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Development of an Analytical Method for the Determination of Congener Specific PCBs in Selected Polymeric Packaging Materials

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PCBs remain in the environment at declining but still unacceptable high concentrations because of their past widespread application and chemical stability (Schmidt & Heselberg, 1992). Recent studies have shown that at least 18 and perhaps up to 36 of the 209 congeners have potential for toxicity due to their abundance in fish/animal tissue and their demonstrated enzyme induction effects (McFarland & Clark 1989, Tanabe 1988). Recent research has focused on the use of polymeric materials as cleanup and bioconcentration tools and for the analysis of PCBs and other organic chemicals from water, soil and lipophilic media (Huckins *et al.* 1990, Zabik *et al.* 1992). In food packaging, there is a need for research on issues such as the migration of PCBs from packaging materials to packaged foods or the reverse case, the sorption of PCBs from contaminated foods by the packaging material. The purpose of this study was to develop the methodology for the determination of specific PCB congeners in selected polymeric packaging materials used for the packaging of foods. Once the method is developed, it will be possible to investigate the effect of the chemical composition and physical characteristics of food polymers on the potential sorption of selected PCB congeners ranging from tri to deca chlorinated PCBs.

MATERIALS AND METHODS

The films used included polyvinyl chloride (PVC) (1.778 x 10^{-3}cm, 1 ply)(Reynolds Metals, Grottoes, VA), polystyrene (3.048 x 10^{-3}, 1 ply)(Dow Chemical, Midland, MI) and polyethylene (2.286 x 10^{-3} cm, 1 ply)(resin from Dow Chemical , Midland, MI). All solvents were analytical HPLC grade. All chemicals were analytical grade. Polychlorinated biphenyl congeners - Accustandard Inc. (New Haven, CT). PCB congeners selected are based on the occurrence of the congeners in Aroclor 1254 and number of chlorine atoms per molecule and shown in Table 1.

For film uptake studies, deionized distilled water was spiked with a mixed acetone solution of PCB standards to produce a 10 ppb solution of each congener. The system was heated at 40°C for 1 hr with frequent shaking, to evaporate the acetone.

Approximately 0.160 g of each polymeric film was prepared by cutting longitudinal strips approximately 4 x 1.5 cm. Each sample was then inserted in a 76 mL serum vial. Each vial was then brim-tilled with the spiked aqueous PCB congener solution,

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Table 1. PCB congeners used in this study.

IUPAC No.	Chlorobiphenyl Systematic Names
30	2,4,6-Trichlorobiphenyl
31	2,4’,5-Trichlorobiphenyl
47	2,2’,4,4’-Tetrachlorobiphenyl
103	2,2’,4,5’,6-Pentachlorobiphenyl
128	2,2’,3,3’,4,4’-Hexachlorobiphenyl
171	2,2’,3,3’,4,5’,6,6’-Heptachlorobiphenyl
200	2,2’,3,3’,4,5’,6,6’-Octachlorobiphenyl
206	2,3,4,5,6,2’,3’,4’,5’-Nonachlorobiphenyl
209	2,3,4,5,6,2’,3',4',5’,6’-Decachlorobiphenyl

sealed, and stored at 25°C in the absence of light. At given time intervals over 12 hrs, samples were removed for PCB congener quantification. All samples were anaylzed in triplicate.

PCBs were extracted for each time interval by Soxhlet extraction for 18 hrs using a single solvent aliquot of 120 mL hexane. A 1 mL aliquot of a 5 ppm PCB congener 2,4,6 trichlorobiphenyl (IUPAC #30) solution was added prior to extraction and used as an internal standard for determination of method recoveries and to correct the final concentration of each of the PCB congeners. Each sample extract was reduced in a Turbo-Vap evaporator (Zymark) to 0.5 mL at ambient temperature.

Cleanup by an automated Gel Permeation Chromatography (GPC) system (Waters 712 WISP, Milford, MA) was used for the removal of plasticizers, antislip agents, antistatic agents, flame retardants, monomers, dimers, polymers, antioxidants, light absorbers, and any other compounds extracted during the Soxhlet extraction. Each sample was diluted to 4 mL with HPLC grade hexane and transferred to a 6 mL GPC vial. A 2 mL aliquot of each extract was injected into the GPC column (Waters 19 x 300 mm Ultrastyragel 500 A) at a solvent (hexane) flow rate of 5 mL/min. This was attached to a Waters/590 Programmable HPLC pump (Milford, MA) and a Waters faction collector using a UV detector set at 254 nm. This was interfaced with a Hewlett Packard 3390A integrator (Avondale, PA). The contaminant portion was dumped while the PCB portion (54 mL) was collected, and reduced in the Turbo-Vap to 1.0 mL. It was reduced to 0.1 mL by nitrogen evaporation using a N-Vap Model III (Organomation Assoc., Shrewsbury, MA), after which the sample was made up with isooctane to 0.5 mL.

