Analytical Procedure for Quantifying Five Compounds Suspected as Possible Contaminants in Recycled Paper/Paperboard for Food Packaging

Yoon S. Song,*,† Hong J. Park,‡ and Vanee Komolprasert†

Division of Food Processing and Packaging, U.S. Food and Drug Administration, National Center for Food Safety and Technology, 6502 South Archer Road, Summit-Argo, Illinois 60501, and Rural Living Science Institute, 88-2 Seodundong, Suwon, Korea

Because contaminants in recycled paper intended for food packaging could be a risk to public health, analytical methods are needed to identify and quantify residues of concern in paper/paperboard. The U.S. Food and Drug Administration is considering development of a guidance document for testing levels of contaminants that might be retained through paper recycling processes. An analytical procedure was developed using paper spiked with suspected contaminants at concentrations of 1−50 ppm in the paper. Benzophenone, dimethyl phthalate, anthracene, methyl stearate, and pentachlorophenol were introduced by soaking the paper in a solution in acetone at 25 °C for 24 h; the paper was removed and dried by evaporating the solvent with nitrogen. The model contaminant residues were extracted from the paper using ultrasonication and quantified by GC with flame ionization and electron capture detectors. Recoveries from the spiked paper were 80−109% with a repeatability of ±4%. The method was also used to analyze commercial recycled paperboard to validate its applicability.

Keywords: *Benzophenone; pentachlorophenol; anthracene; dimethyl phthalate; methyl stearate; analytical methods; ultrasonication; recycled paper*

INTRODUCTION

Paper is the most common packaging material, being utilized in 48% of all packaging (Janda, 1995). Reclaimed fiber is used in some paper and paperboard food-packaging materials. However, very few data are available to show whether recycled paper/paperboard materials are of a purity suitable for food use.

The Code of Federal Regulations (FDA, 1995), 21 CFR 176.260, permits the use of pulp from reclaimed fiber for food-packaging applications as long as postconsumer feedstock for paper recycling facilities does not "contain any poisonous or deleterious substance which is retained in the recovered pulp and that migrates to the food." The regulation does not provide information to help companies determine whether finished food-contact products manufactured by recycling are of suitable purity for their intended use (Paquette, 1998). In response to requests by industry to evaluate specific recycling processes for compliance with applicable food additive regulations, the FDA is considering a testing protocol for recycled paper/paperboard processes (Paquette, 1998) similar to that for recycled plastics (FDA, 1992). The protocol might use several substances, representing specific contaminant classes potentially found in feedstock, to test the efficacy of the recycling processes in reducing these contaminants to levels of no concern.

In this study, five model compounds—benzophenone, pentachlorophenol (PCP), anthracene, dimethyl phthalate, and methyl stearate—were selected on the basis of the FDA's preliminary test protocol (Paquette, 1998). Benzophenone and PCP are relatively nonvolatile, polar contaminants. The former is a common ink component used as a UV photoinhibitor; the latter is a biocide once used to prevent microorganisms from growing on paper packaging products. Anthracene, dimethyl phthalate, and methyl stearate are relatively nonvolatile, nonpolar contaminants commonly found in pulp and paper and are components of polyaromatic hydrocarbons (PAHs), adhesives, and defoamers, respectively. One way to ensure compliance with the FDA regulations is to determine how much of such substances might be present as residues in recycled paper and thereby become contaminants of food. Consequently, analytical methods are needed to quantify residues of concern in paper/paperboard.

To our knowledge, no standard analytical procedure is available specifically for these five compounds in paper/paperboard. Several researchers have indicated that ultrasonication is a simple, precise, and effective method for rapidly extracting various compounds from matrices similar to paper, such as wood and plant leaves. McDonald (1984) determined chlorophenols in wood samples by using ultrasonic extraction (USE) with 1% acetic acid in methanol, followed by ion exchange analysis and high-pressure liquid chromatography (HPLC). Besner et al. (1995) measured PCP and oil contents in wood samples using the USE method with a 1:1 mixture of Freon 113 and methanol, followed by gas chromatography (GC). Extraction recoveries for both studies ranged from 94 to 103%. Okamura et al. (1994) and Tena et al. (1997) also successfully extracted various

* Author to whom correspondence should be addressed [telephone (708) 728-4126; fax (708) 728-4177].

