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Migration of bisphenol A from can coatings—effects of damage, storage conditions and heating

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Bisphenol A (BPA) is an important monomer used in the manufacture of epoxy resins for internal food can linings. Experiments were conducted to investigate the effects of different storage conditions and can damage on the migration of BPA to foods. These experiments were conducted in a systematic fashion by filling empty epoxyphenolic coated cans with four foods: soup, minced beef, evaporated milk and carrots and a food simulant (10% ethanol). Filled cans of each food type or simulant were then sealed and processed using appropriate conditions, before storage at three different temperatures: 5°C, 20°C and 40°C. For each of the storage regimes, 50% of the cans were dented to establish if this would lead to increased BPA migration. Cans were removed from these stocks at intervals of 1, 3 and 9 months storage at 5°C and 20°C or 10 days, 1 and 3 months at 40°C. Some initial problems of heterogeneity between samples was overcome by determining the amount of BPA in food as well as in the can lining. It was found that 80–100% of the total BPA present in the coating had migrated to foods directly after can processing by pilot plant filling with food or simulant, sealing and sterilization. This level was not changed by extended storage (up to 9 months) or can damage, indicating most migration was occurring during the can processing step. There was no noticeable difference, in this respect, between the different foods or the food simulant. Analysis of control samples (foods fortified with ~0.1 mg kg^{-1} BPA and contained in Schott bottles) showed that BPA was stable under both processing and storage. Experiments were also conducted to investigate the potential effects, on the migration of BPA from can coatings, of cooking or heating foods in the can prior to consumption. Food cans were purchased and the food either cooked or heated in the can. BPA was analysed prior to and after the heating/cooking process. It was concluded from the results that there were no appreciable differences in the BPA level before and after cooking or heating.

Keywords: Bisphenol A, migration, can coatings, chromatography.

Introduction

Bisphenol A (BPA) is an important monomer used in the manufacture of epoxy resins for internal food can linings. The Tolerable Daily Intake (TDI) for BPA was reviewed by the Scientific Committee on Food in 2002 (SCF 2002) and the TDI reduced to a temporary value of 0.01 mg kg^{-1} body weight day per day.

Some published data are available on BPA migration from can coatings into foods and food simulants (Biles *et al.* 1997, Kawamura *et al.* 1999, Yoshida *et al.* 2001, Goodson *et al.* 2002, Kang and Kondo 2003, Society of the Plastics Industry 1995).

Low levels of migration of BPA from can linings to food were found in a Food Standards Agency (2001) survey, but little is known about how the migration level in foodstuffs would be influenced by damage to the can or storage conditions. However, some workers have investigated the effects of the can processing conditions on the migration of BPA with food simulating liquids (Kawamura *et al.* 2001, Munguia-Lopez and Soto-Valdez 2001, Kang *et al.* 2003). A further unknown factor is the effect of heating the food in the can prior to consumption. In view of the potentially long shelf-life of most canned foods and the current interest surrounding the exposure to BPA from food packaging it was felt important to obtain information on all of these factors.

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The main aim of the project was to investigate these factors in a systematic fashion by filling empty epoxyphenolic coated cans with four different foods and a food simulant. After sealing and processing, the cans were subjected to reproducible damage and a range of storage times at 5, 20 and 40°C. The cans were opened and the BPA concentration in the food measured with a GC-MS technique with a limit of detection (LOD) of $2\,\mu g\,kg^{-1}$. To enable the proportion of BPA migration to food to be calculated, the BPA remaining in the coating was also determined.

A further aim was to investigate the effect of heating or cooking foods in the can and in this case the experimental work was carried out on retail samples and the BPA levels compared before and after heating.

The overall aim of this study was to provide migration data to help identify any potential risks to the consumer from additional exposure to BPA from damaged cans or cans stored for longer times or those foods heated in the can.

Materials and methods

Samples

Two hundred samples of empty epoxyphenolic coated, 65×95 mm, 300 g size (A1) cans and easy open ends were supplied by Crown Cork and Seal (Wantage, UK) for the experiments to investigate the effects of storage and damage.

Samples of canned foodstuffs for investigating the effects of heating the food in the can were purchased from a UK supermarket.

Effect of storage and can damage

Selection of empty cans—homogeneity testing. The requirements for the empty cans to be used in this part of the project were that they had an epoxyphenolic internal can lining which was typical of the type used for food cans. Additionally, the cans were required to give BPA migration that could be measured with a relative precision of $< 10\%$, so that any effects of storage and can damage could be readily detected. It was also desirable that the cans were homogenous with respect to BPA levels in the coating. Crown Cork and Seal (Wantage, UK) provided examples of candidate epoxyphenolic coated cans for evaluation which were sourced from standard production ~1998, but were no longer current specification.

