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Identification and Quantification of Polychlorinated Biphenyls in Paper and Paper Board Using Fused Silica Capillary Gas Chromatography

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Since 1929, polychlorinated biphenyls (PCB's) have been used in a variety of industrial and domestic applications. In view of their significance as an environmental hazard, the applications of PCB's are divided into those for open and closed systems.
One of the main applications of PCB's in open systems was the use in non-carbon copying paper as an ink carrier. In the period between 1957 and 1971 more than 20 million kg of a technical PCB mixture was used in the USA in the production of carbonless copy paper (Walter and Zambrano 1981). This paper usually contained between 2 and 6% PCB's by weight (Kuratsune and Masuda 1972; Van Esch et al. 1972). The technical mixture used in the manufacture of carbonless copy paper was a type containing 42-43% chlorine by weight (Aroclor 1242). The use of PCB's in the USA and most other OECD countries practically ceased during the seventies (OECD, 1982). However, environmental levels of PCB's have not decreased substantially since then.

One of the possible routes of PCB's being introduced into the environment is the recycling of paper and paper waste (Walter and Zambrano 1981). Although at present no PCB's are found in carbonless copy paper (Belliardo et al. 1979), recycled paper can be contaminated with PCB's originating from the use in carbonless copy paper.

The analysis of PCB's still renders quite a few problems to the analyst. In particular, quantitation of PCB's in environmental samples is a major analytical issue. Most of the analyses until now have been carried out with gas chromatography (GC) using packed columns. Quantitation was done either by pattern comparison or by converting PCB's to a single compound by dechlorination or perchlorination of the sample. Several authors have evaluated the merits of these methods (Duinker et al. 1981; De Kok et al. 1981). The use of glass or fused silica capillary columns instead of packed columns dramatically improves resolution and enables the analyst to separate individual PCB's. Capillary GC, therefore, allows one to determine contents of individual PCB's if he has the appropriate compounds at his disposal as standards. Kerkhoff et al. (1982), for instance, use a standard solution of 27 individual PCB's to determine trace levels in sediments. The use of capillary GC for this type of work has also been advocated in various other recent papers (Duinker et al. 1980; Kerkhoff et al. 1982; Tuinstra et al. 1980, De Kok et al. 1982b). Standard procedures for the routine capillary gas chromatographic determination of PCB's are, however, not available at the moment.

In the Dutch governmental program for the management and control of environmental pollution, special attention is being given to PCB's. In order to evaluate which routes exist for PCB's to reach the environment, waste streams will be monitored. For that purpose reliable standardized methods of analysis must be elaborated.
The aim of this study was to develop a standard analytical method for the determination and quantitation of PCB's in paper and paper board by capillary GC and to determine PCB levels in various types of paper in order to monitor one of the possible and still existing routes of PCB contamination of the environment.

MATERIALS AND METHODS

Various commercially available brands of paper were collected in 1980 and 1982. Paper and paper board samples were cut into small pieces. PCB's were isolated from the pretreated samples, using approximately 5 g of sample, by refluxing it during 1½-2 h with 50-100 ml n-hexane. The resulting solution was filtered over a plug of silanized quartz wool. The remaining paper shreds were washed twice with 25 - 50 ml hexane, the washings were subsequently filtered as described above and combined. The combined phases were concentrated by distillation to about 4 ml and further concentrated under a gentle nitrogen stream at room temperature to a final volume of 2 ml. The samples were dried over anhydrous sodium sulphate.

Cleanup was carried out according to the methods described by De Kok et al. (1982a). 3 g of activated silica or aluminium oxide were deactivated with 3% (w/w) distilled water, put into a glass column (dimensions: 15 x 0.5 cm I.D.) and packed with a vibrator. A layer of 1 cm of anhydrous Na_2SO_4 was put on top of the adsorbent. A volume of 0.5 ml of concentrated sample was quantitively transferred to the top of the column. Next, n-hexane was added and the first fraction of 6 ml, which contains the PCB's was collected. Under the conditions stated above, the recovery for Aroclor 1242 was over 95%, and for Aroclor 1254 and 1268 at least 90%.

