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ANALYSIS OF POLYCHLOROBIPHENYLS FROM USED TRANSFORMERS FOR POLYCHLOROOIBENZOFURANS

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ABSTRACT

The results of analyses for polychlorodibenzofuran (PCDF) content in two samples of polychlorobiphenyl (PCB) from used electrical transformers are presented and discussed. In neither sample was there evidence for enhanced PCDF concentrations even though one of them had been subjected to overheating while in service.

INTRODUCTION

Polychlorodibenzofurans (PCDFs) are trace contaminants of commercial polychlorobiphenyls (PCBs) commonly used in electrical components such as transformers, where overheating can occur. There is a considerable amount of evidence that PCDFs can be formed when PCBs are heated which is of concern because PCDFs are more toxic than PCBs. This paper present measurements of PCDF concentrations from two samples of PCB taken from used electrical transformers, one of which had been overheated while in service.

EXPERIMENTAL

The precise origin and nature of the two PCB samples could not be established although GC-MS analysis with computer matching of the major ions to the National Bureau of Standards library[1] gave either Aroclor 1254 or Aroclor 1260 as the nearest equivalents for both samples. The transformers were apparently made in 1969 and 1977 and the newer one had overheated while in service. The PCB sample from this overheated transformer (PCB-A) contained a suspension of fine black particulates while the other PCB sample (PCB-B) was almost clear.

About 15 g of PCB-A and 25 g of PCB-B were each dissolved in 100 ml samples of aromatic-free hexane (AFH). In the case of PCB-A no attempt was made to exclude or separate out the fine black particulates, but as homogeneous a mixture of oil and particulates as possible was used to prepare the initial solution.

In the clean-up procedure 50 ml burettes were plugged with acetone-washed , glass-wool, packed with about 22 g of activated basic alumina (Woelm Grade B Akt 1) under AFH, and topped with cleaned anhydrous sodium sulphate. The basic alumina used was activated by heating at 440°C

overnight and then stored in an oven set at 250°C. Just prior to use, the required amount of alumina was transferred to an oven kept at 110°C containing a bed of silica gel. The anhydrous sodium sulphate was cleaned by Soxhlet extraction with acetone, hexane and dichloromethane prior to use.

Aliquots (1 ml) of each of the PCB solutions was removed and spiked with 20 ul of a 473.5 ppm octachlorodibenzofuran (OCDF) solution and 200 ul of a 64.6 ppm solution of 1,2,3,4 tetrachlorodibenzo-p-dioxin (TCDD). These spiked solutions were blown dry under N_2, redissolved in AFH and transferred to the alumina column with copious amounts of AFH washings. The columns were first eluted with 80 ml of a freshly prepared 2% CH_2Cl_2/AFH solution and then with 50 ml of a freshly prepared 50% CH_2Cl_2/AFH solution. Both 2% and 50% elutions were separately reduced on a Kuderna-Danish apparatus with final reductions to dryness under a stream of nitrogen gas in screw-topped glass vials. The residue was redissolved in xylene and stored at -10°C prior to analysis.

Analysis was conducted using either a Finnigan 1020 GC-MS with one single-ion monitoring programme for the PCDFs and the 1,2,3,4-TCDD, and another for the PCDDs, or High Pressure Liquid Chromatography (HPLC) using a Zorbax ODS column and UV detection. Details of the analytical conditions are given in Table 1. The concentrated 50% fraction from the column clean-up proved reluctant to dissolve completely in xylene for GC-MS analysis, so small amounts of CH_2Cl_2 and acetone were added to encourage complete solution.

Table 1 Analytical conditions

Instrument	Detector	Column	Oven
Finnigan 1020 GC-MS	70 eV ionization potential Manifold temp = 80°C Separator temp = 310°C	30 m x 0.2 mm ID SE54. WCOT on silica quartz	Injector temp = 100°C Detector temp = 100°C Temp prog: injection at 90°C; ballistic rise to 215°C, temp gradient 15°C/min to 300°C for 12 mins
LDC. HPLC. (Milton Roy)	UV detector: 245 nm	25 cm x 4 mm ID Zorbax ODS reverse phase column. MeOH at 1.0 cm^3/min liquid phase	Ambient

It is difficult to confirm the presence and quantities of the various PCDF isomers with GC-MS because single isomer standards for these compounds, apart from OCDF, were not available at the time of analysis. The presence of PCDFs was confirmed both by comparison of retention times with those from an UV-irradiated solution of OCDF in 1:5 methanol: xylene solvent and by measuring the ratio between the intensity of each of the PCDF isomers' main mass ion (M^+) and its daughter ion ($M^+ -63$), created by the loss of a COCl fragment. Irradiated solutions were found by GC-MS to contain at least two isomers of pentachlorodibenzofuran (PnCDF); three isomers of hexachlorodibenzofuran (HxCDF) and one of heptachlorodibenzofuran (HpCDF). The retention times of these isomers relative to 1,2,3,4-TCDD were measured. Injections of the irradiated sample gave

$M^+/M^+ -63$ ratios for PnCDF, HxCDF, HpCDF and OCDF isomers which were consistent with the literature values[1]. In this study all the peaks identified as PCDFs in the PCB samples had the expected relative retention times and $M^+/M^+ -63$ ion ratios.

