

Considerations for Reuse of Poly(ethylene terephthalate) Bottles in Food Packaging: Migration Study

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Experiments were performed to evaluate the significance of potential contamination of postconsumer poly(ethylene terephthalate) (PETE) on the reuse of such material as food packaging. The protocol in the FDA document *Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations* (FDA, 1992) that are routinely employed to evaluate recycling processes for removal of potential contaminants were used. Two-liter PETE bottles were contaminated separately with benzene, butyric acid, malathion, and lindane at 40 °C for 2 weeks, rinsed, dried, and cut into small chips. The contaminated chips were washed at 73 °C, dried with an IR lamp, and extracted using 8% aqueous ethanol solution at 49 ± 1 °C for 30 days. After 30 days, approximately 60% of the benzene, 30% of the butyric acid, and 30% of the lindane had migrated from the contaminated chips into the 8% ethanol solution, but no measurable concentration of malathion was observed.

Keywords: Reused PETE; migration; residual contaminants; food simulant

INTRODUCTION

The reuse and recycling of beverage bottles are common commercial practices. Reuse of postconsumer poly(ethylene terephthalate) (PETE) beverage bottles by refilling is currently practiced widely in the European Community (Covell, 1995). The postconsumer PETE beverage bottles intended for reuse could become incidentally contaminated with foreign chemicals such as household pesticides due to possible misuse by consumer. These chemicals could diffuse into the polymer matrix, and back into the product, analogous to those reported by Landsberg *et al.* (1977), who studied multiuse of milk containers. As a result, a rigorous quality control program is currently used in the refilling of PETE beverage bottles. State-of-the-art, sophisticated detectors, such as FID, ECD, and MSD used in gas chromatography and extensive visual inspection, form an integral part of the program. These detectors are used to identify and remove any contaminated bottles from the cleaning process prior to being filled. This study investigates the need for a rigorous quality control program in refilling PETE beverage bottles by considering the consequences of relying solely on washing to remove potential contamination. The objective of this study was to test the bottles using analytical protocols developed according to FDA documentation (FDA, 1992) by simulating contamination of 2-L PETE bottles with various test chemicals, determining the effect of a minimal washing procedure on removal of test chemicals from spiked PETE bottle material, and determining the migration of the residual contaminants from the washed PETE into 8% aqueous ethanol, which was used as a food simulant.

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Table 1. Concentrations of Contaminants Used for Spiking 2-L PETE Bottles

surrogate	category	concentration (w/v)
benzene	volatile, nonpolar	10% in hexane
butyric acid	volatile, polar	1% in hexane
lindane	nonvolatile, nonpolar	0.1% in hexane
malathion	nonvolatile, polar	5% in water

MATERIALS AND METHODS

Reagents. All chemicals were of reagent grade.

Contaminants. Benzene, lindane, and butyric acid were of reagent grade. Malathion was of 57% purity, commercial grade (Platte Chemical Co., Inc., Fremont, NE). Selection of these contaminants was based on the recommendations in FDA guidelines (FDA, 1992).

Apparatus. A Varian 3400 gas chromatograph (GC) (Varian Associates, Sugar Land, TX) with flame ionization detector (FID), flame photometric detector (FPD), and electron capture detector (ECD) was used. The Varian system was controlled by a 486 computer using STAR workstation software.

PETE Material. Unused, clean, blow-molded, 2-L clear PETE bottles without caps and base cups were supplied by Eastman Chemical Co. (Kingsport, TN). These bottles were used to simulate refillable PETE bottles.

Contaminated PETE. Contaminated PETE material was prepared according to a spiking method using individual benzene, butyric acid, lindane, and malathion. In the spiking method, clean PETE bottles were separately contaminated with each contaminant at the concentration shown in Table 1. The bottles were completely filled with the contaminant solutions, capped, placed in an incubator, and maintained at 40 °C for 2 weeks. After incubation, the contaminant solutions were removed and the bottles were cut vertically in half and blotted twice with Kimwipes and hexane. The bottle contaminated with the malathion solution became yellowish, while other contaminated bottles did not appear to change. After blotting, the cylindrical wall portion was separated from the shoulder and the bottom and cut into small chips (approximately 0.5 cm × 0.5 cm). Unlike Feron and co-workers (Feron *et al.*, 1994), who used the whole bottle in their migration study, this study used the chips obtained from the cylindrical wall instead. This approach minimized the variability of concentration of the same contaminant present in two different bottles, and it reduced the number of bottles used

to one per contaminant. The uptake concentration of the contaminants in the chips had been determined prior to the washing procedure described below by using the analytical methods developed at the National Center for Food Safety and Technology. Two replicates of chips were used.