GC measurements were carried out on Packard Becker (Delft, The Netherlands) Models 419, 430 and 433 gas chromatographs, equipped with ^{63}Ni electron capture detectors. The glass columns (2 m x 2 mm I.D.) were packed with 3 or 4% OV 101 on Chromosorb WHP (80-100 mesh) or with 1.95% OV17/1.5% OV 210 on Chromosorb WHP (80-100 mesh). Conditions were as follows: isothermal analysis at 220°C, detector 300°C, injector 260°C, carrier gas He or N_2, carrier flow 20 ml/min, bypass N_2 20 ml/min, injection volume 0.5-1.0 µl. For capillary GC, 25 m x 0.22 mm I.D., fused silica CP^{tm}sil5 (Chrompack, Middelburg, The Netherlands) columns were used. Conditions were as follows: temperature programmed analysis from 90 to 150°C at a rate of 30°C/min and from 150 to 225°C at 3°C/min. Detector 300°C, injector 260°C using splitless injection; carrier gas: He, flow rate 1 ml/min; detector bypass: N_2, 29 ml/min; injection volume 0.2-1.0 µl.

Commercial PCB mixtures were obtained from Analabs (North Haven, CT. USA). Clean up was done using Woelm B-super I aluminium oxide (Woelm, Eschwege, GFR), activated at 200°C and deactivated with 3-5% (w/w) water, and silica (Kieselgel 60, 70-230 mesh, Merck, Darmstadt, GFR) activated at 150°C overnight and deactivated with 3% (w/w) water. Anhydrous Na_2SO_4 (Baker, Deventer, The Netherlands) was used to dry the hexane extracts. HPLC-grade n-hexane (Baker) was used for extraction procedures and as the solvent when preparing standard solutions. All-glass containers were used to avoid contamination by plasticizers, etc. All glasswork was rinsed before use with successively acetone, ethanol and n-hexane.

A mixture of 27 individual PCB's was a gift from Drs. M.A.T. Kerkhoff, Netherlands Institute of Fisheries Investigations, IJmuiden.

RESULTS AND DISCUSSION

Seven, out of a total of twelve, paper and paper board samples were used to study PCB recovery. To this end known amounts of Aroclor 1242 were dissolved in n-hexane and added to dry paper shreds. After allowing the solution to soak in, the procedure described in the experimental section was carried out. As can be read from table 1, recoveries for the whole analytical procedure averaged 91%. In the literature some authors have reported a better efficiency for an ethanolic alkali extraction of paper samples (Young et al. 1973; Becker and Schulte 1976) as compared to the relatively simple hexane reflux. Others (De Kok et al. 1982a), however, did not observe any noticeable difference. In the present study, differences were also found to be absent, average recoveries of 93 and 91% being obtained for 4 selected samples with the former and latter method respectively. These included so-called 'difficult' (Becker and Schulte 1976) paper board samples. All further data in this study were obtained using the reflux method in n-hexane as described in the experimental section, which is a more simple, faster and easier method.

Determination of the PCB contents was based on pattern comparison using various methods of calculation as described below. Peak identification was based on relative retention times (RRT) using p,p'-DDE as the internal standard. When this procedure was applied to capillary GC, a peak was considered to be identified as a PCB peak if the RRT matched within the range of 0.01 RRT with a peak in a commercial PCB mixture standard.

In table 1 the results of this study are summarized. In five brands of paper, PCB contents between 1 and 22 ppm by weight were found, in one brand the level was about 0.1 ppm, and in the other six samples the PCB content was below the detection limit of 0.1 ppm.

The GC pattern of each of the six samples that contained PCB's showed a remarkable resemblance to the pattern of Aroclor 1242; examples are shown in figures 1B and 1C. In samples from Japan (Kuratsune and Masuda 1972), Italy (D'Arrigo 1979), the USA (Walter and Zambrano 1981) and The Netherlands (De Kok et al. 1982a) a similar resemblance has been found. However, other workers have reported different types of technical mixtures to be present in paper samples, for instance Aroclor 1254 (Easty 1973), Aroclor

Table 1. PCB levels in paper and paperboard (in µg PCB/g paper)*

sample type	I	II	III	IV	V	VI	VII	recovery %
white A4	<0.1						0.1	-
pink A4	<0.1						0.5	86
sandwich paper	<0.1						0.1	89
airmail	<0.1						0.1	-
magazine text	<0.1						0.1	90
magazine photos	<0.1						<0.1	80
scribble paper (recycled)	0.1	0.10	0.10	<0.1	<0.1	0.10	0.1	96
paperboard 1	1.65	1.70	1.70	1.20	1.55	3.95	5.7	-
paper towels	2.85	2.85	2.75	1.80	2.15	1.40	3.5	93
light toilet paper	3.95	4.90	3.60	2.85	3.25	6.70	3.8	-
paperboard 2	5.35	5.40	5.35	4.25	4.85	4.90	7.1	102
dark toilet paper	12.40	12.50	11.90	7.75	10.85	22.00	15.0	-