Two batches of empty cans (coded 41O and 41P) of A1 size were submitted for homogeneity studies. Measurement of the homogeneity was carried out by selecting 10 cans at random from each batch and extracting the BPA using acetonitrile, by filling the can with this solvent and storage for 24 h at room temperature. The 10 cans were extracted with acetonitrile for 24 h at 25°C. Duplicate aliquots of each extract were injected for analysis by HPLC with fluorescence detection using the conditions given here: Column, Phenomenex MAX RP 250×4.6 mm, 4 μm; Mobile phase, 50%; acetonitrile/50% water held 7 min, programmed to 90% acetonitrile/10% water at 10 min hold 2 min; Flow rate, $1.2\,ml\,min^{-1}$; Detector, Fluorescence λ_{ex} 275 nm, λ_{em} 305 nm; Injection, 25 μl; Retention time, 6.2 min.

The between and within-sample variation was evaluated by analysis of variance (ANOVA). The first batch (coded 41O) was inhomogeneous and exhibited two populations with ranges of 33–44 and 57–63 $\mu g\,l^{-1}$ BPA. A second batch was tested (coded 41P) and the homogeneity experiment was repeated. The cans were again found to be inhomogeneous with a relative standard deviation (RSD) of 10.4%. A further set of 10 cans were taken from batch 41P and the homogeneity test repeated, giving a RSD of 16.8% and mean of $72\,\mu g\,L^{-1}$. Additional analyses conducted on acetonitrile extracts by GC-MS (conditions described below) obtained a mean value of $51\,\mu g\,L^{-1}$, giving a strong indication that there was an interference with the HPLC analysis. All further work on analysis was carried out by GC-MS.

To overcome the apparent inhomogeneity of the cans, the project was extended to cover measurements not only of the BPA content of the food but also the levels remaining in the coating. This approach enabled the proportion of BPA migrating to food to be calculated for each can/food combination; therefore, eliminating the between-can variable. The cans coded 41P were selected for investigating the effects of storage exposure conditions and can damage.

Selection of foods, filling and processing of cans. To systematically investigate the effects of can damage

and storage on the migration of BPA, four different foods and a food simulant were selected for filling the empty 41P cans. The foods were chosen to represent the whole range of canned food from high fat to low fat. The food simulant 10% ethanol was chosen to represent a worst case, as previous research (Cooper *et al*. 1996) has shown that lower migration occurs with the fatty food simulant olive oil. The cans were then filled with the foods given in table 1 and processed at Crown Cork and Seal using the typical conditions given. The cans were sealed using a typical easy-open end.

Blanks (two for each food) and controls (10 for each food) were prepared by dispensing ~ 200 g of the blank food into 250 ml tared Schott bottles. The controls were spiked with 50 µl of a solution of BPA in acetonitrile (419 µg ml^{-1}). This gave controls for each foodstuff containing BPA at ~ 100 µg kg^{-1}. The blanks and controls were processed using the same conditions as for the cans.

Denting of cans. After filling, but before commencing the storage experiments, 100 of the cans were dented using an apparatus which was designed to produce reproducible damage. The apparatus was based on that described in BS EN ISO 6603-1; 2000, 'Determination of puncture impact behaviour of rigid plastics'.

The apparatus comprised a 1 m graduated tube, 51 mm internal diameter and release mechanism and a 28 mm hemispherical impact dart machined from steel fitted with nylon guide rings (a base weight of 500 g).

Each can was impacted at the centre of the sidewall on the face opposite the side seam from a height of 1 m using a dart weight of 500 g.

Table 1. Foodstuffs.

Food/food simulant and declared fat content	Process conditions
Spring Vegetable Soup (0.3% fat)	90 min, 121°C
Carrots in Brine (0% fat)	90 min, 121°C
Evaporated Milk (8% fat)	30 min, 121°C
Minced beef in gravy (prepared *in situ* 20% fat)	90 min, 121°C
10% ethanol	90 min, 121°C

A typical can deformation is shown in figure 1.

Storage conditions. Both dented and undamaged cans were stored at temperatures of 5 and 20°C to represent chilled storage and ambient storage for up to 9 months. In addition, because the shelf-life of some food cans is up to 3 years, an accelerated test was carried out at 40°C for 3 months (this covers ambient storage for ~ 4 years by extrapolation of the accepted convention of 10 days at 40°C being equivalent to 6 months at ambient temperature). For each of the foods and the food stimulant, the following storage and sampling programme was set up as given in table 2.