Small-Scale Washing Experiments. Small-scale washing experiments were performed using a 250-mL beaker containing 21 ± 0.5 g of spiked PETE and 210 mL of deionized water. The deionized water was preheated to 74 ± 3 °C on a hot plate before the spiked PETE chips were added. This temperature was relatively high compared with the temperature 50–60 °C (Feron *et al.*, 1994) used in most commercial processes for washing reusable PETE bottles. However, this temperature was comparable to the 75 °C temperature that is currently used for new refillable PETE bottles in Europe (Covell, 1995). The mixture was stirred with a 3.4 mm i.d. three-blade propeller agitator equipped with a laboratory mixer (Lightnin Model DS 3014, Mixing Equipment Co., Avon, NY) operated at 600 rpm for 30 min. After washing, the chips were removed from the washing solution with a sieve and dried for 15 min by using a sieve shaker and an IR lamp (Kamolprasert and Lawson, 1995). The washed chips shrank as expected because of the thermal warpage.

Extraction Experiments. Migration of residual contaminants in washed PETE chips was measured by extraction experiments using 8% ethanol in water, a food simulant suggested by the FDA (1993). This system was different from that in the work reported by Feron *et al.* (1994), who used carbonated water both with and without modifier addition. In this study, the experiments were performed using a 100-mL glass jar containing 50 mL of 8% ethanol solution and 1.5 g of washed chips (10 mL of 8% ethanol solution per 6.45 cm² of chips). The jar was crimp-sealed with a Teflon-faced septum and placed in an incubator (Precision mechanical oven, Model STM 40, Precision Scientific, Chicago, IL). A temperature of 49 ± 1 °C was maintained for 30 days as suggested by the FDA (1993). For each contaminant, 12 replicates from the same bottle were prepared. The jars were manually shaken for 10 s each day while being incubated, and the concentration of the contaminants in the 8% ethanol solution and PETE chips was determined after 1, 2, 5, 10, 20, and 30 days of storage. Two replicates were withdrawn from the incubator at each storage time.

Quantification of Contaminants in PETE Chips. *Benzene.* Concentrations of benzene in spiked PETE were quantified by using the total dissolution coupled with liquid-liquid partition, which was developed by Pierce and co-workers (D. E. Pierce, A. R. Lawson, and G. D. Sadler, Illinois Institute of Technology, personal communication, 1993) with a modification. In the method, spiked PETE was dissolved in trifluoroacetic acid (TFA) and benzene was then partitioned twice with *n*-pentane instead of *n*-heptane as used by Pierce and co-workers (D. E. Pierce *et al.*, personal communication, 1993). Benzene was then quantified by GC/FID. The limit of quantification (LOQ) was 500 ppb. Recoveries ranged from 65 to 94% with repeatability of $\pm 4\%$ for PETE chips spiked with benzene at concentrations of 5–500 ppm.

Butyric Acid. Concentrations of butyric acid in spiked PETE were quantified with a procedure developed by Komolprasert *et al.* (1995). Spiked PETE was dissolved in a mixture of hexafluoro-2-propanol (HFIP) and methylene chloride (MC). The solution was diluted with MC before polymer precipitation by using acetone. The mixture was vacuum-filtered, and the filtrate was subsequently concentrated by rotary evaporation. The concentrate was filtered, and butyric acid was quantified by GC/FID. The LOQ was 1 ppm and recoveries ranged from 85 to 95% with repeatability of $\pm 5\%$ for PETE chips spiked with butyric acid at concentrations of 1–500 ppm.

