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Quantitation of Mixtures of Polychlorinated Biphenyls Isolated From Paperboard Containing Recycled Fiber

Abstract: Paperboard made from recycled fiber was found to contain small amounts of the polychlorinated biphenyl formulations Aroclor 1242 and Aroclor 1254. Gas chromatograms of each of the two Aroclors had many peaks in common, indicating that the formulations contained many of the same chlorobiphenyls. Thus, determination of the separate amounts of Aroclor 1242 and 1254 in extracts from paperboard samples was quite difficult. A method for determining the amounts of each of the two Aroclor formulations in a mixture was devised, based on the observation that two chromatograms possessing a number of coincident peaks may be viewed as a complex extension of two single chromatographic peaks which partially overlap. Chromatograms of the individual Aroclors were used to predict overlap in Aroclor 1242-1254 mixtures; elementary equations were developed to compute the amount of each Aroclor in a sample. The equations were successfully tested on synthetic mixtures and applied routinely to paperboard.

Keywords: Paperboards · Reclaimed fibers · Quantitative analysis · Chlorine compounds · Computation · Equations · Gas chromatography · Biphenyl* · No-carbon papers

Polychlorinated biphenyls (PCBs) have been detected in paperboard made from recycled fiber as well as in a wide variety of environmental samples (*1, 2*). The primary source of PCBs in paperboard has been recycled carbonless copy paper, although the use of PCBs in the domestic production of that paper was terminated early in 1971. Monsanto's Aroclor 1242 is the PCB formulation that was used in carbonless copy paper, and that is the type which is usually found in paperboard. Occasionally, paperboard extracts show evidence of Aroclor 1254 from environmental and other sources in addition to the 1242.

Gas chromatography, using an electron capture detector, is the most common method of detecting and quantitating PCBs. Because commercial PCB formulations consist of mixtures of chlorobiphenyls, the chromatogram of a single formulation, such as Aroclor 1242, contains a complex series of peaks as shown in Fig. 1. If both 1254 and 1242 are present, the chromatogram is doubly complex, and determining the amounts of each formulation present in the mixture may be quite difficult. It is important to the paperboard manufacturer that the nature and thus the source of the PCBs contaminating his product be identified.

The PCBs commonly found in wildlife are of the Aroclor 1254 and 1260 types (*3*), commercial mixtures containing on the average five and six chlorine atoms per molecule, respectively (*4*). The electron capture response of chlorobiphenyls containing from four to nine chlorine atoms per molecule varies by a factor of less than two (*5*). Thus, semiquantitative methods have been used with some success for PCB mixtures from wildlife (*6*), even though the exact nature of the PCB found could not be reported and the method assumed constant detector response for all peaks on the chromatogram. Improved accuracy seems likely with use of a method based on the electron capture response to each chlorobiphenyl in the sample (*4*). Because this method requires careful measurement of the area of each peak and a determination of the number of chlorines in the isomer producing the peak, quantitation of chromatograms would appear to be quite time-consuming. Perchlorination (*7*) offers the advantages of maximum detector response and the conversion of a complex PCB chromatogram into the single decs-

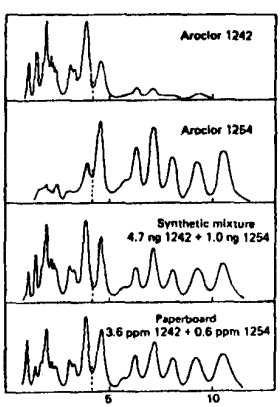


Fig. 1. Gas chromatograms of PCBs.

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chlorobiphenyl peak. Unfortunately, the method "sees" unchlorinated biphenyl as PCB and provides no insight into the nature of the commercial PCB formulation(s) originally present in the sample.

On the basis of total integrated area, the detector response of Aroclor 1254 is three to four times that of Aroclor 1242. Thus, the semiquantitative methods used for wildlife would be less acceptable for paperboard.