† U.S. Food and Drug Administration.

‡ Rural Living Science Institute.

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Table 1. GC Conditions for Determining Five Test Compounds in Paper/Paperboards

	GC-ECD[a]	GC-FID[b]	GC-MSD[c]
surrogate	pentachlorophenol	others[d]	?
injector; temp, °C	SPI,[e] 280	SPI, 280	splitless, 280
column	EC-1	DB-5	DB-5
	30 m × 0.32 mm i.d. × 0.25 μm (Alltech, Deerfield, IL)	30 m × 0.32 mm i.d. × 0.25 μm (J&W Scientific, Folsom, CA	30 m × 0.32 mm i.d. × 0.25 μm (J&W Scientific, Folsom, CA)
column temp, °C	60 °C for 5 min, 12 °C/min to 280 °C, hold 6 min	60 °C for 5 min, 12 °C/min to 280 °C, hold 6 min	60 °C for 5 min, 12 °C/min to 280 °C, hold 6 min
carrier gas, mL/min	nitrogen, 3.0	helium, 3.0	helium, 0.7
makeup gas, mL/min	nitrogen, 27.0	helium, 27.0	none
detector[c]; temp, °C	ECD; 300	FID; 300	MSD; 300
hydrogen flow rate, mL/min	none	30	none
air flow rate, mL/min	none	300	none

[a] ECD, electron capture detector. [b] FID, flame ionization detector. [c] MSD, mass selective detector. [d] Anthracene, benzophenone, dimethyl phthalate, methyl stearate. [e] SPI, septum programmable injector.

phenolic compounds from dried and fresh plant leaves using USE with acetone.

This paper describes an analytical procedure based on USE with modifications of that reported by Tena et al. (1997) for the GC analysis of the five suspected contaminants in paper.

MATERIALS AND METHODS

Reagents. All chemicals were of reagent grade.

Standard Spiking Solutions. Standard solutions in acetone were prepared with 0.5, 2.5, and 12.5 ppm (w/v) each of benzophenone, pentachlorophenol (PCP), anthracene, dimethyl phthalate, and methyl stearate.

Paper Material. Homogeneity is very important in the analysis of recycled paper/paperboard products as the amount of test substances in spiked paper matrices could decrease dramatically in the inner layers. In a test using 0.2% methylene blue in acetone, the dye did not penetrate evenly into commercial paperboard layers with an average thickness of 0.5080 mm. Thus, paper with a thickness of only 0.0762 or 0.0813 mm was used to simulate more closely the contamination expected in postconsumer feedstock.

Two virgin papers with different porosities were used: Staging liner paper with a density of 0.60 g/cm^3 and a thickness of 0.0813 mm (Perseco, Oak Brook, IL) and Kimwipes paper with a density of 0.23 g/cm^3 and a thickness of 0.0762 mm (Kimberly-Clark, Roswell, GA). Paper was cut into strips (0.0254 m × 0.00635 m) with a paper cutter and placed in a mechanical convection oven (Precision model STM 40, Scientific Inc., Chicago, IL) maintained at 60 °C until a constant weight was obtained. The dried paper strips were stored in a desiccator and then exposed to the five test compounds at levels targeted to mimic worst-case postconsumer feedstock contamination.

Three commercial recycled paperboard boxes used for packing cereals were also tested for applicability of the method developed. These were manufactured in January, April, and July 1998 and obtained from Kraft Foods (Rye Brook, NY). The paperboards were peeled to layers with a thickness of ≤0.25 mm to increase the extraction efficiency, cut into small strips, and subjected to the same extraction procedure as the virgin paper.

