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Concentration of Bisphenol A in Highly Consumed Canned Foods on the U.S. Market

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ABSTRACT: Metal food and drink cans are commonly coated with epoxy films made from phenolic polymers produced from bisphenol A (BPA). It is well established that residual BPA monomer migrates into can contents during processing and storage. While a number of studies have reported BPA concentrations in foods from foreign markets and specialty foods on the U.S. market, very few peer-reviewed data for the BPA concentrations in canned food from the U.S. market were available. This study quantified BPA concentrations in 78 canned and two frozen food products from the U.S. market using an adaptation of a previously reported liquid chromatography–tandem mass spectrometry method. The tested products represented 16 different food types that are from the can food classifications that constitute approximately 65% of U.S. canned food sales and canned food consumption. BPA was detected in 71 of the 78 canned food samples but was not detected in either of the two frozen food samples. Detectable BPA concentrations across all foods ranged from 2.6 to 730 ng/g. Large variations in BPA concentrations were found between different products of the same food type and between different lots of the same product. Given the large concentration ranges, the only distinguishable trend was that fruits and tuna showed the lowest BPA concentrations. Experiments with fortified frozen vegetables and brine solutions, as well as higher BPA concentrations in canned food solids over liquid portions, clearly indicated that BPA partitions into the solid portion of foods.

KEYWORDS: bisphenol A, canned foods, LC–MS/MS

INTRODUCTION

Metal, as drink or food cans, caps on glass bottles and jars, and heating trays and lids, is a commonly used material for food transport, storage, and protection. Most, if not all, of these metal surfaces are coated prior to making contact with food.¹ The internal coating plays a dual role, providing protection of the contents from metal contamination and protection of the metal from oxidation or corrosion by the contents.¹ Perhaps the most common examples of internal coatings are epoxy films, often composed of phenolic polymers produced from bisphenol A (BPA) or 2,2-(4,4'-dihydroxydiphenyl)propane. These films are widely used as food can coatings because of their flexibility and corrosion resistance.

It is well established^{2,3} that because a residual amount of monomer remains after the polymerization process, BPA^{4–6} and other components^{7,8} migrate, at very low concentrations (parts per billion), from the epoxy coatings into the contents during processing and storage. Indeed, food has been identified as the primary source of BPA exposure for humans.^{9,10} To characterize this exposure, the exposure estimates from all dietary sources were re-evaluated in 2009.¹¹ During this exposure evaluation, a number of studies were identified that reported BPA concentrations in canned and other packaged foods.^{2–4,12–23} However, many of these studies sampled only a limited number of foods^{3,18,24} or focused on a specific food category, such as infant formulas,^{2,12,16} baby foods,¹⁵ or soft drinks.¹⁴ The remaining publications and larger survey efforts focused on foods from the European Union,^{13,17} Asia,^{21–23} or other markets^{6,20,25} and tested only a small number of U.S. products. It was clear that there were no large scale studies of the U.S. market and that there

were significant gaps in the data for highly consumed canned foods, such as chili, pastas, and pork and beans.

More recently, two publications^{26,27} have reported BPA concentrations in foods available on the U.S. market. Both of these studies were published in mid to late 2010 and were not available when this study was initiated. Given the large number of canned foods, different food and can manufacturers, and the proprietary nature of can coatings,¹ the two previous surveys, when combined with this survey, only begin to assemble a representative sample of BPA concentrations in foods on the U.S. market. Because of the size and diversity of the potential canned food sample pool, the objective of this study was to measure BPA concentrations in canned food types representing the most consumed canned foods. To this end, this study utilized sales data to determine select food types that, on a mass basis, were the most highly purchased canned foods in the United States. Finally, this study investigated the partitioning of BPA between solid and liquid food portions^{23,28,29} as a possible explanation for differences between reported BPA concentrations.

EXPERIMENTAL SECTION

Reagents. Standards of BPA (>99%, Sigma-Aldrich, St. Louis, MO) and [¹³C₁₂]BPA (99%, Cambridge Isotope Laboratories, Andover, MA)

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were tested for purity and suitability by a liquid chromatography–tandem mass spectrometry (LC–MS/MS) method upon receipt. The water, acetonitrile, and methanol used were 99.9% Fischer (Fair Lawn, NJ) Optima LC–MS grade.

