POLYCHLORODIBENZODIOXIN AND POLYCHLORODIBENZOFURAN OCCURRENCE IN POLYCHLOROBIPHENYLS USED IN DIELECTRIC FLUIDS

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Forty-two samples of dielectric fluids from electrical equipment in operation were analyzed in order to assess their content of polychlorinated biphenyls (PCBs), dibenzodioxins (PCDDs), and dibenzofurans (PCDFs). The electrical equipment mainly consisted in transformers and capacitors used by the Italian National Railways Service; they were built in the years 1949 to 1986, had a variety of electrical usage histories, but had never been involved in failures or accidents.

A small (<100 ml) amount of fluid was pipetted out from the charging plug of each apparatus. From each sample, a 100-500 mg aliquot was taken, dissolved with n-hexane, spiked with the ^{13}C-analogs of the PCDD and PCDF congeners to be quantified, and eluted on a 10 cm long 20 mm i.d. multilayer chromatographic column for cleanup.[1] Extracts were reduced to a small volume (<0.5 ml), transferred to 10 cm long 5 mm i.d. columns packed with activated alumina, and eluted to separate PCBs from PCDDs and PCDFs.[1] PCBs were recovered in the first fraction and assessed by GC/ECD; PCDFs and PCDDs were recovered in the second fraction and determined by HRGC-MS(MID).[2]

It is known that PCDD and PCDF cumulative levels in PCBs may range from 1 to approximately 14 mg/kg.[3] Therefore, it was decided not to quantify PCDDs and PCDFs in those samples having a PCB content <1 % (w/w), as the presence of PCDDs and PCDFs in such samples was reckoned not to be of particular concern in case of handling, disposal, or accidental release of the fluid into the environment. Table 1, Section A, shows the PCB levels measured in the set of forty-two samples. For the samples (Nos. 32-42) with a PCB content >1 %, PCB-normalized PCDD and PCDF concentrations are also given, and expressed as per the following equations:

$$Y_A = [PCDD+PCDF]_A/[PCB]$$
$$Y_H = [PCDD+PCDF]_H/[PCB]$$
$$Y_C = [PCDD+PCDF]_C/[PCB]$$

Table 1. PCB, PCDD, and PCDF levels measured in dielectric fluids matrices.

No.	PCB (g/g) [a]	No.	PCB (g/g) [a]	No.	PCB (g/g) [a]	No.	PCB (g/g) [a]
Section A							
1	<1.0 E-8 [b]	9	<1.0 E-8	17	2.7 E-4	25	4.5 E-4
2	<1.0 E-8	10	6.0 E-5	18	3.0 E-4	26	5.0 E-4
3	<1.0 E-8	11	7.0 E-5	19	3.0 E-4	27	5.6 E-4
4	<1.0 E-8	12	1.7 E-4	20	3.0 E-4	28	5.9 E-4
5	<1.0 E-8	13	1.7 E-4	21	3.4 E-4	29	7.4 E-4
6	<1.0 E-8	14	1.8 E-4	22	3.5 E-4	30	7.7 E-4
7	<1.0 E-8	15	1.8 E-4	23	3.9 E-4	31	2.1 E-3
8	<1.0 E-8	16	2.5 E-4	24	4.2 E-4		

Section B

No.	PCB (g/g) [a]	Y_A (g/g) [c]	Y_H (g/g) [c]	Y_C (g/g) [c]
32	2.0 E-2	2.8 E-7	6.3 E-8	6.0 E-9
33	4.0 E-2	1.5 E-6	2.2 E-7	7.6 E-8
34	5.0 E-2	9.4 E-7	9.1 E-8	1.3 E-8
35	4.1 E-1	2.4 E-5	2.2 E-6	5.3 E-7
36	5.0 E-1	4.2 E-6	3.1 E-7	6.5 E-8
37	5.2 E-1	7.6 E-6	7.7 E-7	1.6 E-7
38	6.4 E-1	1.5 E-6	2.7 E-7	5.1 E-8
39	6.6 E-1	3.7 E-7	6.2 E-8	1.8 E-8
40	8.0 E-1	2.3 E-6	3.3 E-7	8.5 E-8
41	8.4 E-1	3.3 E-6	4.7 E-7	8.7 E-8
42	9.9 E-1	8.9 E-7	1.9 E-7	3.6 E-8

(a) PCB amount per unit amount of dielectric fluid. (b) 1.0 E-8 = 10 ng/g. The sign "<" indicates below detection threshold. (c) PCDD plus PCDF cumulative amount per unit amount of corresponding PCBs.