Ultrasonic Extraction (USE). In this method, 30 mL of acetone was added to the 1.25 or 2.50 g uncontaminated (control) or spiked paper strips in a 35-mL centrifuge tube. Each tube was centrifuged at 700*g* for 3 min to remove air bubbles trapped in the tube and then sonicated in an ultrasonic bath (Ultrasonic Cleaner 8891R-DTH, Cole-Parmer, Vernon Hills, IL) for 15 min. The extract was transferred to a 250 mL round, flat-bottom flask, and each paper strip was re-extracted using the same procedure two more times. Each paper strip was then transferred to a porcelain Büchner funnel (5.3 cm i.d. × 10.1 cm high) on a 50 mL vacuum flask and filter-washed with an additional 30 mL of acetone. The filtrate and extract were combined in the 250 mL flask and concentrated to 1−2 mL with a rotary evaporator (Rotavapor RE 120, Brinkmann Instruments, Westbury, NY) at 40 °C and 60 rpm. The concentrate was diluted with acetone to 5 mL and filtered with a 0.5 μm pore PTFE filter unit (Millipore, Milford, MA) to remove any remaining paper residue.

Gas Chromatography Analysis. A gas chromatography system (Varian Analytical Instruments, Sugar Land, TX) consisting of a Varian 3400 chromatograph, a flame ionization detector (FID), an electron capture detector (ECD), and STAR workstation software (Varian Analytical Instruments) was used to separate the benzophenone, dimethyl phthalate, anthracene, methyl stearate, and PCP in paper extracts: 1 mL of extract was transferred to a 2 mL vial and placed on the carousel tray of the autosampler; 2−4 μL of extract was injected into the GC system for analysis. A Hewlett-Packard 5890 series II gas chromatograph with a 5971 series mass selective detector (MSD) (Hewlett-Packard, Avondale, PA) was used to confirm the identities of these contaminants when they were detected in the extracts of the commercial recycled papers by other detectors. The conditions of GC analysis for determining each contaminant are described in Table 1.

Limit of Detection (LOD). The LOD of standard solutions of the five test compounds was determined at a signal-to-noise (S/N) ratio of 3. With this criterion, the LODs of benzophenone, PCP, anthracene, dimethyl phthalate, and methyl stearate in the paper extracts were 200, 10, 400, 500, and 500 ppb, respectively. However, the limits of quantitation (LOQs) in extracts from the paper matrix were ∼50 ppb for PCP and 1 ppm for the other compounds.

Recovery Studies. For these studies, 1.25 or 2.50 g of uncontaminated cut paper was placed in the 35 mL centrifuge tube, followed by 5 mL of standards solution, which almost entirely soaked into each 2.5 g sample in the tube. For 1.25 g samples, <15% of the solution was left on the bottom of the tube. In both cases the paper absorbed all of the residual solution during nitrogen purging. The purging system used directed the nitrogen flow toward the top of the glass tube and its paper layers, so that the solvent already soaked into the paper was evaporated first, not the residual solution at the bottom of the tube. Thus, the paper remained wet after all residual solution had disappeared from the bottom of the tube.

The tube was tightly sealed with a screw cap, wrapped with aluminum foil, and stored at 25 °C for 24 h. Any solvent trapped in the paper was evaporated to dryness under a stream of nitrogen (500 mL/min), and the dried and spiked paper remaining in the tube was subjected to the extraction procedure described previously. At least three replicates were used. The extraction was initiated without transferring the dried and spiked paper to a new tube because the paper had adsorbed all of the solutes, as was confirmed by analyzing an empty tube with its paper removed to test whether any residues remained on the tube surface after purging. The residual amount in the tube was negligible, below the LOQ.

The appropriateness of the spiking conditions for ensuring complete uptake of the contaminants by the paper was tested by using a Staging liner paper spiked with benzophenone, anthracene, dimethyl phthalate, and methyl stearate at a 10

Table 2. Recoveries of Benzophenone, Anthracene, Dimethyl Phthalate, and Methyl Stearate from Paper Samples Spiked at 10 ppm and Stored under Different Conditions

storage conditions	av % recovery ± RSD[a]				
	replicates	benzophenone	anthracene	dimethyl phthalate	methyl stearate
1 day, 25 °C	3	93 ± 2	97 ± 2	91 ± 3	99 ± 3
7 days, 40 °C	3	91 ± 3	95 ± 2	89 ± 3	99 ± 3
14 days, 40 °C	3	90 ± 3	95 ± 1	ND[b]	98 ± 2

[a] Relative standard deviation. [b] Not determined.