Blanks and controls were set up alongside each experiment.

Extraction of cans using acetonitrile. After taking appropriate aliquots of the foodstuff for analysis, each can was emptied and the internal surfaces wiped clean with a tissue. The can was then filled with

Figure 1. Typical can deformation after impact.

Table 2. Storage and sampling programme.

	Dented			Not dented		
Storage time	5°C	20°C	40°C	5°C	20°C	40°C
10 days			x			x
1 month	x	x	x	x	x	x
3 months	x	x	x	x	x	x
9 months	x	x		x	x	

x = test samples analysed for BPA .

Table 3. Analytical performance data.

Food	BPA $\mu g\,kg^{-1}$ Mean level	Repeatability (r) ($n=6$)
Baby food 1	19.2	3.3
Baby food 2	41.8	3.4
Rice pudding 1	20.4	2.6
Rice pudding 2	20.5	2.3

acetonitrile and stored at ambient temperature for 24 h. After this time, a 10 ml aliquot was taken for analysis using the method given below.

Heating food in the can

Selection of suitable canned foods (initial experiments). Ten different canned food types were selected for purchase. For each canned food type, six replicates with the same batch numbers were then purchased from a UK supermarket. These canned foods were chosen because it was judged that they might be heated in the can by the consumer or instructions were given on the can requiring the food to be cooked in the can. One can of each type was opened and the internal coating examined by Fourier transform infra-red spectroscopy (FTIR) to ensure that an epoxy-based coating (therefore based upon BPA) was present. This judgement was made by comparison against reference IR traces and the main absorptions at 830, 1610, 1500 and 1260 cm^{-1}, which are characteristic for epoxy based coatings.

Two of the remaining cans of each of the 10 canned food samples were opened and the contents homogenized and the BPA concentration determined. Another two cans were taken from each of the samples and the food cooked according to the manufacturers' instructions or the contents heated in the can by immersing the can in boiling water for 15 or 30 min depending upon the can size. The results were inconclusive because of apparent variations in the BPA levels in the can coatings. To try and overcome the apparent variability in the BPA contents of the can coatings, the final can from three of the canned food types (Spaghetti Bolognese, baby food and soup) was opened, two aliquots of each food were removed for BPA analysis and the remainder heated in the can for 15 or 30 min in boiling water with the can covered with a watch glass. This exploratory approach was followed by further experiments.

Follow-up experiments on heating food in the can. A further three canned foods (two baby food and rice pudding), which were judged to be easily mixed and reasonably homogenous in nature, were purchased in replicate ($n=8$). To evaluate the effects of heating in the can, experiments were then conducted by taking duplicate sub-samples for analysis from each can before heating and quadruplicate sub-samples after heating. This replicate sampling was carried out for each of the food types using triplicate or duplicate dented and triplicate undamaged cans. The cans were dented as described above. Care was taken to mix the food well before taking sub-samples for analysis and to cover the can with a watch glass during the heating. The temperature in one of the baby food cans and one of the rice pudding cans was monitored using a digital thermometer and a K-type thermocouple during heating the cans in a beaker of boiling water for 15 min (for the baby food) or 30 min (for the rice pudding) and the final temperature recorded.

Following the heating procedure, the cans were emptied, wiped clean and extracted with acetonitrile for 24 h at ambient temperature to estimate the levels of BPA remaining in the coating.

Analytical method

The method used for analysis of foodstuffs was reported in the survey (Food Standards Agency 2001) and by Goodson *et al.* (2002). Some minor modifications to this method were made to determine BPA in 10% ethanol and acetonitrile.

Determination of BPA in 10% ethanol food stimulant. A 25 ml aliquot of the simulant was taken and transferred to a 250 ml separating funnel. Internal standard, BPA-d_{16} was added (0.1 ml of 10 $mg\,l^{-1}$ solution) at a concentration of $\sim 40\,\mu g\,kg^{-1}$ in the food simulant.

Ten millilitres of 72% (w/v) aqueous potassium carbonate solution and 10 ml methanol were added to the food simulant in the separating funnel and the contents swirled to mix. Ten millilitres of acetic anhydride were then added to the separating funnel and, after the initial reaction had subsided, the contents were swirled gently and left to stand for 15 min.