As shown in Fig. 1, chromatograms of Aroclor 1242 and 1254 have many peaks in common, indicating that the formulations contain many of the same chlorobiphenyls. The peaks which are not in common, such as the early peaks of 1242 and the latest peak of 1254, might be used to measure the amounts of each formulation in a mixture. However, the early peaks of 1242 are quite subject to distortion and loss due to volatilization during drying of the paperboard. That would produce unacceptable errors in mixture determinations.

Two chromatograms possessing a number of coincident peaks may be viewed as a complex extension of two single chromatographic peaks which partially overlap. Methods for the quantitation of two overlapping peaks have been reviewed by Pecsok (8), but they do not appear to be adequate for mixtures of Aroclor formulations. The elementary treatment described in the following section is more laborious than is usually needed for computation of two overlapping peaks, but it has been readily adapted for the task of calculating amounts of Aroclor 1242 and 1254 on the same chromatogram. This technique is somewhat similar to the well-known method of spectrophotometric analysis of mixtures of two absorbing substances (9).

INTERPRETATION OF OVERLAPPING CHROMATOGRAMS

Idealized chromatographic peaks for Species A and B are shown in Fig. 2, drawn as they would look if the other species were not present. Curve C is the sum of the two peaks, showing the additive character of the overlapping areas. The vertical dotted line has been drawn at an arbitrary time so that only small portions, A_0 and B_0, lie on the opposite sides of the line from A and B, respectively, the areas representing major portions of the species. The dotted line is drawn at the same time on Curve C, and it separates the left area, composed of A and B_0 from the right area, B and A_0.

$$\text{Left area} = X = A + B_0 \quad (1)$$

$$\text{Right area} = Y = B + A_0 \quad (2)$$

From chromatograms of Species A and B alone, the relationships of areas A_0 to A and B_0 to B may be determined. For example, if the relations below are found,

$$A_0 = A/2 \quad (3)$$

$$B_0 = B/6 \quad (4)$$

Eqs. (1) and (2) become

$$X = A + B/6 \quad (5)$$

$$Y = B + A/2 \quad (6)$$

Areas X and Y may be measured from the chromatogram of an unknown mixture of the two species, and Eqs. (5) and (6) may then be solved for A and B. A_0 and B_0 are computed from Eqs. (3) and (4), and the areas corresponding to total amounts of the two species, A_T and B_T, are computed from Eqs. (7) and (8) below.

$$A_T = A + A_0 \quad (7)$$

$$B_T = B + B_0 \quad (8)$$

Chromatograms of the individual species may be used to prepare working curves, plots of Area A_T vs. weight of Compound A injected and B_T vs. weight of Compound B. Thus, for an unknown mixture, A_T and B_T computed as described above from measured areas X and Y may be taken to the working curves and the weights of each component in the mixture determined. In actual practice, the equations are combined and simplified.

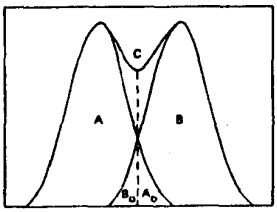


Fig. 2. Overlapping chromatographic peaks.

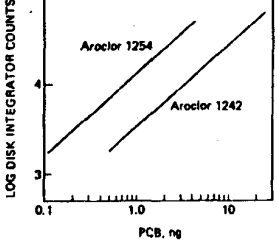


Fig. 3. Typical working curves.

QUANTITATION OF PCB MIXTURES ISOLATED FROM PAPERBOARD

The technique for interpreting overlapping chromatograms described in the preceding section has been applied to the interpretation of PCB mixtures. Aroclor 1242 and 1254 may be considered analogous to Species A and B in the equations. The vertical dotted line is drawn as shown in Fig. 1. Thus, Area A is that due to 1242 to the left of the dotted line, and Area B is that due to 1254 to the right of the dotted line. X is the total area to the left of the dotted line on the chromatogram of a 1242-1254 mixture, and Y is the total area to the right of the line.