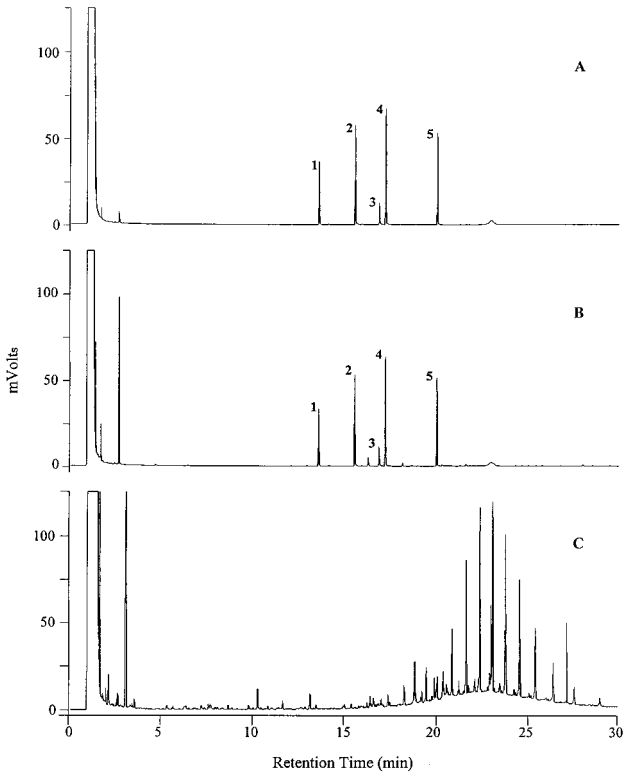

Figure 1. GC-FID chromatograms of (A) standards cocktail, (B) extract of virgin paper spiked with standards (50 ppm, dry paper basis), and (C) extract of one recycled paperboard sample: dimethyl phthalate (1); benzophenone (2); pentachlorophenol (3); anthracene (4); methyl stearate (5).

ppm level under three different storage conditions: 1 day at 25 °C, 7 days at 40 °C, and 14 days at 40 °C. Statistical analysis of the data in Table 2 showed no significant difference among these storage conditions ($P < 0.05$). We, therefore, assumed that storage at 25 °C for 24 h was sufficient to obtain a homogeneous distribution of test substance in the paper, the condition used for further recovery studies.

RESULTS AND DISCUSSION

Typical GC-FID chromatograms of the five standards, all present at 12.5 ppm, are shown in Figure 1A; those of extracts from Staging liner papers spiked with 50 ppm of each on a dry paper basis are shown in Figure 1B. Figure 2A shows typical GC-ECD chromatograms of 0.5 ppm standards and Figure 2B those of a Staging liner paper spiked with 1 ppm standards.

Virgin Paper. Recoveries of benzophenone, PCP, anthracene, dimethyl phthalate, and methyl stearate from the Staging liner paper spiked at concentrations of 1, 10, and 50 ppm were determined. The results are presented in Table 3. The recoveries of the "polar" compounds benzophenone and PCP were 90−97 and