The contents were then extracted with 3 ml n-heptane. The heptane layer was removed and dried over

sodium sulphate then transferred, through a 0.2 μm syringe filter if necessary, to a 2 ml vial for analysis by GC-MS using selected ion monitoring.

Determination of BPA in acetonitrile extracts. A 10 ml aliquot of the extract was taken and transferred to a 250 ml separating funnel. The internal standard BPA-d_{16} was added (0.1 ml of the 10 mg l^{-1} solution) to the solvent extract. Forty millilitres of water was added. The solution was mixed and taken through the derivatization procedure, as described above.

Calibration. Stock solutions of BPA were accurately prepared in acetonitrile at a concentration of ~500 μg ml^{-1}. One millilitre of the stock solution was diluted to 50 ml with acetonitrile in a volumetric flask, to give a dilute stock solution of concentration ~10 μg ml^{-1}.

Aliquots (0, 10, 25, 50, 100, 200, 300 and 500 μl) of the dilute stock solution were transferred with a syringe to a series of 250 ml separating funnels, each containing 50 ml water. One-hundred microlitres of the BPA-d_{16} internal standard solution was added to each, then, after mixing, the derivatization procedure was followed as described above.

Instrument parameters. BPA migration was measured by GC-MS, SIM using the following parameters: Instrument, Agilent 5890 GC with 5972 mass selective detector (MSD), Agilent 6890 GC with 5973 MSD; Data collection, Hewlett-Packard Chemstation: Injector, 290°C, splitless, on time 1 min; Column, 30 m × 0.25 mm (id), 0.25 μm film thickness, 5% phenylmethyl siloxane, e. g. HP5-MS (Agilent); Oven programme, 70°C hold for 1 min, ramp to 120°C @ 10°C min^{-1}, ramp to 300°C @ 20°C min^{-1}, hold 5 min; Carrier gas, He, constant flow 8psi @ 70°C; Detector, MSD, SIM; Ions, mz^{-1}, BPA: 213, 228, 244, BPA-d_{16}: 224, 242; Retention times (min), BPA: 14.3, BPA-d_{16}: 14.3.

Data analysis and calculation of results. Quantification was by interpolation from the appropriate calibration graph constructed by plotting amounts of BPA in μg against the peak area ratio of BPA/BPA-d_{16} using the ions m/z 213/224. Visual qualitative inspection of the ratios of the ions m/z 213, 228 and 244 was used for confirmation of BPA.

The percentage of BPA migrating into the food and food simulant was calculated by dividing the BPA value determined in the food by the total BPA (which was obtained by summing the content in the food and the acetonitrile extraction).

Results

Validation of food analysis

Calibration and blank foods analysis. All calibration graphs were linear with correlation coefficients of 0.997 or better and with a range spanning ~0.1–5 μg of BPA, corresponding to 5–250 μg kg^{-1} in foods. BPA was not detected in the blank foods at any of the exposure times or temperatures with a LOD estimated to be 2 μg kg^{-1}.

LOD and repeatability. The LODs were estimated by calculating the concentration of BPA equal to 3 × the signal to noise. For foods and acetonitrile, the LODs were calculated to be 2 μg kg^{-1} and for 10% ethanol 0.5 μg kg^{-1}. These values are conservative estimates and varied over the course of the project. The repeatability (95% confidence level) was calculated from the standard deviation (Sr) obtained from the analysis of six replicates of the baby foods and rice pudding and is expected to be typical for the different foods examined in this project ($r = 2.8 \times Sr$) see table 3. The analytical recovery for three of the foodstuffs; baked beans, peas and toffee pudding, was determined by fortifying sub-samples of the food with BPA (~100 μg kg^{-1}) and analysis alongside the unfortified sub-samples. The recoveries obtained are given in table 4.

Proficiency test. Pira participated in FAPAS Specific Migration Series 12, Round 19 (Central Science Laboratory 2003) as laboratory number 007. The *z*-scores obtained were −0.4 and −0.2 for analysis of BPA in olive oil and 3% acetic acid, respectively, and are well within the limit of ±2 which is deemed to be satisfactory.

Table 4. Analytical recovery from foodstuffs.

Food	% Recovery	Mean % recovery
Baked beans	91, 93	92
Peas	100, 121	110
Toffee Pudding	108, 109	108

Table 5. Results from spiked controls.