Equipment. Highly crystalline 50 and 15 mL polypropylene (PP) centrifuge tubes (Corning, Corning, NY) were used for sample storage and processing. Solid foods were homogenized using a stainless steel homogenizer (PRO250, Pro Scientific, Oxford, CT). Aliquots were centrifuged on a Fischer Marathon 2100R centrifuge (Thermo Fisher, Pittsburgh, PA). HPLC–MS/MS analyses were performed using an Agilent 1100 Series HPLC system (Agilent Technologies, Wilmington, DE) with a micro volume mixing and degassing chamber, a Pursuit XRs C18 column (Agilent Technologies; 2 mm × 150 mm, 3 μm) or a Luna C8(2) column (Phenomenex, Torrance, CA; 2 mm × 150 mm, 3 μm), and an API-4000 Q-trap MS/MS instrument (Applied Biosystems, Foster City, CA). Data analysis was performed using Analyst and Excel (Microsoft, Redmond, WA). A Branson 3510 ultrasonic bath purchased from VWR (Radnor, PA) was used for all sonication experiments.

Sample Collection. Eighty different products, 78 canned and two frozen foods, were purchased from retail stores in Washington, DC, and surrounding Maryland counties. The majority of samples were purchased from large chain grocery stores, but a number of cans were purchased from local cooperatives and ethnic food markets. Brands were chosen to represent a variety of available manufacturers, including national brands, store brands, value brands, organic brands, and specialty brands. None of the foods collected were labeled as “BPA free”. Food types and brands chosen for analysis were many of the most commonly consumed canned food products on the basis of available sales survey data from 2007 to 2009 (The Nielsen Co., New York, NY). For example, using the Nielsen data from 2007 to 2009, it was determined that chili is the most highly consumed canned food, while ravioli and pork and beans are the second and third most consumed canned foods, respectively (Table 3). The 16 types of foods analyzed for this study constitute more than 65% of the canned food sales and canned food diet. All canned samples were stored at room temperature prior to being opened and were sampled prior to the “use by” dates stamped on the cans. Any frozen foods were stored frozen (below −10 °C) and thawed at 4 °C prior to use. The manufacturer or distributor, food type, can size, can type, expiration date, and manufacturing code were recorded for all products prior to opening.

Sample Preparation. The analytical method utilized for this work is a simplification of the LC–MS/MS method previously reported for the determination of BPA in liquid and powder infant formula.¹² Because of the higher BPA concentrations generally found in canned foods, the solid phase extraction cleanup and extract concentration steps were not performed. After the cans had been opened, any brine or liquid was decanted, processed, and analyzed as an independent sample. The remaining solid food was placed in a glass beaker and homogenized into a smooth paste using a stainless steel homogenizer. An aliquot (1 g) of the liquid or solid food was placed in a 15 mL polypropylene centrifuge tube, spiked with [¹³C]BPA (50 μL of a 1 ng/μL solution), and vortexed. Acetonitrile (2 mL) was added, and the samples were thoroughly mixed by being vortexed for 1–2 min. After being mixed, the samples were centrifuged (4000 rcf) for 10 min at room temperature. An aliquot (0.75 mL) of the supernatant was transferred to a glass autosampler vial and diluted 1:2 with water. The vials were sealed with PTFE-lined caps, briefly vortexed to ensure mixing, and then immediately analyzed or held at 4 °C until analysis.