The polystyrene solvent extracts were cleaned up using florisil followed by silica gel low pressure chromatography. The extracts were eluted through the florisil column with a 6% (by volume) of diethyl ether in petroleum ether. The column (1 cm i.d. x 51 cm), was prepared by placing 1 cm of granular anhydrous sodium sulfate on a glass wool plug, followed by 5 g of 60-80 mesh florisil (activated by heating overnight at 130°C), then another 1 cm of granular anhydrous sodium sulfate. The column was then washed with a 20 mL portion of hexane. When the hexane reached the top of the upper layer of sodium sulfate, the Turbo-Vap concentrate was transferred to the column bed. A 40 mL aliquot of elution solvent was then added to the column. Care was taken not to allow the florisil bed to go to dryness. The collected (approximately 35 mL) eluent was then reduced to 1 mL in the Turbo-Vap.

The silica gel column was prepared similar to that described for the florisil column, but with silica gel 60 (70-230 mesh) activated at 130°C for 16 hrs. Fifty mL of 0.5% toluene in hexane was used as the elution solvent. The eluent from the florisil column was added to this silica gel column, eluted, collected, and reduced to 1.0 mL in the Turbo-Vap and then to 0.1 mL by nitrogen evaporation using the N-Vap Model III instrument. Each sample was then made up with isooctane to exactly 0.5 mL.

In order to evaluate the PCB method, a corrected mass balance was calculated based on the PCBs analyzed in the polymer and remaining water solution as compared to the level in the original spiked water. To do this, the water solutions were also analyzed for their PCB concentrations. After the polymers were removed from the vials, the spiked water was transferred to 250 mL separatory funnels. To each sample, a 30 mL aliquot of hexane was added and vigorously shaken for approximately 30 sec. After standing for several min, the hexane layer rose to the top. This was drawn off and transferred to a 100 mL flask fitted with a stopper. This extraction procedure was repeated 2 more times. The extracts were combined, then a 10 g quantity of granular anhydrous sodium sulfate, was added to each flask to remove any traces of water. After allowing 30 minutes for drying the extracts were reduced in the Turbo-Vap to 1.0 mL volume at ambient temperature. Each sample was and then reduced to 0.1 mL by nitrogen evaporation using the N-Vap Model III instrument then made up with isooctane to 0.5 mL.

The concentration of individual PCB congeners in each extract was determined by Gas Chromatography (GC) with a ^{63}Ni electron capture detector (Hewlett Packard 5890 series II, Avondale, PA), and equipped with DB-5 capillary column (60 m x 0.25 mm id.). The standard PCB congeners used are listed in Table 1. The data were recorded on a HP level 4 intergrator. All concentrations were corrected for % recovery. The limits of quantitation were 0.13 ng/g for the polymers and 2 pg/g for the water. All quantification was based on peak area relative to the recovery of congener #30. A standard curve was constructed for each PCB congener. The GC conditions were as follows: Detector temperature-300°C Injector temperature-160°C Inject volume3 µL, Carrier gas-helium at 1 mL/min, Detector makeup gas-nitrogen at 1 ml/min. The oven was programmed from an initial temperature of 160°C. with no hold time, then programmed at 8°C/min to 200°C, held for 5 min, then programmed at 2°C/min to 280°C and held for 10 min.

RESULTS AND DISCUSSION

A chromatogram of a standard 10 ppm solution of the eight PCB congeners is shown in Figure 1. The efficiency of the cleanup procedure for polyethylene is shown in Figures 2a and 2b, a polyethylene/l ppm extract with no cleanup and with cleanup, respectively. A chromatograph of a polystyrene/10 ppm PCB extract without cleanup is seen in Figure 3a, while that of polystyrene/10 ppm PCB after the cleanup procedure is seen in Figure 3b. The polystyrene cleanup did not use the GPC method because it contained compounds with the same retention time as the PCB congeners used in this study. Figures 4a and 4b are chromatograms of PVC/10 ppm PCB without cleanup, and after cleanup, respectively. The cleanup procedures used in this study were necessary in order to aid in the quantitation of the PCB peaks, and to reduced the chances of overlapping these peaks with that of the extraneous compounds and therefore introducing errors in the integration of the peak areas.

Use of the internal standard, 2,4,6-trichlorobiphenyl, allowed for evaluation of the effectiveness of the procedure and for correcting the value of each of the PCB congeners based on the actual recovery for each analysis. Average recoveries of the internal standard for the polymeric materials were: polyethylene 60.3 ± 16.6%; polystyrene 87.2 ± 17.8%; and PVC 60.6 ± 25.5%. Values ranged from a low of 0.3 µg/g for tetra-, penta-, nona-, and decachlorobiphenyl in polystyrene to a high of 2.1 µg/g of trichlorobiphenyl in polyethylene. Table 2 shows the corrected mass balance ratios for PCB concentrations in the polyethylene, polystyrene and PVC respectively, and the water to which they were exposed. The ratios were obtained by taking the sum of the corrected PCB concentrations in the water and the plastic and dividing by the initial PCB concentration in the water for two time periods, 1 and 12 hours.