Temperature/time (months)	Recovery %				
	10% ethanol	Milk	Soup	Carrots	Minced beef
5°C					
0	124.5	117.5	93	94	85
1	92.5	116.5	95.5	87	92
3	103.5	103.5	93	100	90
9	104.5	108.5	100	104	94
20°C					
1	105.5	117.5	100	87	90.5
3	101.5	89	97.5	106	96.5
9	104	114.5	95.5	91.5	98.5
40°C					
0.33	103.5	94.5	96.5	84	94.5
1	102	124	77	81	91
3	102	103	90	102	104
Mean	104.4	108.9	93.8	93.7	93.6
Standard deviation	7.9	11.2	6.7	8.9	5.2

Experiments to assess the effects of storage and can damage

Analysis of spiked controls and blank foods. BPA was not detected (LOD estimated to be $2\,\mu g\,kg^{-1}$) in the blank foods at any of the exposure times or temperatures studied. No trend in the BPA concentration in the spiked controls was evident at the different timepoints for each food. The mean recoveries of the duplicate analyses for the control samples at each of the three storage temperatures are given in table 5. Also given is the grand mean and standard deviation for each food across the three temperatures showing the mean recovery to be in the range 90–110% and standard deviation approximating to the expected precision of the method.

These results show that BPA is stable in the four foods and 10% ethanol food simulant under both processing at 121°C and the storage temperatures examined. They, thus, also demonstrate that the analytical method was under control during the course of the project. For each food type and the 10% ethanol, the data at time = 0 for the three temperatures have the same value and represent the recovery obtained for the control samples after processing, but before storage.

BPA migration results for damaged and undamaged cans stored at 5, 20 and 40°C. Cans were removed at the appropriate sampling time and BPA determined. Two cans were taken for analysis of the 5°C storage tests and the initial time-point and a single can for all other temperatures. Triplicate or quadruplicate cans were taken for analysis at the 3 months at 40°C timepoint and 2–3 cans for the 9 month at 20°C timepoint. An exception to this was for 10% ethanol filled cans where only a single replicate can was available. Graphs illustrating the pattern of results obtained for each foodstuff, at the selected study temperatures, are given in figures 2–6.

Examination of the can with the naked eye after emptying of the contents revealed no cracking or flaking of the inner coating on either the dented or undamaged cans. A small amount of corrosion was noticed around the inner area of the can seam with the cans filled with 10% ethanol and stored for 9 months at 20°C or 10 days at 40°C. However, no corrosion was seen with the foodstuffs, even the carrots in brine after storage for 9 months at 20°C. This is probably because of lower oxygen levels remaining in the foods after processing.

Heating food in the can

Table 6 describes the samples selected for the initial experiments and the results obtained on each of the four replicate retail cans tested of each

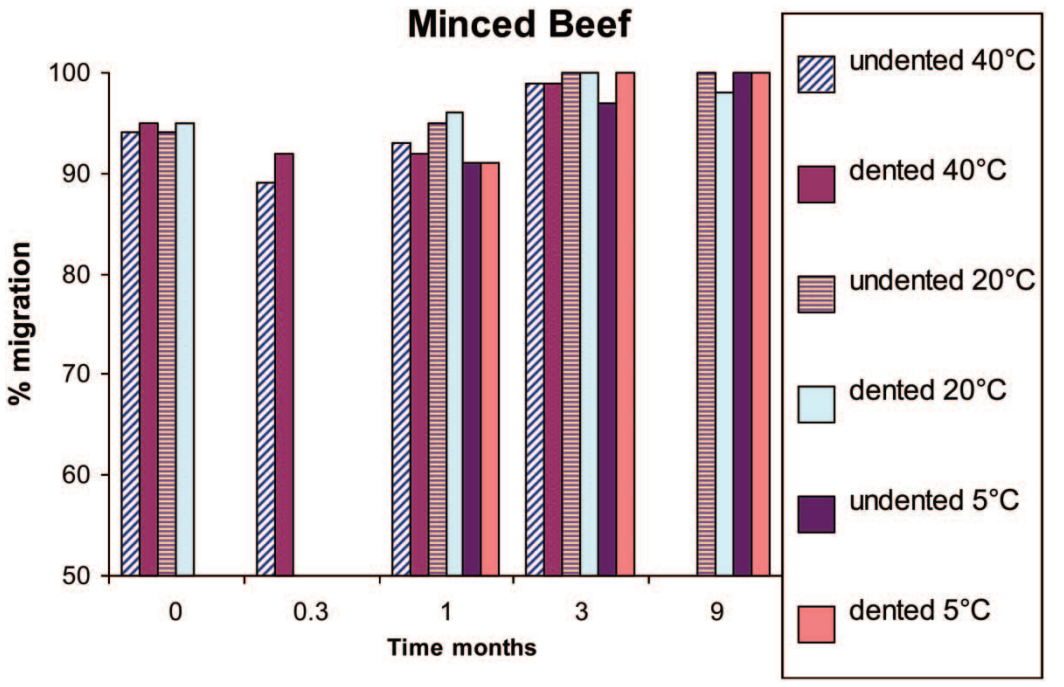

Figure 2. Results showing proportion of BPA migrating into foods after storage/damage.