where subscripts "A", "H", and "C" indicate, respectively: the cumulative analytical concentration, the concentration expressed as "TCDD toxicity equivalents" (cumulative TE units) obtained by multiplying each homologous group by the most conservative TEF in that group, and the TE concentration from congener-specific determination. As a source of TEFs, the US EPA scale of 1987 was used.[4] The distributions of Y_A, Y_H, and Y_C data sets were statistically analyzed (Table 2). Shapiro and Wilk's normality test was carried out on the ln-transformed values of each set. The three distributions turned out to be characterized by a high level of normality. Based on confidence

Table 2. Outcome of the statistical analysis of PCB-normalized PCDD plus PCDF concentrations Y_A, Y_H, and Y_C.[a]

Parameter	Y_A		Y_H		Y_C	
N	11		11		11	
Mean	-11.9	6.56 E-6[b]	-15.2	2.57 E-7	-16.8	5.24 E-8
SD[c]	1.49	4.46	1.07	2.93	1.23	3.42
LCL(95%)[d]	-12.9	2.40 E-6	-15.9	1.25 E-7	-17.6	2.29 E-8
UCL(95%)[e]	-10.9	1.79 E-5	-14.5	5.29 E-7	-15.9	1.20 E-7
W[f]	0.97		0.95		0.97	

(a) For each variable Y, data are reported in logarithmic (left column) and corresponding linear (right column, g/g or gTE/g) coordinates. (b) 6.56 E-6 = 6.56 μg/g. (c) Standard deviation. (d) Lower confidence limit. (e) Upper confidence limit. (f) Level of normality (Shapiro and Wilk's W test; normality threshold, W = 0.90).

limits, the analytical amount of PCDDs and PCDFs relative to PCBs (Y_A) appears to range from approximately 2 to 20 mg/kg, with a mean of 6.6 mg/kg. These data are in excellent agreement with the literature;[3] however, contrary to this study, the latter refers to presumably fresh, unused PCBs. Based on averages, the PCDD and PCDF toxicologically active fraction ($\langle Y_C \rangle$ = 0.052 mgTE/kg) is over two orders of magnitude lower than the corresponding analytical value; the more conservative mean based on homolog-specific determinations ($\langle Y_H \rangle$ = 0.26 mgTE/kg) is approximately 1/25th of the analytical value, but is overestimated by a factor of 5 with respect to the congener-specific datum.

In order to assess the reliability of PCB analytical procedure, parallel but independent determinations were carried out by our two laboratories (Laboratory 1 and Laboratory 2) on a group of 46 samples including a subgroup of samples from Table 1 with PCB concentrations above analytical threshold, and another subgroup of samples of fluids with accident histories. X_1 and X_2 were set as the PCB results from parallel assays of a given sample, and the following variable was defined:

$$Z = [X_1 - X_2]/X_1$$

The Z distributions of both subgroups were Gaussian only when converted to their (natural) logarithms; therefore, the logarithmic transform of the variable

$$Z_{abs} = abs[X_1 - X_2]/X_1$$

was chosen to be used for statistical analysis, which provided the outcome summarized as follows (Table 3). It was observed

Table 3. Outcome of the statistical appraisal performed on 46 pairs of results from parallel PCB determinations carried out by our two laboratories.

Parameter	$\ln(Z_{abs})$	Z_{abs}	Z
N	46	43	43
Outliers[a]	3		
Mean	-1.501	0.223	0.060
SD[b]	1.319	3.738	0.521
LCL(95%)[c]	-1.907	0.149	-0.100
UCL(95%)[d]	-1.095	0.335	0.221
W[e]	0.90		0.96

(a) According to Chauvenet's criterion. (b) Standard deviation. (c) Lower confidence limit. (d) Upper confidence limit. (e) Level of normality (Shapiro and Wilk's test; normality threshold, W = 0.90).

that the mean of the maximum deviation Z_{abs} and its upper confidence limit were equal to 22 and 34 %, respectively. However, the absolute relative deviation represents the most conservative deviation estimate. The distribution of the relative deviation Z was characterized by a mean +6.0 %, which indicated that Laboratory 1 had a small positive bias compared to Laboratory 2. Based on the upper confidence limit, the bias could be as high as +22 %. On the whole, it was deemed that the above statististical figures were reasonable, considering that the laboratories had determined PCBs by somewhat different GC techniques and without implementing an interlaboratory quality control and quality assurance program. The data reported in Table 2 have been evaluated and corrected for biases.

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