Determination of Polychlorinated Biphenyl (Aroclor 1242) Migration Into Food Types

by
RICHARD P. STANOVICK, S. I. SHAHIED, and EMIL MISSAGHI
Biochemistry Department
Hazleton Laboratories, Inc.
Vienna, Virginia 22180

Polychlorinated biphenyl (PCB) residues were first identified in fish from different Swedish waters by JENSEN (1,2). He also recognized these as potential food contaminants.

A significant portion of PCB's found in paperboard products is contributed by recycled waste paper containing PCB's carbonless "carbon" paper.

Low levels of PCB's were found in numerous foodstuffs by WESTOO, et al., (3). Their report showed that PCB residues were present in all 22 samples of human milk analyzed with 11 samples between 0.0 and 0.50 and the other 11 between 0.60 and 1.0 mg/kg fat.

The purpose of this study was to determine the migration of Aroclor 1242 from treated paperboard of known concentrations (15.0 and 150.0 ppm) into various food types (ready-to-eat flake cereal, cereal grain, packaged cake mix and table spread). This study was also designed to determine if various barriers (polyvinylidene chloride (PVDC) coated paper, waxed glassine and polyethylene) could prevent or reduce the migration of Aroclor 1242 into food.

Experimental

A. Materials

Paperboard:
Aroclor 1242 treated paperboard:
Furnish: 50% bleached hardwood Kraft pulp, 50% bleached soft wood Kraft pulp plus repulped carbonless copy paper to give estimated PCB concentrations of 15.0 and 150.0 ppm

Barriers:
PVDC Coated Paper
Coating Weight: 8 lb/ream
Caliper: 2.0 MILS

Waxed Glassine Paper:
Type: Cereal bag grade waxed glassine
Caliper: 2.4 MILS

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Polyethylene Film:

Type:	Low density
Caliper:	1.4 MILS

Foods:

Ready-to-eat- flake cereal
Cereal grain
Packaged cake mix:
  Dry mix comprised of:
    43% flour
    45% sugar
    12% shortening with emulsifiers
Table spread

B. Design of Study

The study was designed to simulate the commercial packaging of similar food types (ready-to-eat flake cereal, cereal grain, packaged cake mix and table spread). Commercially packed foods were obtained from a local grocery store and the paperboard to food ratio determined, and the most severe ratio was used in this study. The paperboard to food ratios determined are summarized as follows:

Type of Food	Ratio Paperboard to Food	Grams of Paperboard to Grams of Food Used in Study
Ready-To-Eat Flake Cereal	1 to 2	10 to 20
Cereal Grain	1 to 10	5 to 50
Packaged Cake Mix	1 to 10	5 to 50
Table Spread	1 to 15	3 to 45

One-pint hermetically sealed Mason jars were lined with treated paperboard at either the 15.0 or 150.0 ppm level. The food types were placed in the jars in four different ways as follows: direct contact with board, with PVDC barrier between the food and board, with a glassine barrier between the food and board, and with a polyethylene barrier between the food and board. Each jar represented an individual sample. The samples were all stored at room temperature. Ready-to-eat flake cereal and cereal grain were sampled for analysis at two-, 14-, 30-, 60- and 90-day time intervals after initiation of the study. Packaged cake mix and table spread were scheduled for analysis at two, seven, 14, 30 and 60 days.

C. Sample Extraction

Samples were removed from the Mason jars, mixed and 10-gm subsamples were taken for analysis from the ready-to-eat flake cereal and cereal grain. Three-gram subsamples were taken from the packaged cake mix after mixing and table spread as described later.

The subsamples were placed into a 500-ml round-bottomed flask, except for the table spread. One-hundred milliliters of 2% methanolic potassium hydroxide were added and the samples were refluxed for 30 minutes.