*calculation methods used:

I sum of peak heights of peaks 1-27 (see table 2 and figure 1) relative to sum in Aroclor 1242 standard
II mean of individual peak concentrations of peaks 1-27
III sum of peak heights of peaks 3,6,7,9,10,13,16,17,18 and 19
IV sum of peaks 1-10, as I
V sum of peaks 1-19, as I
VI sum of peaks 9 and 13, as I
VII packed GC, sum of 10 selected peaks
<0.1 = below detection limit; - = not determined

1260 (Serum et al. 1973; Woidich et al. 1978) and Aroclor 1248 or no recognizable pattern (Williams and Benoit 1979); these authors used packed columns for their analyses. All these authors, however, also mention the presence of peaks in the lower chlorinated (Aroclor 1242) range in their samples.

In some of the paper samples analysed in this study, peak heights of late eluting peaks (cf. figure 1B, peaks no. 24, 26, 29 and 32) are somewhat elevated when compared to the usual ratio's between peaks in the late and the early eluting regions in the Aroclor 1242 pattern. Yet, these peaks (cf. figure 1B) are not likely to originate from another technical mixture, since the corresponding more highly chlorinated components are absent from the chromatograms. Rather, environmental breakdown of some of the earlier eluting peaks may account for this phenomenon. If the presence of a technical mixture with a higher chlorine content is suspected in samples, quantitation should be based on either pattern comparison with a standard mixture of Aroclor 1242 and 1254 (Easty 1973) or calculation of contents of individual components (Kerkhoff et al. 1982).

In Europe, the technical mixtures formerly used in carbonless copy paper can be Aroclor 1242 (USA), Clophen A30 (GFR) or Fenclor 42 (Italy). Since chromatographic patterns of the former two do not

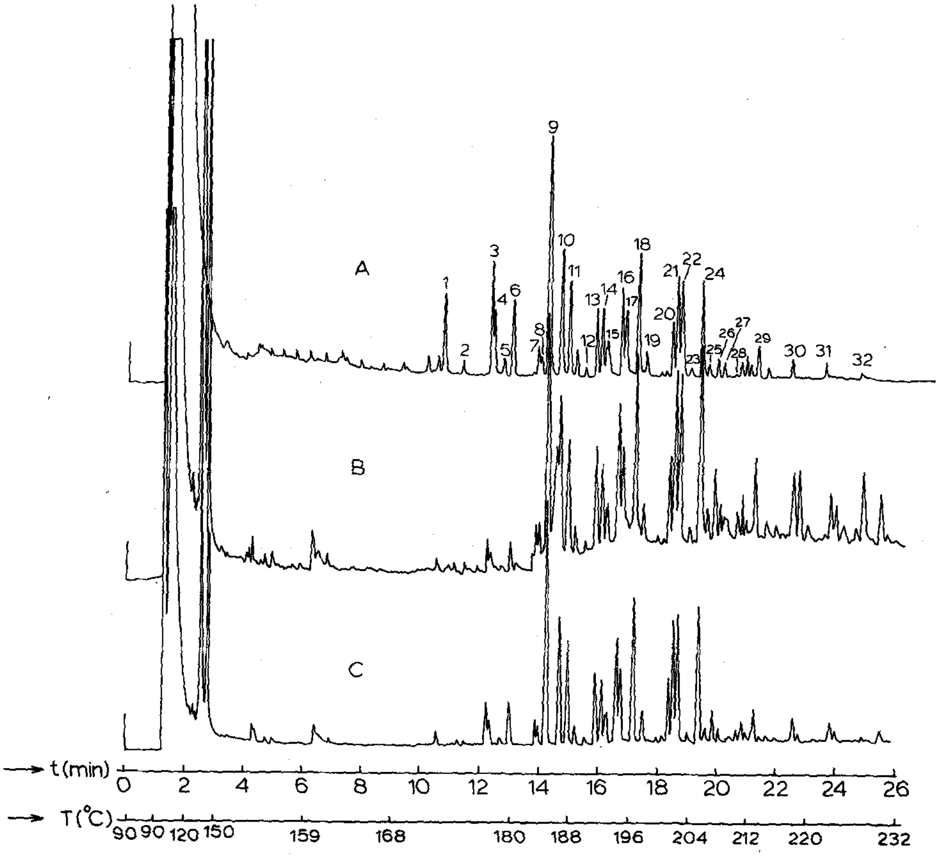

Figure 1: Capillary chromatograms of Aroclor 1242 (A) light toilet paper (B) and dark toilet paper (C). Conditions, see methods section.

