30	29,240	33,060	113
13	183		0,00075	0,0032	0,0176	1,22	4,280	-3,065	-72
14	181		0,00110	0,0026	0,0161	1,17	3,953	-2,784	-70
15	170		0,0055	0,0150	0,0648	3,62	16,732	-13,109	-78

Table 3b: elimination of peak no 12

Peak-no.	Ball. no.	technical clophen mixtures content in massquotient A 30 fiA	A 40 fiB	A 50 fiC	A 60 fiD	Conc. µg/g (meas.) Cm.	Conc. µg/g (calc.) Cc.	Difference of conc. Cm.-Cc.	relative difference (%) (Cm-Cc)*100/Cc
1	8	0,0668		0,0035		107,30	111,480	-4,180	-4
2	16	0,0323	0,0070	0,0011		50,50	55,288	-4,788	-9
3	20	0,0751	0,0308	0,0048		138,50	131,822	6,678	5
4	52	0,0173	0,0552	0,0440	0,0056	46,60	45,874	0,726	2
5	44	0,0194	0,0476	0,0194		46,00	44,375	1,625	4
6	42	0,0212	0,0211	0,0022		37,50	39,883	-2,383	-6
7	70	0,0229	0,0649	0,0357	0,0013	52,50	55,799	-3,299	-6
8	101		0,0058	0,0597	0,0359	10,88	11,772	-0,892	-8
9	81	0,0035	0,0273	0,0753	0,0174	14,56	21,961	-7,401	-34
10	77	0,0095	0,0529	0,1730	0,0487	55,00	51,735	3,265	6
11	153		0,0027	0,0266	0,0643	16,72	10,213	6,507	64
13	183		0,00075	0,0032	0,0176	1,22	2,327	-1,112	-48
14	181		0,00110	0,0026	0,0161	1,17	2,176	-1,007	-46
15	170		0,0055	0,0150	0,0648	3,62	9,506	-5,883	-62

Table 3c: further elimination of peak no 11

Peak-no.	Ball. no.	technical clophen mixtures content in massquotient A 30 fiA	A 40 fiB	A 50 fiC	A 60 fiD	Conc. µg/g (meas.) Cm.	Conc. µg/g (calc.) Cc.	Difference of conc. Cm.-Cc.	relative difference (%) (Cm-Cc)*100/Cc
1	8	0,0668		0,0035		107,30	111,533	-4,233	-4
2	16	0,0323	0,0070	0,0011		50,50	55,250	-4,750	-9
3	20	0,0751	0,0308	0,0048		138,50	131,684	6,816	5
4	52	0,0173	0,0552	0,0440	0,0056	46,60	46,062	0,538	1
5	44	0,0194	0,0476	0,0194		46,00	44,485	1,515	3
6	42	0,0212	0,0211	0,0022		37,50	39,776	-2,276	-6
7	70	0,0229	0,0649	0,0357	0,0013	52,50	56,065	-3,565	-6
8	101		0,0058	0,0597	0,0359	10,88	10,263	0,617	6
9	81	0,0035	0,0273	0,0753	0,0174	14,56	22,144	-7,584	-34
10	77	0,0095	0,0529	0,1730	0,0487	55,00	51,528	3,472	7
13	183		0,00075	0,0032	0,0176	1,22	0,989	0,226	23
14	181		0,00110	0,0026	0,0161	1,17	0,942	0,227	24
15	170		0,0055	0,0150	0,0648	3,62	4,637	-1,014	-22

Result of regression:

Regr. no.	elim. Ball. no.	technical clophen mixtures µg/g A 30 A	µg/g A 40 B	µg/g A 50 C	µg/g A 60 D	Σ PCB µg/g (meas.) Cm.	r^2
1		1664	199	134	210	2207	0,928
2	105	1663	207	115	102	2088	0,988
3	153	1662	200	139	22	2024	0,991