Instrumental Analysis. Separations were performed at a flow rate of 0.4 mL/min and a column temperature of 60 °C. A water–methanol gradient from 40 and 100% methanol during the first 6 min led to elution of BPA around 6.1 min. Following BPA elution, the analytical column was washed with methanol for 1 min and returned to 40% methanol for a 9 min equilibration time. Negative ion electrospray at −5 kV, curtain gas

at 20, ion source gas 1 at 40, ion source gas 2 at 70 (arbitrary units), and a temperature of 600 °C were used. A declustering potential of −70 V, an entrance potential of −10 V, and a collision cell exit potential of −10 V were used. Two MS/MS transitions were monitored for each of the analytes (BPA, *m/z* 227.1 to 211.9 and 133.1; [¹³C₁₂]BPA, *m/z* 239.1 to 223.9 and 139.1). Collision energies of 28 and 35 eV were used for the first and second transitions, respectively. Analyte confirmation required both mass transitions to peak at a >3:1 signal-to-noise ratio (S/N) and within ±0.02 min of the expected retention time and the relative intensity of the two transitions to match their ratio in the standard within ±20%. Calibration solutions ranged from 1.0 to 1000 ng/mL BPA, with 50 ng/mL [¹³C₁₂]BPA in each calibration solution. Calibration solutions were analyzed prior to and throughout daily sets of sample extracts, and BPA was quantified as the area ratio of one BPA transition (*m/z* 227.1 to 211.9) to the internal standard [¹³C₁₂]BPA transition (*m/z* 239.1 to 223.9). All resulting calibration curves were linear between 1.0 and 1000 ng/mL (*r*² > 0.99).

A second quantification method for the confirmation of BPA concentrations, which used different chromatographic conditions, was performed on a subset of sample extracts. The confirmatory analysis was performed on a Luna C8(2) column (150 mm × 2.0 mm, 3 μm) using a 0.4 mL/min flow rate and 60 °C column temperature. A water (5% acetonitrile)–acetonitrile (5% water) gradient between 40 and 100% acetonitrile during the first 6 min led to elution of BPA around 3.4 min. The analytical column was washed by being held at 100% acetonitrile for 2 min and then returned to 40% acetonitrile for an 8 min equilibration time. The mass spectrometer source and MRM conditions were identical to those described previously.

Partitioning Experiments. Frozen peas and green beans were thawed and dried of excess water. Approximately 25 g of the vegetable was placed in 50 mL glass bottles. An aqueous BPA solution (25 mL of a 100 ng/mL solution) was added to each bottle, and the samples were held at 100 °C for 4 h or 40 °C for 24 h. Additionally, experimental controls, including a BPA solution without vegetables and vegetables covered in LC–MS grade water, were also held at 100 and 40 °C. After the allotted time, the bottles were removed from the heat and allowed to cool for 10–15 min at room temperature. The liquid was decanted from the vegetables, and the entire solid portion was homogenized to a smooth paste. Subsamples (1 g) of the solid homogenate and liquid were prepared and analyzed separately to determine potential partitioning. Additionally, to determine background BPA concentrations, samples of the thawed green beans and peas were homogenized, extracted, and analyzed without incubation.

Fourier Transform Infrared Spectroscopy. Fourier transform infrared (FTIR) analyses of select can coatings were conducted with a Nicolet 6700 (Nicolet Analytical Instruments, Madison, WI) spectrometer equipped with a Smart Performer single-bounce ATR (attenuated total reflectance) attachment (Thermo Scientific, Madison, WI) using a germanium crystal. Spectra were processed with Omnic (Nicolet Analytical Instruments) with comparisons to Hummel (Thermo Inc.) and in-house spectral libraries for polymers and additives. After being emptied, cans were washed with soap and water and air-dried. After the cans had dried, small pieces (1 cm²) were cut from the side and ends of each can. The exterior of the can was marked to ensure that spectra were collected (4 cm^{−1} resolution) using the inside can surface. Using the empty reflectance cell, background spectra were collected prior to the analysis of each can piece. To ensure there was no carryover, the ATR crystal was cleaned with ethanol and allowed to air-dry between each can sample.