The PCDFs and PCDDs were quantified using calibration curves constructed from the GC-MS analysis of a series of mixed PCDD/PCDF standards, containing 1,2,4,6,7,9-and/or 1,2,4,6,8,9-HxCDD; 1,2,3,4,6,7,9-HpCDD; OCDD and OCDF with 1,2,3,4-TCDD as the internal standard dissolved in xylene. The PCDFs detected in the PCB sample were quantified using a series of standards containing 1,2,3,4-TCDD and OCDF. Values for the concentration of tetrachlorodibenzofuran (TCDF) present were calculated from a calibration curve derived from 1,2,3,4-TCDD but adjusted for the relative response factors between 2,3,7,8-TCDF and 1,2,3,4-TCDD found from the literature[2]. The concentrations of PnCDFs, HxCDFs and HpCDFs present in the cleaned samples were determined by interpolation between TCDF and OCDF.

A particulate-rich sample of 10 g of PCB-A taken from the bottom of the container after settlement, was dissolved in 50 ml AFH and centrifuged to separate out the particulate matter. The particulates were Soxhlet-extracted for 8 hours using 50 ml of a 1:4 mixture of xylene and AFH. The resulting solution was concentrated and then blown dry under a steam of clean nitrogen gas, the residue was taken up in AFH, column chromatographed and analysed as described above. No PCDDs or PCDFs were detected.

RESULTS AND DISCUSSION

Recovery efficiencies for the 1,2,3,4-TCDD and OCDF spikes after column chromatography were calculated from HPLC analyses; the results are presented in Table 2. The clean-up procedure used gave the most consistent and highest recovery from the several alternatives that were examined. Table 3 contains the results of the GC-MS analyses expressed as ng PCDF or PCDD per g PCB.

Table 2 HPLC-determined recovery efficiencies for 1,2,3,4-TCDD and OCDF after column chromatograph

Chemical	PCB	Initial amount of spike added µg	Post column chromatography recovery determined by HPLC µg	Recovery efficiencies
1,2,3,4-TCDD	PCB-A	12.9	11.1	86%
	PCB-B	12.9	10.7	83%
OCDF	PCB-A	9.5	7.3	77%
	PCB-B	9.5	7.3	77%

Sample PCB-A, the overheated PCB, has marginally higher PCDF concentrations than sample PCB-B but all the PCDFs are within the range quoted for 10 Aroclor and Clophen PCB samples in the literature[3] (see Table 4) and since PCB-A and B had different origins the differences in PCDF concentrations cannot be considered significant.

Table 3 Results of GC-MS analyses

Chemical	Retention time (relative to 1,2.3,4-TCDD)	PCB-A (μg g^{-1} PCB)	PCB-B (μg g^{-1} PCB)
TCDF	0.94	0.06	ND
	0.96	0.05	0.04
	0.98	0.09	0.07
TCDD	1.0	spike	spike
PnCDF	1.14	0.46	0.15
PnCDD	-	ND	ND
HxCDF	1.39	0.53	0.13
	1.47	0.59	0.16
HxCDD	-	ND	ND
HpCDF	1.79	spike	spike
HpCDD	-	ND	ND
OCDF	2.45	spike	spike
OCDD	-	ND	ND

Notes: 1 The analytical error associated with these results, estimated from repeat determinations is 46 per cent for the TCDF and TCDD and 52 per cent for the HxCDF and HxCDD values.

2 ND = not detected. The detection limit for TCDD and TCDF was 0.04 μg/g PCB; for OCDF 0.06 μg/g PCB; and for OCDD 0.05 μg/g PCB.

3 'Spike' indicates that only the spiked chemical was detected, the OCDF contained traces of HpCDF.

Table 4 Measured concentrations of PCDFs

	Total PCDF (μg g^{-1})		
	TCDF	PnCDF	HxCDF
Range of literature concentrations (mean)	0.04-1.4 (0.34)	0.1-5.0 (1.1)	0.02-2.45 (1.0)
PCB-A	0.2	0.5	1.1
PCB-B	0.1	0.2	0.3

Thus there is no evidence for significant PCDF production in the overheated transformer. The presence of black particles, assumed to be carbon, in the overheated sample indicates that during overheating, conditions inside the transformer were reducing rather than oxidizing. This is consistent with the observation of no significant PCDF formation from PCBs because such

reactions would require oxidizing conditions. Neither PCB sample contained detectable concentrations of PCDDs and it is noticeable that even in fires, where oxygen is presumably more freely available, PCDF production predominates over PCDD formation[4].

Results of PCB analyses from an intact capacitor involved in a fire[5] have been reported giving comparable PCDF concentrations to those in Table 4 whereas residual fluid from a ruptured capacitor involved in the same fire had markedly enhanced PCDF concentrations[5]. This supports the speculation above and implies that provided the PCB-containing vessel does not contain air and remains intact and sealed during overheating, formation of PCDF will be negligible.

CONCLUSIONS

The PCDF concentrations in two samples of PCB from used transformers, one of which had overheated, are within the range of values previously published for the industrial product. These results indicate that in this case there is no evidence for PCDF formation during overheating. This is the expected result if the overheating occurs in the absence of oxygen and implies that if electrical components remain intact and sealed while in use and during overheating, conversion of PCB to PCDF should be negligible.

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