The hydrolized samples were filtered and the volume recorded for later correction of each sample weight taken. The entire methanolic hydrolyzates were concentrated, using a vacuum rotary film evaporator, to 10-ml volumes in a water bath maintained at 24 C. Ten milliliters of distilled water were added to each sample and further concentrated to 10 ml. The concentrated samples were transferred quantitatively using 250 ml of 2% sodium chloride solution into 500-ml separatory funnels. The flasks were rinsed with two 50-ml portions of petroleum ether and the rinsings were added to the separatory funnels. The separatory funnels were shaken for one minute and left to stand. The aqueous layers were discarded and the organic petroleum ether layers were washed twice with 50.0 ml of 2% sodium chloride solution. The washings were discarded and the petroleum ether extracts dried through 50 gm of anhydrous sodium sulfate.

The entire table spread sample was removed from the Mason jar and melted down. The molten sample was mixed well and a 3-gm subsample taken and transferred quantitatively with 50 ml of petroleum ether into a 125-ml separatory funnel. The sample was further extracted four times with 25 ml of acetonitrile, previously saturated with petroleum ether. The four acetonitrile extracts were combined and placed into a 500-ml separatory funnel containing 250 ml of 2% sodium chloride and 100 ml of petroleum ether. The separatory funnel was shaken for one minute. After the separation of the layers, the aqueous layer was discarded, the petroleum ether layer was washed twice with 50 ml of 2% sodium chloride and the washings were discarded. The petroleum ether extract was dried through 50 gm of anhydrous sodium sulfate.

D. Florisil Column Chromatographic Clean-Up

The above extracted samples were further cleaned up using florisil column chromatography. The florisil column was prepared as follows: a 25-mm O.D. x 300-mm glass column with teflon stopcock was plugged with glass wool, and filled to 4 inches (after settling) with florisil (Floridin Company, Berkeley Springs, West Virginia) which had been activated at 100 C for a 24-hr period and topped with one-half inch of anhydrous sodium sulfate. The column was prewetted with 100 ml of petroleum ether by allowing the petroleum ether to percolate through to the top of the sodium sulfate. The petroleum ether prewash was discarded.

The petroleum ether extracts were transferred to the columns and eluted into 500-ml round-bottomed flasks at a rate of about 5 ml per minute. The containers were rinsed with petroleum ether. The rinsings were poured on the columns and the walls of the columns were rinsed with additional small quantities of petroleum ether. The columns were eluted with 110 ml of 6:94 ethyl ether/

petroleum ether eluting mixture. The samples were concentrated under flash evaporation to about 10 ml and were transferred quantitatively with rinsings into graduated centrifuge tubes. The samples were further concentrated to 2 ml or as needed under a stream of nitrogen in a water bath at room temperature.

E. Preparation and Extraction of Barriers and Treated Paperboard

The three barriers and the Aroclor-treated paperboard were also assayed for Aroclor 1242 residues as follows. Ten-gram samples of treated paperboard and barriers were accurately weighed, shredded into small pieces and transferred into 500-ml round-bottomed flasks. One-hundred milliliters of 2% methanolic potassium hydroxide were added and refluxed for 30 minutes. The hydrolyzed samples were filtered and 40.0-ml aliquots were transferred to 500-ml separatory funnels. The aliquots were shaken vigorously with 50 ml of petroleum ether and 100 ml of distilled water. Each aqueous layer was drained into a second separatory funnel containing 100 ml of petroleum ether. The separatory funnels were shaken vigorously and the aqueous layers were discarded. The petroleum ether extracts from each sample were combined and washed twice with 50 ml of distilled water. The petroleum ether extracts were taken through anhydrous sodium sulfate and the volumes were adjusted to the required amount for analyses.

F. Analysis by Gas Chromatography

The analyses were carried out on a Micro-Tek Model MT-220 gas chromatograph equipped with an Ni^{63} electron capture detector system. Two- to 5-µl aliquots of the above concentrated samples (from the Florisil clean-up) were injected into the gas chromatograph for analysis. The instrument was operated using the follow-conditions:

Gas Chromatographic Column:	6' x 1/4" O.D. glass, packed with 3% OV-17 on Gas-Chrom Q, 100/120 mesh size
Column Temperature:	220 C
Detector Temperature:	280 C
Inlet Temperature:	275 C
Carrier Gas (Nitrogen):	86 ml/min flow

A typical standard curve was plotted each day for Aroclor 1242. The amount of Aroclor 1242 detected was determined by peak height.