differ substantially (Ballschmiter and Zell 1980), we only used Aroclor 1242 as a reference.
Two samples were analysed with EI-GC/MS (Finnigan 3200, 70 eV) to verify the presence of PCB's. In both cases, di-, tri-, and tetra-chlorobiphenyls were identified. Moreover, several substituted polycyclic aromatics, as well as terphenyls and hydrogenated terphenyls were found to be present. The latter have been reported to be present in paper by other authors (Thomas and Reynolds 1973; De Kok et al. 1982b).

Quantitation via pattern comparison can be done in a variety of ways. Either one can take into account all the peaks in the chromatogram, or one selects individual peaks. The latter method is less time consuming, but a proper selection must be made to avoid biased results. In the present paper, PCB contents were calculated in different ways, as indicated for columns I-VI in table 1. The data in columns I and II have been calculated on the basis of peaks 1-27 in the Aroclor 1242 chromatogram (see figure 1A and table 2), the difference being that the results in column I were obtained by comparing sums of peak heights in sample and standard, whereas the results in column II were obtained by averaging the ratios of peak heights in sample and standard of every single peak. The latter method will yield substantially higher results if the contribution of peaks having low peak heights in the standard is relatively high in the sample chromatogram. As can be seen from table 1, this is the case with some higher chlorinated components (cf. peaks no. 24, 26, 29 and 32 in figure 1B) in light toilet paper. No such discrepancy was noted for any of the other paper brands. For all further work, the first method of calculation was preferred.

Table 2 Retention times of peaks* in Aroclor 1242 relative to p,p'-DDE

peak no.	RRT	peak no.	RRT
1	.4996	17	.7969●
2	.5480	18	.8164●
3	.5785●	19	.8313●
4	.5828	20	.8725
5	.5994	21	.8799
6	.6141●	22	.8866
7	.6598●	23	.9085
8	.6644	24	.9200
9	.6727●	25	.9366
10	.6927●	26	.9485
11	.7062	27	.9463
12	.7382	28	.9550
13	.7498●	29	1.012
14	.7587	30	1.070
15	.7676	31	1.134
16	.7905●	32	1.203

* peak numbers refer to figure 1A; GC conditions, see text
● peaks used for quantitation of column III in table 1

Calculations for column III were analogous to those for the first column, this time, however, using 10 instead of 27 peaks from the capillary GC chromatogram (see table 2). These peaks were selected on the basis of abundance, retention time and resolution in order to get a selection representative for an Aroclor 1242 mixture. As can be seen from table 1, there is a close fit between the data in columns I and III for all types of paper found to contain PCB's. This is an important result, since the method used here significantly reduces the complexity of the calculation.

In columns IV and V results are summarized that were obtained using relatively early eluting peaks only, which might seem advisable in order to eliminate interferences due to more highly chlorinated PCB mixtures. The results, however, demonstrate that if a non-representative part of a chromatogram is used for the quantitation, completely erroneous results may be obtained.

In column VI, data are summarized which were obtained using two individual components (peaks 9 and 13 in table 2) for the quanti-

tation. These two chlorobiphenyls are part of a selection of 6 to 10 components proposed (Tuinstra et al. 1983) as a reliable means to quantify PCB contents in environmental samples. Although, in that proposal, the selection has not been made with the intention to quantify in terms of technical mixtures, we calculated the PCB contents in terms of Aroclor 1242 in order to be able to make a comparison with other calculation methods. It is evident from the data in table 1 that the mode of calculation used for column VI does not yield reliable results. This is according to expectations, since the 2-peak selection certainly cannot be considered a representative one for paper samples (cf. previous paragraph).
Finally, in column VII, the results of packed GC are shown. Generally speaking, they are seen to be distinctly higher than those obtained in capillary GC. Several reasons for this discrepancy may be advanced, the most important one probably being the poor resolution in packed GC, as has been pointed out by DUINKER et al. (1981).