Malathion. Concentrations of malathion in spiked PETE were quantified by using the procedure developed by Komolprasert *et al.* (1995) with modifications. Spiked PETE was dissolved in a mixture of TFA instead of HFIP and MC. The solution was diluted with additional MC before polymer precipitation by using methanol. The mixture was vacuum-filtered, and the filtrate was subsequently concentrated by rotary evaporation. The concentrate was dissolved in potas-

sium acetate buffer solution (pH 5.3), and the mixture was filtered through a C₁₈ cartridge for cleanup prior to determination of malathion by GC/FPD. The LOQ was 1 ppm, and recoveries ranged from 72 to 93% with repeatability of $\pm 8\%$ for PETE chips spiked with malathion at concentrations of 1–500 ppm.

Lindane. Concentrations of lindane in spiked PETE were quantified by using the procedure for malathion determination (Komolprasert *et al.*, 1995) with modifications. The modifications included the use of deionized distilled water instead of the buffer solution and determination of lindane by GC/ECD instead of GC/FPD. The LOQ was 15 ppb. Recoveries ranged from 70 to 80% with repeatability of $\pm 5\%$ for PETE chips spiked with lindane at concentrations of 15 ppb and 5 ppm.

Quantification of Contaminants from 8% Ethanol/Water Solution. *Benzene.* Concentrations of benzene in 8% ethanol/water solution were determined by using the liquid-liquid partition that was used with the PETE chips. In the procedure, benzene was extracted from 8% ethanol solution with *n*-pentane, separated on an SPB-5 column (30 m \times 0.53 mm \times 0.5 μ m) (Supelco, Bellefonte, PA), and quantified by GC/FID. The LOQ was 500 ppb by GC/FID. Recoveries of benzene from the 8% ethanol solution spiked at concentrations of 500–1000 ppb were 78–91% with repeatability of $\pm 6\%$.

Lindane. Concentrations of lindane in 8% ethanol/water solution were determined by using liquid-liquid partition. In the procedure, lindane was extracted from 8% ethanol solution with hexane, separated on an SPB-5 column (30 m \times 0.53 mm \times 0.5 μ m) (Supelco), and quantified by GC/ECD. The LOQ was 0.1 ppb. Recoveries of lindane from the 8% ethanol/water solution spiked at concentrations of 0.1–10 ppb were 92–98% with repeatability of $\pm 3\%$.

Butyric Acid. Concentrations of butyric acid in 8% ethanol/water solution were determined simply by concentration using rotary evaporation. The concentrate obtained was diluted with acetone, and butyric acid was separated on a Nukol column (30 m \times 0.32 mm \times 0.25 μ m) (Supelco) and quantified by GC/FID. The LOQ was 20 ppb. Recoveries of butyric acid from the 8% ethanol/water solution spiked at concentrations of 20–200 ppb were 84–85% with repeatability of $\pm 2\%$.

Malathion. Concentrations of malathion in 8% ethanol/water solution were determined according to the procedure used with PETE chips, but without the polymer dissolution and polymer precipitation steps. Malathion was eluted from a C₁₈ cartridge with xylene, separated on an SPB-5 column (30 m \times 0.53 mm \times 0.5 μ m) (Supelco), and quantified by GC/FPD. The LOQ was 50 ppb. Recoveries of malathion from the 8% ethanol/water solution spiked at concentrations of 50–100 ppb were 114–118% with repeatability of $\pm 1\%$.

Statistical Analysis. Chi-square mean comparison test of StatMost Statistical Analysis and Graphics Software for Windows (DataMost Corp., 1994) was used to analyze the obtained data.

RESULTS AND DISCUSSION

Effects of Simple Washing on Removal of Contaminants from Spiked PETE Bottle Material. The concentrations of benzene, butyric acid, lindane, and malathion in PETE bottle material before and after washing are shown in Table 2. The results indicate that simple washing at 74°C significantly ($P < 0.05$) reduced the concentrations of benzene to 74%, malathion to 64%, lindane to 58%, and butyric acid to 51% of their initial concentrations.