Results and Discussion

The results obtained for Aroclor 1242 migration from treated paperboard into different types of food (for the longest time intervals) are summarized in Tables 1 and 2. The sensitivity of the method for Aroclor 1242 is 0.10 ppm for the various food types.

TABLE 1

Summary of Aroclor 1242 migration from treated paperboard into food (90 days).

Food Type	Sample Number	Barrier	Treated Paperboard Used ppm	Aroclor 1242 Found ppm
Ready-To-Eat	1	No Barrier	20.0	0.57
Flake Cereal	2	PVDC	"	<0.10
"	3	Glassine	"	<0.10
"	4	Polyethylene	"	0.26
"	17	No Barrier	159.0	4.30
"	18	PVDC	"	0.13
"	19	Glassine	"	0.89
"	20	Polyethylene	"	1.98
Cereal Grain	5	No Barrier	20.0	0.26
"	6	PVDC	"	<0.10
"	7	Glassine	"	0.18
"	8	Polyethylene	"	<0.10
"	21	No Barrier	159.0	1.80
"	22	PVDC	"	<0.10
"	23	Glassine	"	0.50
"	24	Polyethylene	"	0.63

Prior to initiation of the study the foods, barriers and treated paperboard were analyzed. The results of the treated paperboard analyses indicated 20.0 ppm (average) Aroclor 1242 at the lower level and 159.0 ppm (average) at the higher level. The treated paperboard was also analyzed upon termination of the study and the results indicated 10.0 ppm (average) at the low level and 84.0 ppm (average) at the high level. When the paperboard was received at Hazleton it was assumed that the level of Aroclor 1242 would be homogenous throughout the roll, which it was not. This will explain the reason that the residue level detected in the food types doubled in amount between the 30-day time interval and the 60-day time interval. The latter time intervals (60 and 90 days) represented the first paperboard that came off the rolls.

TABLE 2

Summary of Aroclor 1242 migration from treated paperboard into food (60 days).

Food Type	Sample Number	Barrier	Treated Paperboard Used ppm	Aroclor 1242 Found ppm
Packaged Cake Mix (12% Shortening)	9	No Barrier	20.0	0.38
"	10	PVDC	"	0.19
"	11	Glassine	"	0.20
"	12	Polyethylene	"	0.10
"	25	No Barrier	159.0	1.33
"	26	PVDC	"	<0.10
"	27	Glassine	"	0.34
"	28	Polyethylene	"	1.20
Table Spread	13	No Barrier	20.0	0.33
"	14	PVDC	"	<0.10
"	15	Glassine	"	0.14
"	16	Polyethylene	"	0.10
"	29	No Barrier	159.0	0.93
"	30	PVDC	"	<0.10
"	31	Glassine	"	0.78
"	32	Polyethylene	"	0.90

Conclusions

1. The investigation was designed to elucidate the mechanism of migration of Aroclor 1242 to packaged foods. It was conducted in sealed glass jars and the packaging materials used had been treated to contain higher levels of Aroclor 1242 than are commonly found in food packaging materials presently used in the food industry. The data indicate that migration is a vapor-phase phenomenon. Accordingly, interposing barrier materials between Aroclor bearing paperboard and food significantly reduces the migration to food. The degree of the reductions appears inversely correlated with the known gas permeabilities for the classes of barrier materials studied. Of these, PVDC-coated paper prevented Aroclor migration for the 90-day test period. Waxed glassine paper was found to be second most effective of the barriers included in this study. Polyethylene film was relatively ineffective at the longer storage intervals.

2. In the absence of an effective barrier, Aroclor 1242 was shown to migrate from paperboard to food in measurable amounts when food is packaged in paperboard containing a significant amount of Aroclor 1242.

3. Pick-up of Aroclor 1242 by packaged foods is predominately an adsorption phenomenon. The equilibrium adsorption of Aroclor 1242 on food is primarily dependent on the surface area of the food and only secondarily dependent on the fat content of the food. This suggests that adsorption is a surface condensation mechanism.

4. The effectiveness of other barrier materials commonly used in food packaging, e.g., foil laminates, copolymer films, paper laminates was not investigated. The results of this study would suggest that materials of low gas permeability would be effective barriers to PCB migration.

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