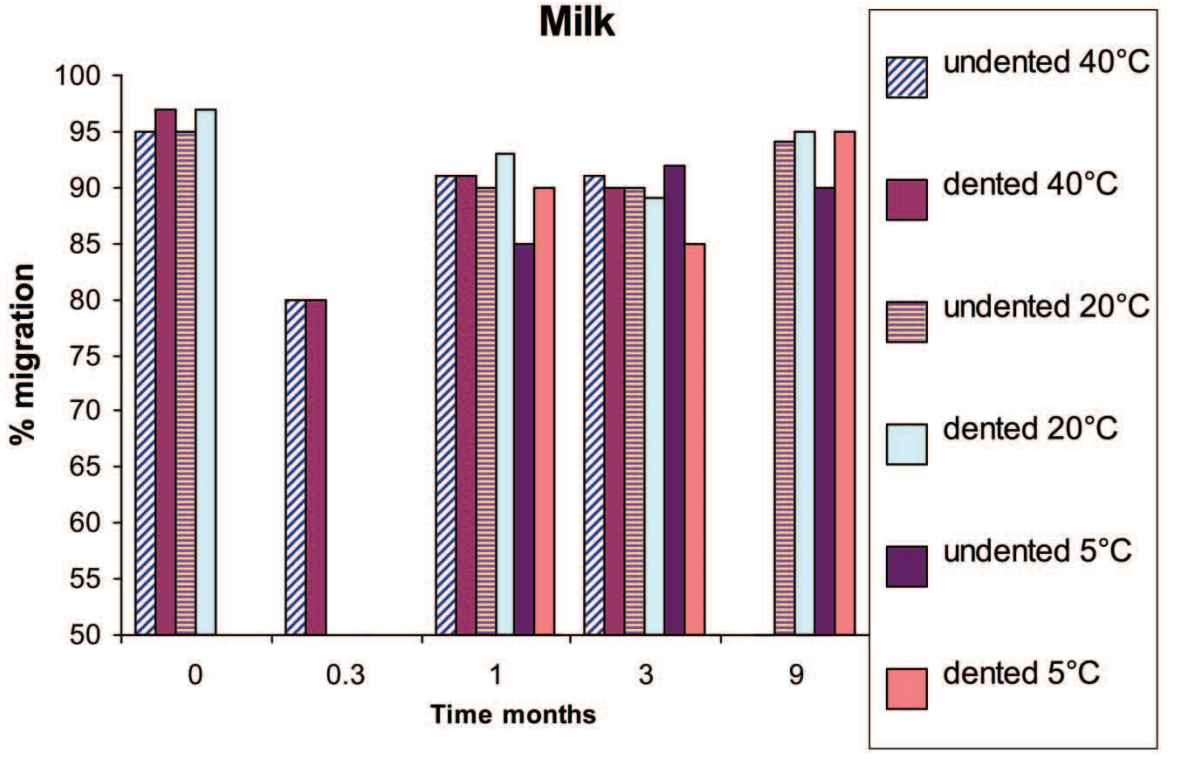

Figure 3. Results showing proportion of BPA migrating into foods after storage/damage.