RESULTS AND DISCUSSION

Method Validation. The method used in this study had previously undergone extensive single-laboratory validation;¹²

Table 1. BPA Spike Recovery

food	description	[BPA] (ng/g)			recovery (%)
		initial	initial and spike ^a	measured	
green beans	frozen	<2	10.	11	105
			49	46	94
			220	240	110
pork and beans	national A	43	91	94	104
			64	66	104
			420	400	94
chili	store E, chicken	98	150	140	94
			190	190	102
			490	490	99
pasta	organic E	60	110	110	102
			78	130	94
			40	90.	88
			40	91	100
fruit cocktail	store A	<2	48	48	99
pineapple	national K	<2	45	43	97
vegetables	import B, liquid	<2	50.	50.	101
	import B, solid	10	380	390	104
tomatoes	national B	24	72	72	100
fish	import E	22	390	380	97

^a Nominal 1 g sample aliquots were used for all spike samples.

however, that work addressed only a single matrix (infant formula). Therefore, to evaluate the performance of the method in the wide variety of food matrices tested in this study, we analyzed a series of reagent blanks, replicates, and spike samples. BPA was spiked into every food type sampled and also spiked at various levels (10–400 ng/g) in a number of foods, to ensure that the BPA concentration did not affect the accuracy of the method. Additionally, extraction using sonication (30 min) in addition to vortex mixing was evaluated for a number of the solid food matrices.

BPA was not detected (<2 ng/g) in any of the reagent blanks or frozen vegetables. These reagent blank data are consistent with the background concentrations previously reported for the infant formula method (0.01–0.14 ng/g) falling well below the limit of detection (LOD) for the current method (2 ng/g). The nondetectable results for frozen vegetables are consistent with the theory that epoxy can coatings and not environmental or other processing conditions are the primary source of BPA in canned foods.

Spike recovery data across a large concentration range (10–400 ng/g) and a variety of food products are presented in Table 1. Eighteen of the 19 spiked samples showed BPA recoveries between 94 and 104%. The final sample had a recovery of 110% with a spike concentration of 220 ng/g. There was no correlation between the spike concentration and the recovery, and none of the food types showed consistently lower or higher recoveries.

Eleven food samples were analyzed in at least triplicate to determine the precision of the method. All aliquots were taken from the same can, but samples were processed and analyzed on different days. All but two of the samples had a relative standard deviation (%RSD) of ≤10, with the remaining two samples, ravioli and pork and beans, having %RSD values of 12 and 16, respectively.

Table 2. Repeatability and Sonication

food	description	average [BPA] (ng/g)	RSD (%)	BPA concentration for sonication (ng/g)
soup		55	1.5	
pork and beans	national E	13	7.7	
	national F	46	16	
ravioli	national F	50	8.4	52
	store E	54	12	55
chili	store E	98	7.7	110
red beans	national J	200	6.4	200
black beans	national J	720	5.9	710
green beans	national B	24	8.2	
	national B	310	2.7	
spinach	national B	22	10	

The majority of samples show good reproducibility, and there was no correlation between the precision and BPA concentration. Indeed, samples with BPA concentrations ranging from 13 to 700 ng/g varied between %RSD values of 6 and 8. Additionally, no single matrix consistently yielded poor precision. Although the largest %RSD for replicate analysis was a pork and beans sample, another product of this same food type yielded a %RSD of 7.7. On the basis of the good precision of the method across the variety of food types, the remaining survey samples were analyzed in duplicate. All but two samples had a <10% difference between the duplicate values. One of the two samples was pineapple (national D), where both values (2.6 and 4 ng/g) were below the limit of quantitation (LOQ). The other sample was chili (store A), which had BPA concentrations of 26 and 33 ng/g, a difference of 25%. Because both values were well within the range reported for this food type and other chili samples showed good precision, no further replicate testing of this food type was performed.

To ensure that vortex mixing was quantitatively extracting BPA from different homogenized food types, we investigated a more rigorous extraction method for a number of solid food matrices. Sonication (30 min) at room temperature was used in place of vortex mixing, after the addition of acetonitrile. The use of sonication did not change, within experimental error, the BPA concentrations determined for those samples (Table 2). All six sonicated samples showed BPA concentrations within the 95% confidence limit of the mean BPA concentration determined using vortex mixing. On the basis of these data, vortex mixing was used during the remainder of the sample processing.