Migration of Residual Benzene, Lindane, Butyric Acid, and Malathion from Washed, Spiked PETE Bottle Material to 8% Ethanol/Water Solution. The amount of benzene in the 8% ethanol/water solution and in the extracted PETE chips was determined, normalized, and plotted (Figure 1). The percent of benzene left in the PETE chips decreased with respect to the concentration of the pre-extracted chips, whereas that in the 8% ethanol/water solution increased loga-

Table 2. Concentrations of Benzene, Butyric Acid, Lindane, and Malathion in PETE Bottle Material before and after Washing with Deionized Water at 74 ± 3 °C for 30 min and Drying for 15 min with an IR Lamp

surrogate	concentration (ppm, $\mu\text{g/g}$) \pm SD		
	before washing	after washing and drying	% residue after washing \pm SD ^a
benzene	308 \pm 8	223 \pm 18	74 \pm 5 ^S
butyric acid	57 \pm 2	29 \pm 2	51 \pm 4 ^S
lindane	100 \pm 14 ^b	58 \pm 3 ^b	58 \pm 3 ^S
malathion	1286 \pm 244	818 \pm 44	64 \pm 3 ^S

^a SD, standard deviation. A superscript S indicates significance based on Chi-square test between before and after washing and drying. ^b Concentration in ppb, ng/g.

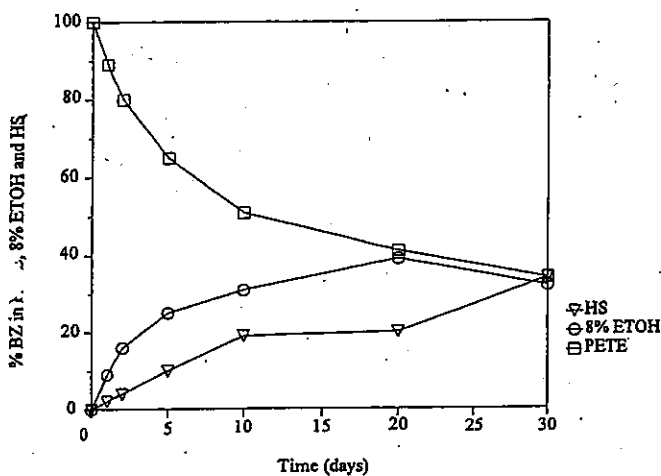


Figure 1. Percentage of benzene (BZ) in PETE chips, 8% ethanol (ETOH)/water solution, and headspace (HS) calculated by the difference between 100 and the sum of the percentage of BZ and ETOH during extraction at 49 ± 1 °C after 1, 2, 5, 10, 20, and 30 days of storage.

arithmically. Benzene in the 8% ethanol/water solution also partitioned into the headspace. It was not measured but was calculated as the difference. The calculation was based on assumptions that the variation in initial concentration of the benzene in pre-extracted, washed PETE chips from different jars was negligible, as was the loss of benzene through the crimp-top seal during storage. As a result, the amount of benzene in the headspace at each storage time equaled the difference between the average benzene amount measured in the pre-extracted PETE chips and the sum of the benzene amounts measured in the 8% ethanol solution and in the extracted PETE chips at each corresponding storage time. The calculated amounts of benzene in the headspace were also normalized to the benzene concentrations of pre-extracted chips and are plotted in Figure 1. The benzene in the headspace increased with time but did not seem to reach equilibrium. It is possible that the headspace affected the rate of benzene migration from the chips to the 8% ethanol solution. An additional experiment with no headspace is required. Regardless of the headspace, approximately 65% of benzene diffused into the 8% ethanol solution after storage at 49 ± 1 °C for 30 days.

The percentage of butyric acid in the 8% ethanol/water solution and in the extracted PETE chips was determined and is plotted in Figure 2. Except for the data at the 10th day of storage, results are similar to those observed for benzene. The amount of butyric acid in the extracted PETE chips decreased, whereas the level in the 8% ethanol/water solution increased and reached equilibrium after 10 days of storage. On the