The present study demonstrates that, in GC, PCB patterns in paper and paper board samples closely resemble that of the 42-43% chlorine containing technical mixture formerly used in the manufacture of carbonless copy paper. Peak height comparison - by means of capillary GC - for a representative set of ten peaks offers a rapid and reliable means to calculate PCB levels in the said type of samples. GC on packed columns may well be useful for preliminary screening purposes; however, it cannot be recommended for quantitative analysis. For the rest, it should be realized that the pattern comparison technique is not applicable for those types of samples in which partial breakdown of individual PCB's has altered the original pattern. In such cases, quantitation based on peak height comparison for each individual PCB component should be the alternative.

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REFERENCES

Ballschmiter K, Zell M (1980) Analysis of PCB by glass capillary gaschromatography. Fres Z Anal Chem 302:20-31
Becker G, Schulte E (1976) Zum Vorkommen von PCB in Verpackungsmaterial. Lebensm Chem Gerichtl Chem 30:101-107
Belliardo F, Nano GM, Pavan I, Scansetti G (1979) Sulla presenza di policlorobifenili in carte autocopianti. Med Lavoro 5:391-397
D'Arrigo V (1979) Indagine sul contenuto di policlorobifenili in carte autocopianti chimiche. Ind Carta 17:220-222
De Kok A, Geerdink RB, Frei RW, Brinkman UATh (1981) The use of dechlorination in the analyses of polychlorinated biphenyls and related classes of compounds. Intern J Environ Anal Chem 9:301-318

De Kok A, Geerdink RB, Frei RW, Brinkman UATh (1982a) Limitations in the use of perchlorination as a technique for the quantitative analysis of polychlorinated biphenyls. Intern J Environ Anal Chem 11:17-41

De Kok A, Geerdink RB, De Vries A, Brinkman UATh (1982b) An evaluation of chromatographic methods for the analysis of polychlorinated terphenyls in environmental samples. Intern J Environ Anal Chem 12:99-122

Duinker JC, Hillebrand MTJ, Palmork KH, Wilhelmsen S (1980) An evaluation of existing methods for quantitation of PCB's in environmental samples and suggestions for an improved method based on measurement of individual components. Bull Environ Contam Toxicol 25:956-964

Easty DB (1973) Quantitation of mixtures of polychlorinated biphenyls isolated from paperboard containing recycled fiber. Tappi 56:131-134

Kerkhoff MAT, De Vries A, Wegman RCC, Hofstee AWM (1982) Analysis of PCB's in sediments by glass capillary gas chromatography. Chemosphere 11:165-174

Kuratsune M, Masuda Y (1972) PCB's in non-carbon copy paper. Environ Health Perspect 1:61-62

OECD (1982) Protection of the environment by control of PCB's. Paris

Serum JW, Tong SC, StJohn LE Jr, Bache CA, Mertens DR, Lisk DJ (1973) Electron-capturing compounds and selected elements in paper. Bull Environ Contam Toxicol 10:88-96

Thomas GH, Reynolds LM (1973) Polychlorinated terphenyls in paperboard samples. Bull Environ Contam Toxicol 10:37-41

Tuinstra LGMTh, Traag WA, Keukens HJ (1980) Quantitative determination of individual chlorinated biphenyls in milkfat by splitless glass capillary gas chromatography. J Assoc Off Anal Chem 63:952-958

Tuinstra LGM, Driessen JJM, Keukens HJ, Van Munsteren TJ, Roos AH, Traag WA (1983) Quantitative determination of specified chlorobiphenyls in fish with capillary gas chromatography and its use for monitoring and tolerance purposes. Intern J Environ Anal Chem 14:147-157

Van Esch GJ, Freudenthal J, Greve PA, Wit SL (1972) PCB's in self copying paper (in Dutch).RIV report 107/72 Tox-RoB, Utrecht.

Walter KJ, Zambrano JJ (1981) PCB's and wastepaper. Ind Wastes 3/4: 12-15

Williams D, Benoit F (1979) The determination of PCB's in selected household products. Bull Environ Contam Toxicol 21:179-184

Woidich HW, Pfannhauser W, Scheidl I, Blaicher G (1978) Polychlorierte Biphenyle in Verpackungsmaterial und Zweitfaser. Deut Lebensm Rundschau 74:61-64

Young SJV, Finsterwalder C, Burke JA (1973) Extraction and cleanup for determination of PCB's in paper and paperboard. J Assoc Off Anal Chem 56:957-961

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