These results can be used to determine the effectiveness of the method in spiked water solutions before and after contact with the polymers. In an ideal system, the mass balance ratio should be equal to one. Analysis of variance showed significant differences among polymers and PCB congeners but not time. Nevertheless, the overall average corrected mass balances for the polymers were as follows: 1.05 for polyethylene, 1.17 for polystyrene and 0.93 for PVC. These values are all very close to 1. Small experimental errors can lead to small fluctuations above and below this ideal. One factor likely to contribute to errors may be the low concentration of the PCB analyte in some samples.

Overall average mass balance ratios for the PCB congeners were: 1.11 for tri, 0.86 for tetra, 0.71 for penta, 1.12 for hexa, 1.27 for hepta, 1.17 for octa, 1.02 for nona and 1.26 for deca. The low concentration of the PCB analyte may account for the low ratios for the pentachlorinated congeners in polystyrene and PVC and the high ratios for the trichlorinated analogues in these same polymers. The ratios for the corrected

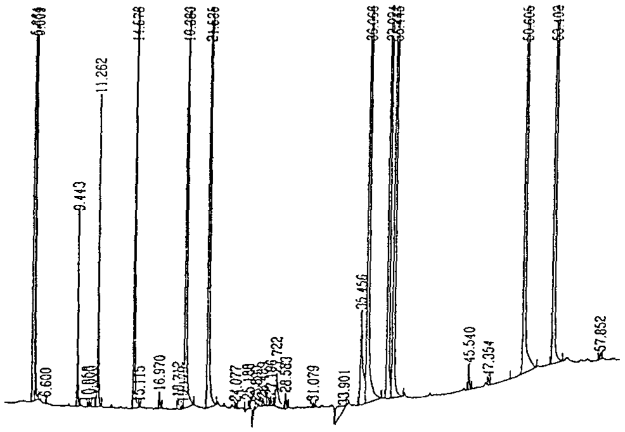

Figure 1. Gas chromatogram of standard PCB congeners-mono(9.443), di(11.262), tri(14.578) tetra(19.380), penta(21.535), hexa(36.068), hepta(37.924). octa(38.445), nona(50.605) and deca(53.402).

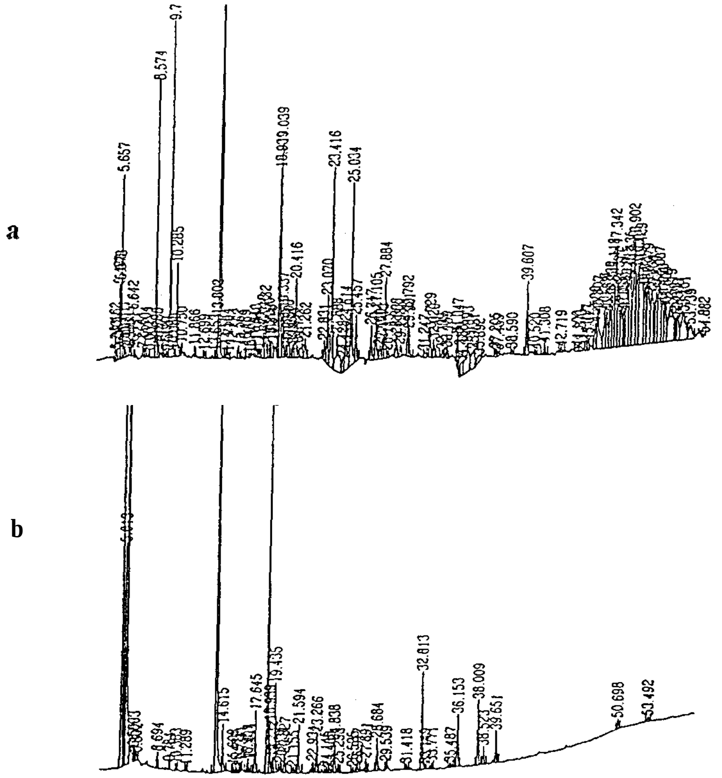

Figure 2. Gas chromatogram of polyethylene/PCB extract before cleanup (a) and after cleanup (b).