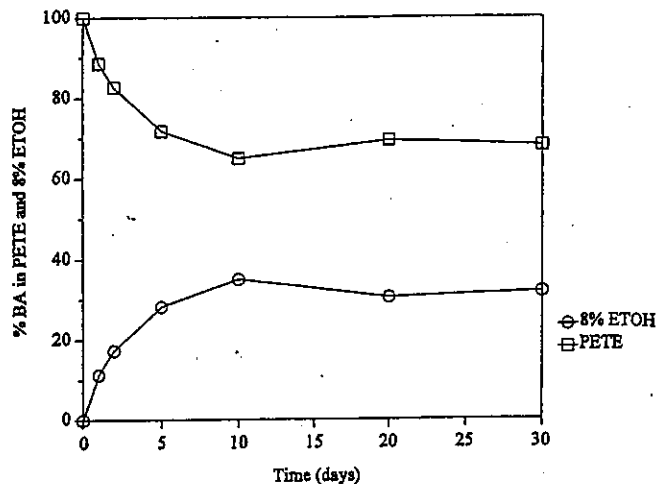


Figure 2. Percentage of butyric acid (BA) in PETE chips and 8% ethanol (ETOH)/water solution during extraction at 49 ± 1 °C after 1, 2, 5, 10, 20, and 30 days of storage.

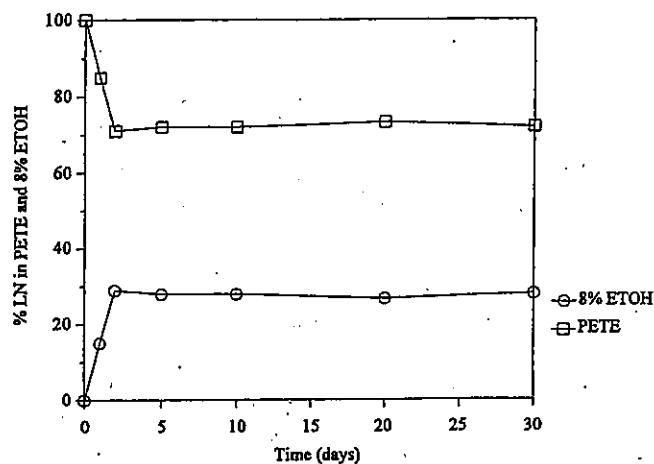


Figure 3. Percentage of lindane (LN) in PETE chips and 8% ethanol (ETOH)/water solution during extraction at 49 ± 1 °C after 1, 2, 5, 10, 20, and 30 days of storage.

basis of a mass balance calculation, the amount of butyric acid partitioning into the headspace was negligible, regardless of the variation in quantitation. The overall results indicate that approximately 30% of the butyric acid migrated from the PETE chips into the 8% ethanol/water solution after storage at 49 ± 1 °C for 30 days.

The percentage of lindane in the 8% ethanol/water solution and in the extracted PETE chips was determined and is plotted in Figure 3. The results indicate that the amount of lindane in the 8% ethanol/water solution increased during the first 2 days of storage and then became constant. This may be a result of desorption of lindane from the surface of the chips, which occurred before the actual migration of lindane from the matrix, which was slow to reach saturation. The overall results indicate that approximately 30% of the lindane migrated from the PETE chips into the 8% ethanol/water solution after storage at 49 ± 1 °C for 30 days.

The percentage of malathion in the extracted PETE chips at various storage times was determined and is plotted in Figure 4. The amount of malathion present in the 8% ethanol/water solution was unmeasurable; this result may have been due to slow migration or instability of the malathion in the 8% ethanol solution. The instability of malathion in aqueous ethanol solution may be explained by the significant effects of pH, temperature, and storage time on decomposition of

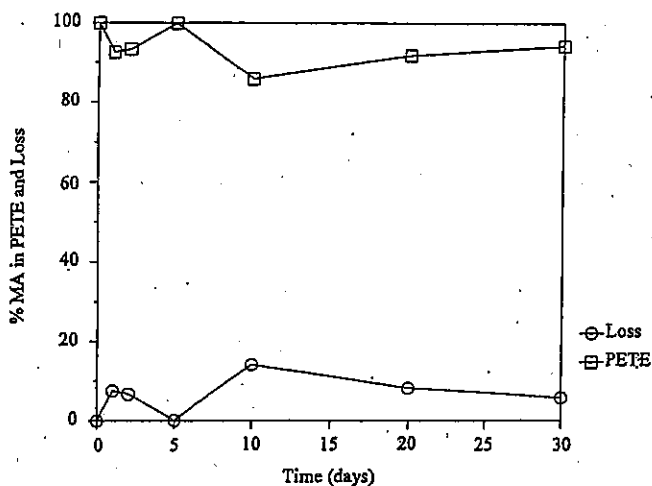


Figure 4. Percentage of malathion (MA) in PETE chips and unaccountable amount (loss) during extraction at 49 ± 1 °C after 1, 2, 5, 10, 20, and 30 days of storage.