As a sample calculation, assume that the relations of Eqs. (3) and (4) have been found from chromatograms of each Aroclor alone. Eqs. (5) and (6) are solved for A by multiplying (5) by 12 and (6) by 2 and subtracting (6) from (5).

$$11A = 12X - 2Y \quad (9)$$

Therefore,

$$A = 1.091X - 0.182Y \quad (10)$$

From (3),

$$A_0 = 0.546X - 0.091Y \quad (11)$$

Substituting Eqs. (10) and (11) into Eq. (7),

$$A_T = \text{Area}_{1242} = 1.64X - 0.27Y \quad (12)$$

$$B_T = \text{Area}_{1254} = 1.27Y - 0.64X \quad (13)$$

Eq. (13) may be computed in a similar fashion or may be written by inspection, knowing that $\text{Area}_{1242} + \text{Area}_{1254} = X + Y$. Eqs. (12) and (13) are final working equations for areas corresponding to total amounts of the two Aroclors in a mixture. These equations apply only to the gas chromatograph for which they were developed, and they should be updated whenever there is any change in the performance of the instrument. They can readily be developed for any instrument in the manner described above. When interpreting chromatograms of mixtures, integrated Areas X and Y are measured and substituted into Eqs. (12) and (13) to obtain the area due to each Aroclor. These areas are then taken to working curves, such as shown in Fig. 3, to ob-

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Table I. PCBs in Synthetic Mixtures and Paperboard from Recycled Fiber

Synthetic mixture			Calculated from chromatogram			Calculated as only Aroclor 1242, ng
Aroclor 1242, ng		Aroclor 1254, ng	Aroclor 1242, ng		Aroclor 1254, ng	
1.0	+	4.0	0.9	+	4.0	...
4.0	+	1.0	4.3	+	1.0	10.0
4.7	+	2.6	4.4	+	2.6	17.0
4.7	+	1.0	4.6	+	1.0	9.5
2.6	+	2.6	2.6	+	2.7	...
4.7	+	0.5	4.4	+	0.4	6.6
4.7	+	0.2	8.0	+	0.2	9.4
4.7	+	2.6	4.4	+	2.5	19.0
4.7	+	1.0	4.4	+	1.0	9.6
Recycled paperboard			3.6 ppm	+	0.3 ppm	5.1 ppm
Recycled paperboard			7.2 ppm	+	3.0 ppm	25.0 ppm
Recycled paperboard			4.8 ppm	+	1.1 ppm	9.5 ppm
Recycled paperboard			3.8 ppm	+	0.6 ppm	6.2 ppm
Recycled paperboard			2.6 ppm	+	<0.1 ppm	...

tain the ng of each Aroclor in the injected sample. Instead of solving both equations, Eq. (12) may be solved for the area due to 1242, which may be *subtracted from* the total area of the chromatogram to obtain the area due to 1254.

Table I shows results obtained from the use of this technique on synthetic mixtures of Aroclor 1242 and 1254. Also included are some results typical of the hundreds of paperboard analyses performed in this laboratory. The amounts of the individual Aroclor formulations computed from the chromatograms agreed quite well with the known composition of the synthetic mixtures. Chromatograms containing small amounts of Aroclor 1254 in the presence of greater amounts of 1242, such as 5 ng 1242 + <1 ng 1254, resemble 1242. Table I shows the errors that might be incurred if these mixtures are quantitated as 1242 alone. Serious errors result if samples containing larger amounts of 1254 are quantitated as containing only 1242. This might occur in laboratories which report PCB results in terms of the single Aroclor which the sample chromatogram most closely resembles.

Because of the high temperature history of paperboard, chromatograms of paperboard extracts frequently exhibit distortion not observed on chromatograms of PCB reference formulations. Fortunately, this distortion tends to be less than that on chromatograms from wildlife and other environmental samples. Errors due to this problem have been partially compensated for by the periodic injection of an extract from an experimental paperboard known to contain only Aroclor 1242. The chromatogram of this sample, which exhibits distortion typical of machine-made paperboard, has been used as a practical standard for determining the A to A_0 relationship described previously.

EXPERIMENTAL

The procedure used for isolation of PCBs from paperboard is essentially that which has been recommended by the Food and Drug Administration (*10*) and which is based upon Sections 211.15d (saponification) and 211.14d (cleanup on Florisil column) of the Pesticide Analytical Manual (*11*).