Survey Results. It should be noted that the BPA concentrations reported represent the BPA concentration in the canned food and are not corrected for food preparation steps, which could change the “as consumed” BPA concentration. Also, no adjustments were made for can size (i.e., surface area-to-mass ratio). In general, the can sizes and food amounts throughout the survey were similar, ranging from 383 to 454 mL, even between food types. However, there are a few exceptions, including tuna (142 mL), crushed pineapple (567 mL), a number of condensed soups (298 mL), one ready-to-eat soup (538 mL), value A products (794 and 1130 mL), and plum tomatoes (794 mL). Additionally, the frozen peas and green beans were packaged in polyethylene bags.

The majority (71 of 78) of the canned food samples tested in this survey contained detectable concentrations of BPA, while BPA was not detected in either of the two frozen foods (Table 3).

Table 3. Descriptions of Samples and BPA Concentrations in Food Samples

food (canned diet %) ^a	brand (description)	volume (mL)	can pieces	average [BPA] (range) ^b (ng/g)	
				solid	liquid
green beans (6.9)	store A	411	3	22	8.3
	store A (frozen)	not available	not available	<2	
	organic A	411	2	230 (32–440)	21 (4.2–38)
	national A	411	2	38 (33–43)	3.6 (2.7–4.7)
	national B	411	2	490 (280–600)	30 (20.–42)
	national B (no salt)	411	2	500 (300–730)	28 (15–47)
	national B (organic)	411	3	33	4.2
	value A	794	3	16	<2
corn (5.5)	import A	425	3	76	7.6
	store B	432	3	4.2	2.6
	national B	432	3	25	3.1
tomatoes (0.6)	national C (sauce)	425	2	2.6	
	store B (plum)	794	3	5.8	
	store A (diced)	411	3	43	
	organic A (diced)	411	3	<2	
	national B (diced)	411	3	24	
peas (1.2)	national B (no salt)	425	2	310	11
	national A	425	2	170	12
	store A (no salt)	425	2	12	<2
	organic A	425	3	2.6	<2
	store D	425	3	3	<2
fruit cocktail (4.1)	store A	425	3	<2	
	national B	432	3	19	
	store D	425	3	2.7	
	store C	425	3	4.6	
	national D	567	3	3.1	
pineapple (3.6)	store C	567	3	<2	
	national K	567	3	<2	
	organic B	396	3	13	
	store A	567	3	<2	
	store A	432	3	9.3	
sliced peaches (5.8)	store C	432	3	<2	
	national B	425	3	6.3	
	national B	425	3	7.0	
	store E	425	3	<2	
	national F	425	2	43 (22–54)	
ravioli (7.4)	value A	1130	3	7.5	
	organic C	425	2	39	
	national E	425	3	10.	
	store E	418	2	50. (44–62)	
	national F	425	3	46	
pork and beans (7.1)	national E	446	3	13 (12–14)	
	store E (chicken)	425	2	98 (95–110)	
chili (8.3)	store E (turkey)	425	2	76	
	national G	425	2	61 (34–91)	
	national G (hot)	425	2	30.	
	national H	425	2	130	
	national H (country)	425	2	150	
	organic E	416	2	75	
	store A	425	2	30.	
	store A (no beans)	425	2	65 (45–81)	
	organic E	425	2	59	

Table 3. Continued

food (canned diet %) ^a	brand (description)	volume (mL)	can pieces	average [BPA] (range) ^b (ng/g)	
				solid	liquid
refried beans (4.5)	import D (black)	454	3	10 (6.3–21)	
	import D (red)	454	3	23	
	national J (black)	454	3	680 (280–790)	
	national J (red)	454	3	210 (160–240)	
pasta (4.2)	organic C (tomato sauce)	425	2	39 (34–43)	
	national E (tomato sauce)	425	3	12	
	store E (tomato sauce)	418	3	40.	
	national F (cheese)	425	2	15	
	national F (tomato sauce)	425	2	21	
	store D (tomato sauce)	418	2	35	
fish (0.4)	national I (tuna)	142	2	17	<2
	national I (albacore)	142	2	12 (11–13)	<2
	national M (tuna)	142	2	5.8	<2
	national M (tuna, oil)	142	2	4.5	<2
	national L (albacore)	142	2	11	<2
	import E (mackerel)	400	3	22	5.4
soups (0.9)	national E (condensed chicken)	298	2	54	
	national E (condensed chicken)	298	2	74 (55–110)	
	national A (ready-to-eat chicken)	538	2	56	
	store B (clam chowder)	425	2	32	
	store B (organic tomato)	411	2	63	
	national E (chicken broth)	396	3	13	
miscellaneous vegetables (0.3)	national B (wax beans)	411	2	140	14
	national B (spinach)	396	3	23	2.9
	import B (stir fry vegetables)	425	3	11	<2
	import C (oyster mushrooms)	425	3	13	4.0
miscellaneous	import F (almond jelly)	538	3	4.6	