Table 3. Average Concentrations (ppb, ng/mL) of Benzene, Butyric Acid, and Lindane in 8% Ethanol/Water System after Extraction at 49 ± 1 °C for 1, 2, 5, 10, 20, and 30 Days of Storage

contaminant	storage time					
	1 day	2 days	5 days	10 days	20 days	30 days
benzene	600	1060	1660	2060	2620	2140
butyric acid	120	180	300	260	300	300
lindane	0.25	0.42	0.4	0.5	0.4	0.52
malathion	ND ^a	ND	ND	ND	ND	ND

^a ND, not detected (less than limit of quantification, 50 ppb).

malathion in the aqueous systems as reported by Garcia-Repetto *et al.* (1994), Larcorte *et al.* (1995), and Lartiges and Garrigues (1995). In Figure 4, the unaccountable or unmeasurable malathion is the difference between the initial amount of malathion and the residual amount of malathion at each storage time.

Concentration of Benzene, Butyric Acid, Lindane, and Malathion in 8% Ethanol in Water Solution. Table 3 summarizes the average concentration (parts per billion) of benzene, butyric acid, and lindane in 8% ethanol/water food-simulating system after extraction at 49 ± 1 °C for 1, 2, 5, 10, 20, and 30 days of storage. These concentrations (0.25 ppb of lindane to 2620 ppb of benzene) are in the same range as many other compounds (<0.1 ppb of methalaxyl to 615 ppm of methanol) that were tested and reported by Feron *et al.* (1994).

CONCLUSIONS

Although the simple washing significantly removed the contaminants from washed PETE, the residual contaminant concentrations were still high. As a result, approximately 60% of the benzene, 30% of the butyric acid, and 30% of the lindane migrated from the chips to the 8% aqueous ethanol food simulant. However, no measurable concentration of malathion was observed in the 8% aqueous ethanol after 30 days of storage.

These results indicate that the simple washing procedure used in this study was not effective enough in removing the contaminants from the contaminated 2-L PETE bottles. The results support the use of sophisticated instrumental detector systems and visual inspections, which are currently used in refilling PETE beverage bottles. These safeguards are necessary to assure that any contaminated bottles are detected and

removed prior to the cleaning process and subsequent refilling. Therefore, thorough and specifically designed cleaning processes could dramatically reduce residual contaminants in the PETE intended for reuse as food packaging.

The above safeguards protect the consumer from exposure to contaminants derived from potentially misused refillable PETE bottles. Nevertheless, studies were performed to assess the hazard in the highly unlikely event that a misused refillable bottle should reach the consumer. To assess the safety of reused PETE in food packaging applications, toxicological data must be considered. On the basis of the extensive, collaborative work of Feron *et al.* (1994), reused PETE beverage bottles present no health risk to the consumer. This conclusion was reached by evaluating the actual level of a broad range of toxic chemicals found in simulated beverage stored in PETE refillable bottles after contamination with these chemicals under worst-case conditions. The evaluation was based on comparing the levels found in the beverage by using standard measures of toxicity, *i.e.*, maximum potential exposure (MPE), acceptable daily intake (ADI), and probability of multiple exposures (chronic exposure) versus a single exposure (acute exposure).

It should be noted that, instead of reuse, the PETE may be recycled by using a process that effectively removes any residual contaminants from postconsumer material. Additional studies are underway in our laboratory to evaluate the migration of contaminants from the secondary recycled PETE material. Reprocessing by extrusion under conditions of thorough mixing can be expected to distribute uniformly any residual contaminants throughout the recycled material. As a result, the migration of any residual contaminant would be expected to be less than what was observed in this study.

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Received for review May 30, 1996. Revised manuscript received November 14, 1996. Accepted November 20, 1996.*

This research was supported by Cooperative Agreement FD-000431 from the U.S. Food and Drug Administration and by the National Center for Food Safety and Technology.

JF9603801

* Abstract published in *Advance ACS Abstracts*, January 15, 1997.