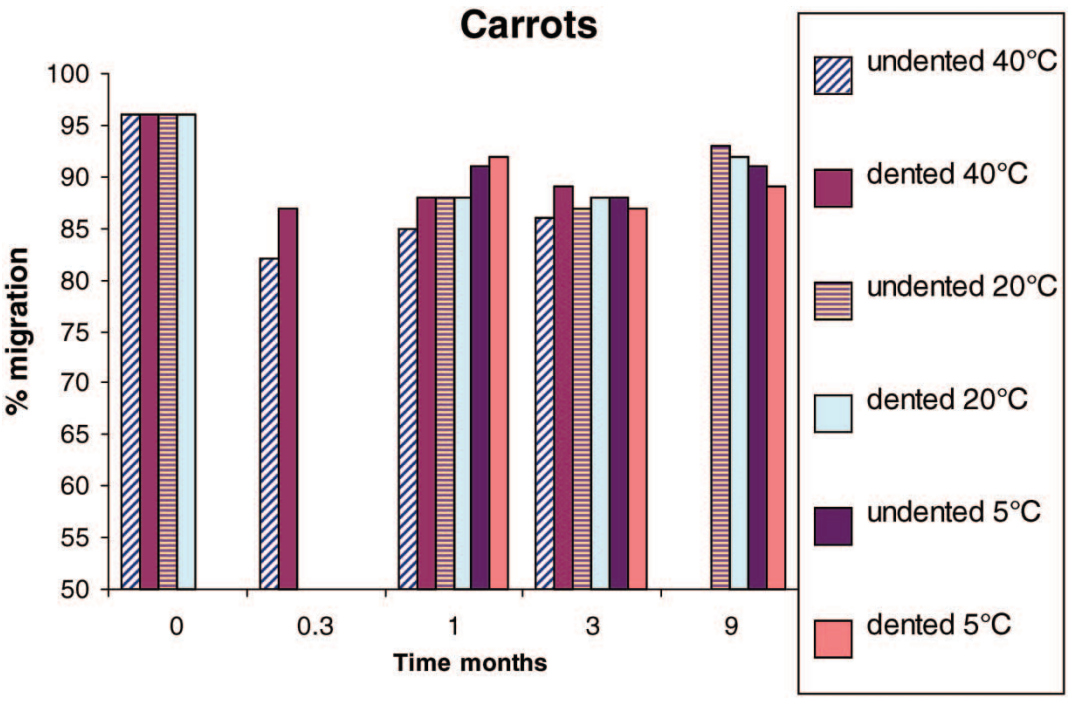

Figure 4. Results showing proportion of BPA migrating into foods after storage/damage.

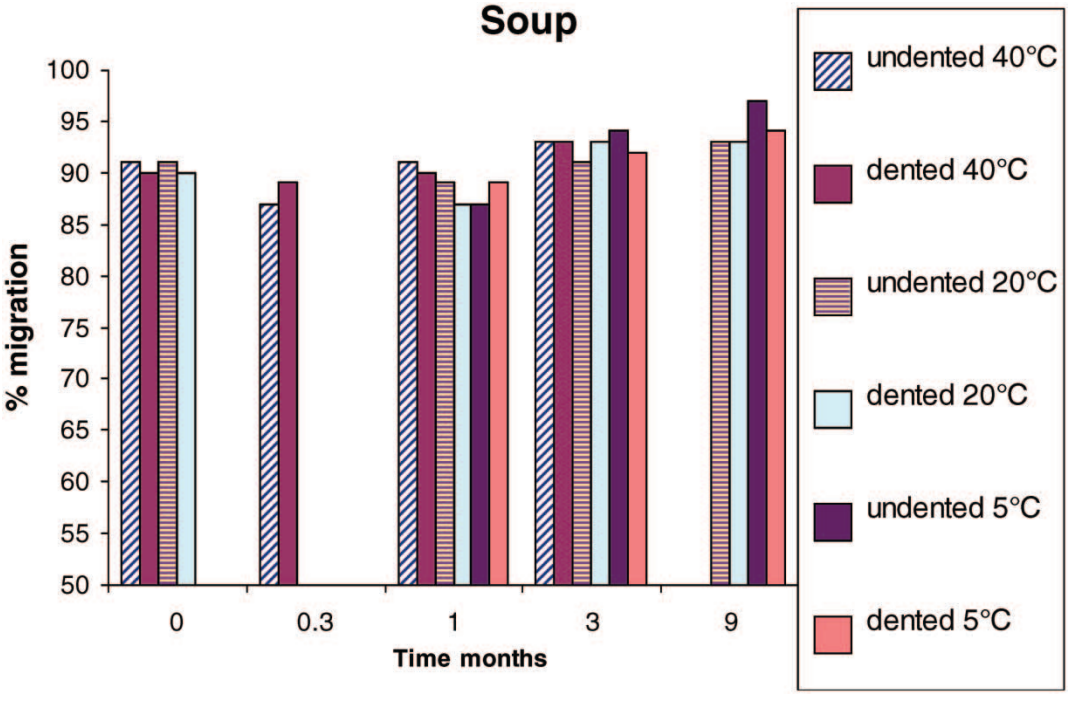

Figure 5. Results showing proportion of BPA migrating into foods after storage/damage.