^a The percentage of canned food diet based on register receipt data from 2007 to 2009. ^b Range used to show BPA concentrations determined when multiple lots of a product were analyzed.

These findings are consistent with previously reported data and the fact that the epoxy resins used as liners for metal cans result in migration of BPA and are the main source of BPA in canned foods.

There was a large range between the lowest detectable (2.6 ng/g) and highest (790 ng/g) BPA sample concentrations. This high variability was noted between food types, and also within many of the food types. For example, BPA concentrations determined for peas showed a 10-fold difference (2.6 to 310 ng/g) between the minimal and maximal values, while green beans had a 30-fold difference (22 to 730 ng/g) between brands. Refried beans showed the largest range with more than 2 orders of magnitude (6.3 to 790 ng/g) between brands. A number of foods, such as tomatoes and corn, exhibited large relative (20-fold) but smaller magnitude (40 and 70 ng/g, respectively) differences between manufacturers. These variations within food types are consistent with previously reported data. Cao et al.^{26,30} reported 60- and 40-fold differences for tuna and condensed soups, respectively. The large variation in BPA concentration is also consistent with multiple can manufacturers using different proprietary coatings and with food producers using different can styles or coating choices for different products.¹ Although a number of foods did show large variations in BPA concentrations, approximately half of the food types, including pasta, pork and beans, chili, soups, ravioli, and fruits, showed smaller relative

and absolute variation, with differences in BPA concentrations from 3- to 5-fold or from 10 to 80 ng/g.

Multiple lots of the same food type and brand were collected for 16 of the 78 canned products. Additionally, for 10 of the products, similar products (e.g., chili with and without beans) in similar can types from the same manufacturer were purchased. In all cases, multiple lots were tested only in products that exhibited detectable levels of BPA. Overall, the lot-to-lot variability was smaller than the variability between and within foods, but it varied greatly between food types and manufacturers. For example, tuna and pork and beans samples showed very little difference between lots, while refried bean and green bean lots differed from 3- to >10-fold. Lot-to-lot variability was only evaluated on similar product information; therefore, it is possible that for certain foods, different food production lots used the same can type and lot, while for other foods both the can and food production lot differed. Additionally, because different lots were collected at different times and locations, there were no controls or methods to evaluate if the same can coating or can manufacturer was used for both lots of food.

As described above, the presence of BPA was confirmed in all of the samples by the intensity ratio of both mass transitions compared to that of the standard. However, it has been reported that comigrants (hydrolyzed forms of the BADGE monomer) from epoxy can coatings can dissociate during electrospray

ionization and produce the $(M - H)^-$ ion of BPA (m/z 227.1) in the source and thus the same MRM transitions.^{12,31} These previous reports established that the chromatographic method used in this survey resolved these comigrants from BPA. However, because of the large variation in BPA concentrations within food types and the relatively high BPA concentrations reported for a number of foods, a secondary chromatographic method was used to confirm the initial results. Refried beans, green beans, ravioli, peas, chili, and soups were reanalyzed to evaluate if comigrants or other compounds were interfering with the quantification of BPA. The alternate chromatographic conditions, described above, shortened the BPA retention time and changed the elution order of BPA and known comigrants.³¹ Such changes were consistent with the retention and elution profiles previously reported by Petersen et al.³² for bisphenol A diglycidyl ether derivatives. All of the BPA concentrations determined with the Luna C8(2) chromatographic conditions were comparable, within the 95% confidence limit, to those reported using the standard method. On the basis of the results from the confirmatory quantification method, it is clear that the BPA concentrations reported (Table 3) are not affected by the previously identified comigrating epoxy derivatives³¹ and unlikely that they are affected by other coeluting interference.