Apparatus

Erlenmeyer flasks with standard taper necks for saponification, 125 ml.

Air condensers, 30 in. long.

Separatory funnels with Teflon stopcocks, 125 ml.

Glass tubes 12 mm o.d. drawn to a tip with o.d. about 4 mm at one end and with a length of 25 cm exclusive of the tip (for the Florisil cleanup).

A gas chromatograph equipped with a tritium source electron capture detector, a ⅛-in. × 4-ft stainless steel column packed with 3% OV-17 on acid-washed and dimethyldichlorosilane-treated Chromosorb W, 80/100 mesh.

A strip chart recorder equipped with a Disc integrator.

Rotary evaporator.

Solvents and Reagents

Petroleum ether suitable for pesticide residue analysis (Burdick and Jackson Laboratories, Inc., Muskegon, Mich.).

Diethyl ether suitable for pesticide residue analysis.

Alcoholic KOH, 10 g of reagent grade potassium hydroxide pellets dissolved in 500 ml 95% ethanol, and kept in a glass-stoppered bottle.

Hexane, reagent grade (J. T. Baker Chemical Co.).

Activated Florisil, PR grade, 60/100 mesh (Floridin Co., Berkeley Springs, West Va.).

Sodium sulfate, anhydrous, reagent grade.

Standard Solutions

Hexane solutions of Aroclor 1242 and 1254 containing 0.2, 1, and 5 μg/ml prepared fresh each week.

Isolation of PCB Solutions

A 2.00-g sample was cut into pieces having an area of about 80 mm² or less, and refluxed gently for 30 min with 20 ml of alcoholic KOH. After cooling to room temperature, the solution was transferred to a 125-ml separatory funnel, using 4-10-ml portions of petroleum ether to wash the saponification flask and the residual paper. Twenty ml water were added to the separatory funnel, and shaken well. The lower layer was drained into a second separatory funnel and extracted with 20-ml petroleum ether. The two petroleum ether solutions were combined and washed with three 20-ml portions of water. Finally, the stem of the funnel was dried with a strip of paper towel.

A loose plug of cotton was placed in one of the 25-cm glass tubes, and sufficient Florisil added to give a 10-cm column after tapping. (Previously the Florisil was heated for 5 hr or longer at 130°C, and any Florisil reheated that had been kept at room temperature for 24 hr or more.) A 5-cm column of anhydrous sodium sulfate was poured on top of the Florisil column. Forty-ml petroleum ether was added to the column, then the PCB solution prepared from the above saponification step, and finally the column was eluted with 100 ml of petroleum ether–diethyl ether 94:6. The above additions were made one after another such that the column did not run dry. The first effluent was discarded, but the effluent was collected as soon as the PCB solution was added to the column. The effluent from the column was concentrated to about 3 to 6 ml. The solution was transferred to a 10-ml volumetric flask and diluted to 10 ml with petroleum ether. PCB was determined in the solution by gas chromatography.

Gas Chromatography

New columns were conditioned using the Environmental Protection Agency procedure (*12*). The following instrument conditions were used for analysis: injector temperature 225°, column temperature 210°, detector temperature 225°, carrier gas flow 25 ml/min as measured in a soap bubble meter.

The standing current was determined and appropriate standard solu-

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tions run each day. Five μl samples of both the standard and the unknown solutions were injected. If the response for any peak in the unknown was more than 40% of the standing current, the unknown solution was diluted and the diluted solution injected. Working curves, log-log plots of Disc integrator units vs. nanograms of PCB, were prepared for each of the Aroclors.

Quantitation

The total area under the PCB chromatogram was measured using a Disc integrator or a planimeter. Peaks which did not appear in PCB standards and peaks having retention times less than about 1.7 min were ignored. From the chromatogram, the Aroclor in the sample was qualitatively identified. Then the integrated area was taken to the working curve for that particular Aroclor and the nanograms of PCB in the injected sample determined. When the chromatogram indicated that two PCB formulations were present, the amounts of each formulation were determined by use of the procedure described above.

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