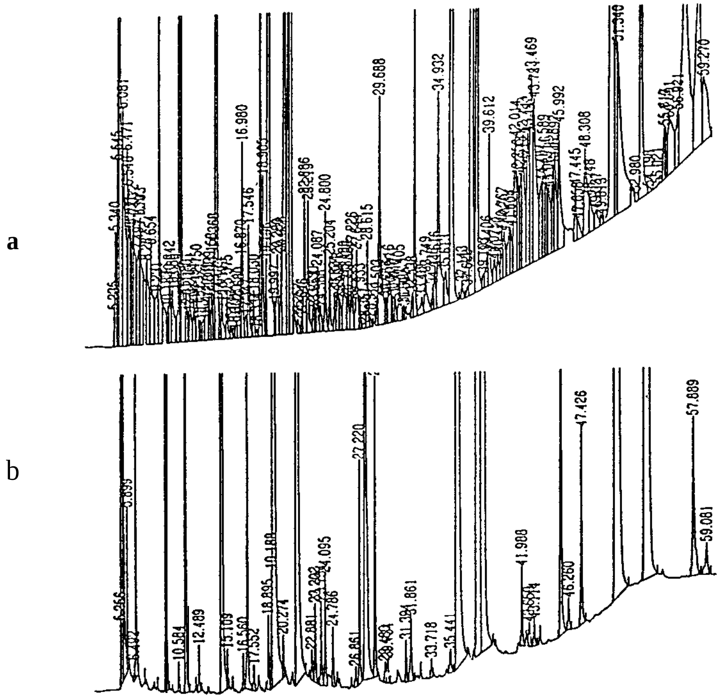

Figure 3. Gas chromatogram of polystyrene/PCB extract before cleanup (a) and after cleanup (b).

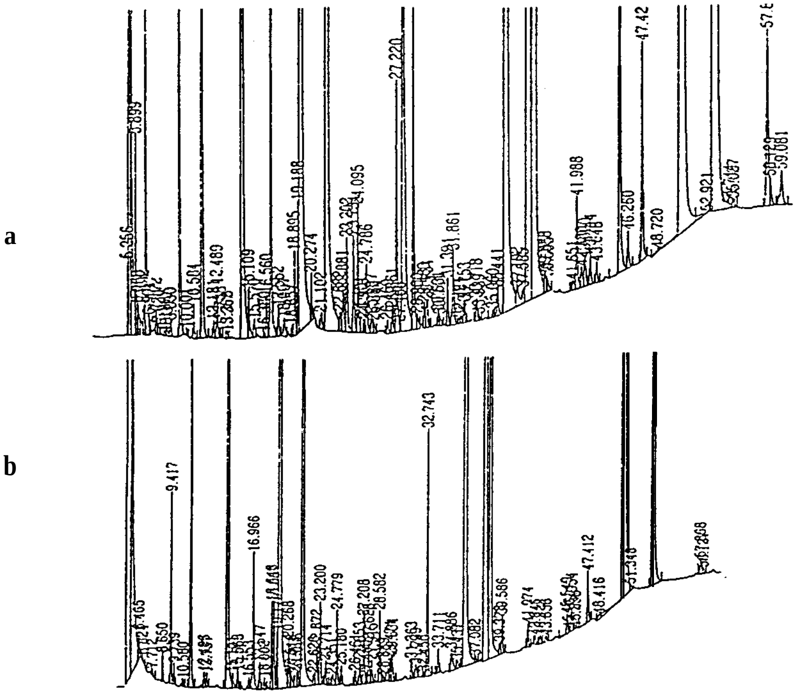

Figure 4. Gas chromatogram of PVC/PCB extract before cleanup (a) and after cleanup (b).

Table 2. Mass balance ratios for PCB congeners in polymeric materials/water.

Congener	Polyethylene/Water		Polystyrene/Water		Polyvinylchloride/Water	
	1hr	12hr	1hr	12hr	1L	12hr
Tri	1.21	0.98	1.09	1.04	1.52	nd
Tetra	1.06	0.97	0.75	0.55	0.92	nd
Penta	0.91	0.95	0.67	0.40	0.66	nd
Hexa	0.99	0.91	1.49	1.53	0.83	nd
Hepta	1.12	1.05	1.56	1.56	0.96	nd
Octa	1.10	1.06	1.47	1.46	0.92	nd
Nona	0.88	1.06	1.30	1.58		
Deca	1.01	1.32	1.28	1.42		

nd= not determined

mass balance for the PCB congeners at 1 and 12 hour intervals were consistant and not significantly different. This shows that the method is equally effective even when the concentration of PCBs in the polymeric materials after 12 hours was more than 1/3 greater than the values of the PCB congeners in the polymers after 1 hour.

Since PCBs can be determined in polymeric packaging materials using the analytical procedures described, studies can now be undertaken to determine the effect of polymer composition and PCB chemical characteristics upon sorption constants. From the partition (K_e) and sorption diffision (D_s) coefficients , the relationship of the package material to the particular PCB congener can be determined. The resulting K_e values can be used to determine the extent of sorption since they indicate the affinity of PCBs for the plastic films.

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