Given the large variability in BPA concentration combined with the variety of foods and manufacturers, there are few clear trends in the data. For example, the survey data do not show a correlation between the type of manufacturer (national, store, organic, or import) and the concentration of BPA in the foods. This lack of correlation is consistent with epoxy linings being the primary source of BPA and multiple can manufacturers supplying cans to numerous food producers. One clear trend is that fruits, excluding tomatoes, and tuna samples had the lowest BPA concentrations of the samples analyzed. Six of the 14 fruit samples showed no detectable BPA, and six of the eight remaining samples had BPA concentrations of <10 ng/g. These findings are in agreement with those of Thomson and Grounds,²⁵ who reported canned fruits from Australia, New Zealand, and Asia to contain <10 ng of BPA/g. Braunrath et al.¹³ and Yoshida et al.²³ also report similar results in smaller surveys of canned fruits from Asia and Australia. Finally, Schecter et al.²⁷ also reported on a single pineapple sample from the U.S. market, which had no detectable BPA concentration (<0.2 ng/g).

The low BPA concentrations found in canned fruits (pineapple, peaches, and fruit cocktail) are consistent with the general industry practice of using tin and not epoxy phenolic films in canned fruit containers.¹ Using FTIR spectroscopy, organic films were not detected on the side walls of any of the fruit cans sampled for this survey. Some, but not all, of the cans did have epoxy phenolic films on the can ends. However, the presence of an epoxy phenolic coating did not always correlate with the detection of BPA in the fruit sample. For example, the spectra of the can ends for store A pineapple were consistent with the use of an epoxy phenolic coating; however, BPA was not detected in the contents. Alternatively, organic films were not detected on the ends or side walls of the national D pineapple can; however, an average BPA concentration of 3.1 ng/g (below the LOQ) is reported for this sample (Table 3).

Given the large variation of BPA concentrations within food types and between manufacturers, the comparison of BPA data from overseas markets and products to U.S. products is not overly informative. However, the results presented here are in good agreement with recent reports on BPA concentrations in canned foods from the Canadian market.^{26,30} Many of the foods

and food manufacturers tested in that survey are products available on the U.S. market. Specifically, the range and mean of the BPA concentrations reported for condensed and ready-to-serve soups, tomatoes, miscellaneous vegetables, and single-serving canned pasta are consistent with the values reported in Table 3. The green bean values also are within the range reported here; however, Cao et al.²⁶ do not report any of the higher concentrations found in this survey. Tuna is the only product for which there is limited agreement between the two data sets. While there is an overlap in the concentration ranges, the data from Cao et al. show a wider range (9.0–534 ng/g) and a higher mean (137 ng/g) than the results found in this study (4.5–17 and 10 ng/g, respectively). The tuna products sampled in the Canadian study were not available for purchase for this survey. It is likely the differences in BPA concentration are due to differences in can coatings used by the manufacturers.

While the values of this study are in good agreement with those of the Canadian survey, there is less agreement with BPA concentrations in canned foods recently reported.²⁷ In general, the values reported by Schecter et al.²⁷ are biased low compared to the ranges reported in Table 3. Pineapple is the only commodity for which the two surveys report comparable BPA concentrations (below the LOD). Green beans (50.5 ng/g) and peas (3.12 ng/g) are the only foods for which the BPA concentrations reported by Schecter et al. fall within, but at the low end, of the ranges reported here, 22–730 and 3–310 ng/g, respectively.²⁷ BPA concentrations reported here are higher for a number of commodities, including chili, pasta, soups, and tuna fish.

It is possible that the differences in BPA concentrations simply represent differences in can size, can lot, or manufacturer. However, they may also represent differences in sample processing or analytical methodology. Schecter et al. do not describe the procedure used for sample homogenization or if solid and liquid portions were combined or separated.²⁷ While the entire can contents were used in foods such as soups, chili, and pasta, the inclusion of the supernatant in tuna and green bean samples would lower the BPA concentrations compared to those in Table 3. Additionally, Schecter et al.²⁷ used a freeze-drying step, prior to the addition of internal standard, which was not used by Cao et al.²⁶ or in our analysis. It should be noted that while the overall instrumental method used by Cao et al.²⁶ is different from that reported here, the initial sample handling steps were comparable. Both methods separated the supernatant from solid food, homogenized the entire canned solid sample, added internal standard prior to extraction, and extracted the wet homogenized aliquot with acetonitrile.