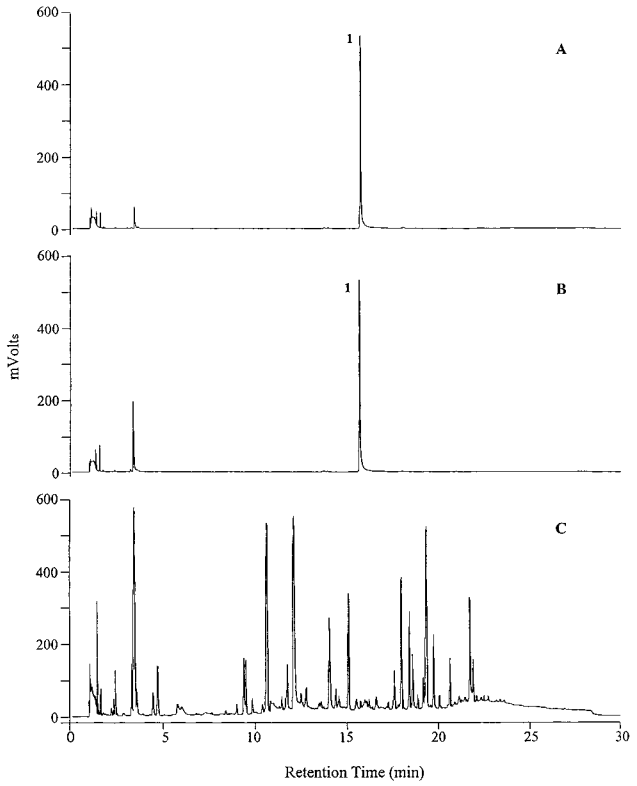

Figure 2. GC-ECD chromatograms of (A) standards cocktail, (B) extract of virgin paper spiked with standards (1 ppm, dry paper basis), and (C) extract of one recycled paperboard sample: pentachlorophenol (1).

Table 3. Recoveries of Benzophenone, Pentachlorophenol, Anthracene, Dimethyl Phthalate, and Methyl Stearate from Paper Samples Spiked at Various Concentrations

spike concn in paper, ppm	av % recovery ± RSD[a]					
	replicates	benzophenone	PCP	anthracene	dimethyl phthalate	methyl stearate
1[b,d]	4	94 ± 3	92 ± 2	95 ± 2	85 ± 3	103 ± 4
10[b,e]	4	93 ± 2	94 ± 2	97 ± 2	91 ± 3	99 ± 3
10[c,e]	4	93 ± 2	92 ± 3	101 ± 2	94 ± 3	101 ± 3
50[b,e]	4	95 ± 1	98 ± 2	95 ± 2	92 ± 4	101 ± 3

[a] Relative standard deviation. [b] Spike concentration in Staging liner paper with a density of 0.60 g/cm^3. [c] Spike concentration in Kimwipes paper with a density of 0.23 g/cm^3. [d] 2.50 g of cut paper (dry basis). [e] 1.25 g of cut paper (dry basis).

91−100% with relative standard deviations (RSDs) of 3%, respectively. The recoveries of the "nonpolar" compounds anthracene, dimethyl phthalate, and methyl stearate were in the ranges of 90−100, 80−95, and 96−109% with RSDs of 4%, respectively. The results indicate that USE is effective for extracting nonvolatile surrogates from recycled paper for subsequent quantification by GC. Statistical analysis of the data in Table 3 showed that the effect of porosity of the paper on the recoveries of standards spiked at a concentration of 10 ppm each was not significant ($P < 0.05$).

Commercial Recycled Paper. Extracts from the commercial recycled papers were analyzed using GC-FID/ECD and compared with extracts prepared after the addition of an internal standard. The GC-FID and GC-ECD chromatograms of the extracts from a recycled paper manufactured April 1998 are presented in Figures 1C and 2C, respectively. Chromatograms of extracts from the recycled paperboard samples (not shown) manufactured in January and July 1998 were compa-

rable to those shown in Figures 1C and 2C. The recycled paper contained several unidentified contaminants when compared to the virgin paper, especially a group of hydrocarbons at longer retention times in Figure 1C, which may result from waxes coated on the inner layer of the recycled paperboard.

Quantitative results based on recovery test data and LODs showed that benzophenone was present in all of the recycled paperboards at an average concentration of 1 ppm. The presence of benzophenone was confirmed by GC-MSD analysis of the extracts with mass scans of 18−270 Da in the electron ionization (EI) mode, under the GC-MSD conditions described in Table 1.

Conclusion. A procedure for analyzing five chemical contaminants in recycled paper/paperboard products has been developed and validated. The method is based on an ultrasonic procedure that can simultaneously extract benzophenone, PCP, anthracene, dimethyl phthalate, and methyl stearate at concentrations of 1−50 ppm each. Applicability of the method was illustrated using commercial recycled paperboard. The results suggest that USE is suitable for the analysis of indirect or direct recycled food-contact paper/paperboards to determine acceptable purity for their intended use. The procedure may be applicable to the determination of other contaminants in recycled paper/paperboard.

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