BPA Partitioning. In an effort to measure BPA in the common edible portion, the sample preparation step of the analysis took care to separate the solid food from the liquid supernatant. The supernatant was then analyzed to provide complete data, in case there is disagreement about the consumption of the liquid portion. Because of this approach, the survey results clearly showed that in foods with separate liquid and solid portions, the BPA concentrations are higher, generally ≥ 10 -fold, in the solid food (Table 3). A few samples did have smaller solid:liquid ratios, but these samples had relatively low levels (<20 ng/g) of BPA in the solid portion or BPA concentrations at or near the method LOQ. These results agree with data reported for Japanese canned fruits and vegetables²³ and in a Belgian market survey.²⁹ However, other researchers have reported BPA concentrations determined with solid phase microextraction gas chromatography and mass spectrometry to be higher in the liquid supernatant of a variety of canned

Table 4. Partitioning of BPA into Solid Food

sample	[BPA] (ng/g)			
	40 °C		100 °C	
	liquid	solid	liquid	solid
positive control	110	not available	110	not available
green beans				
blank	<2	<2	<2	<2
BPA-spiked	7.3	110	18	77
frozen peas				
blank	<2	<2	<2	<2
BPA-spiked	2.9	90	10	100

vegetables.²⁸ That study did not utilize an internal standard during extraction and derivatization, which may impact the accuracy of the recovery from solid foods and thus the quantification. Additionally, water was utilized as a solvent during the direct injection solid phase microextraction (SPME) procedure for the solid food portions. If BPA partitions into the food at a concentration greater than that at which it partitions into water, as our results indicate, then the choice of water as an extraction solvent would impact the accuracies of the SPME quantification.

To further address the question of BPA partitioning with a controlled sample set, a series of partitioning experiments were performed using frozen green beans and peas. The green beans and peas held at 40 °C for 24 h had the same texture and color as the samples processed directly from the bag. Both were bright green, with a slight hard, crisp texture that made homogenization more difficult. However, the samples that had been held at 100 °C for 4 h had a texture and color more consistent with canned vegetables. The vegetables had a faded green color and a soft texture, allowing for easy homogenization.

All of the blanks and negative control samples, including samples taken directly from the package and samples incubated with water, showed no detectable levels of BPA (Table 4). Additionally, all of the positive control samples, which consisted of BPA solutions incubated under the different conditions without the addition of vegetables, showed excellent recoveries. The results for blanks and positive controls clearly established that under the incubation conditions investigated, contamination from storage containers or loss of BPA through degradation or adsorption to the storage container did not affect BPA concentrations. For the incubated vegetable samples, all of the liquid supernatants contained significantly lower concentrations of BPA than the corresponding solid portion. The results were generally similar between green beans and peas and between the different incubation conditions. The loss of BPA from the liquid water and the increase in the level of BPA in the vegetables are in agreement with data reported by Yoshida et al.²³ with similar experiments using corn. That study used lower temperatures and longer storage times but reported comparable solid/liquid partitioning values at the end point of the storage.

It is clear from our findings that the BPA concentrations in canned foods vary greatly not only between food types but also within food types and even between production lots from the same manufacturer. Additionally, the results established that because of partitioning of BPA into the solid portion of foods, the inclusion or exclusion of a brine solution can significantly affect the BPA concentrations reported. Both of these factors

may contribute, solely or in combination, to the discrepancies between published BPA concentrations. On the basis of these survey results, no specific type of manufacturer (national, store, value, or organic) had significantly higher or lower BPA concentrations in the food. While it is tempting to correlate BPA concentrations with food composition (fat content, salt content, and pH), the lack of knowledge about and control of differences in can coatings and can processing makes such conclusions erroneous.

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