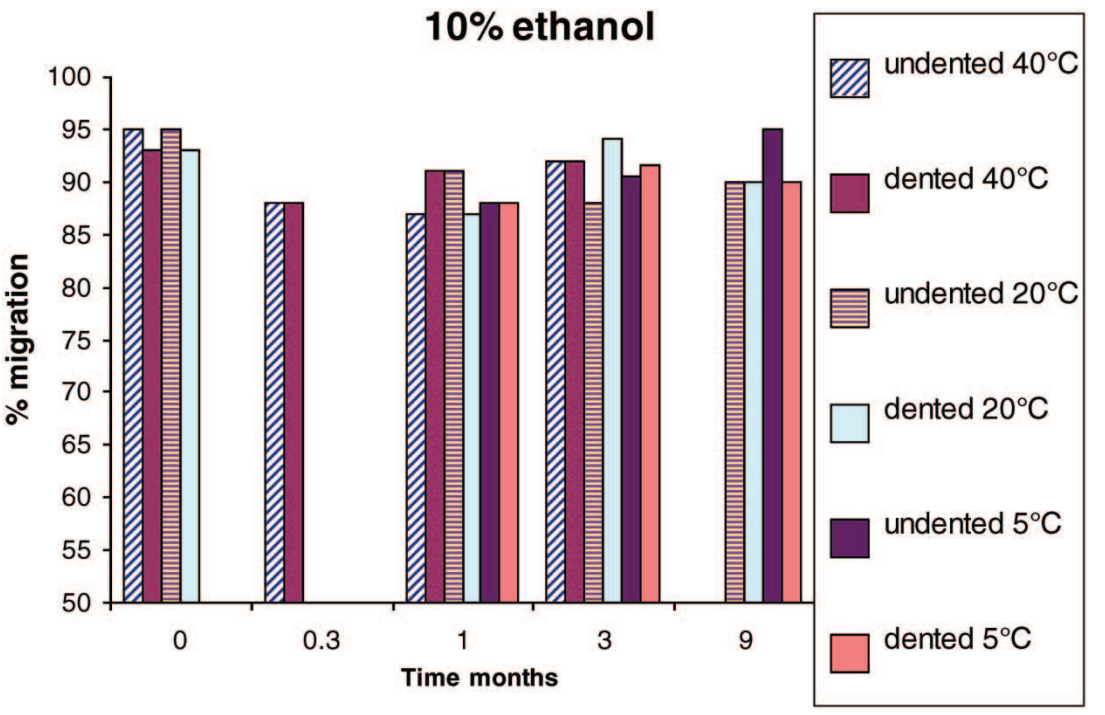

Figure 6. Results showing proportion of BPA migrating into foods after storage/damage.

Table 6. etail food cans—initial results with different cans.

Canned food	Results expressed as $\mu g\,kg^{-1}$ BPA		
	Not heated	Heated	Heating conditions
Steak and kidney pudding (140 g)	9.2, 8.6	9.5, 9.5	Boiling water 20 min
Steak and kidney pie (213 g)	25.7, 21.0	21.1, 22.4	230°C 30 min, lid removed
Spaghetti bolognese (200 g)	90.7, 67.3	129.5, 103.3	Boiling water 15 min
Baked beans (220 g)	13.0, 12.7	12.8, 11.3	Boiling water 15 min
Peas (300 g)	11.9, 13.0	12.9, 14.4	Boiling water 15 min
Carrot and coriander soup (415 g)	18.5, 22.0	28.5, 39.1	Boiling water 30 min
Baby food dessert (128 g)	77.3, 57.4	49.2, 58.9	Boiling water 15 min
Rice pudding (425 g)	34.5, 25.8	53.2, 27.5	Boiling water 30 min
Toffee pudding (300 g)	14.1, 10.5	6.4, 3.8	Boiling water 35 min
Treacle sponge pudding (200 g)	16.8, 20.0	18.2, 20.6	Boiling water 35 min

foodstuff (two heated, two not heated). FTIR analysis demonstrated that the cans contained an epoxy based internal coating.

The results in table 6 indicate that, in most cases where the BPA was at a lower concentration in the unheated sample, there was not a discernable difference in concentration found on heating in the can. However, where the concentration of BPA is higher, such as the spaghetti bolognese and the baby food, and a difference between the respective heated and unheated samples was seen, it was considered that it was not clear if this difference might arise owing to can-to-can variability. Therefore, no firm conclusions could be made from these experiments and the differences seen were attributed to four separate cans being tested.

To investigate ways of overcoming the problem of can-to-can variability, the last remaining can

purchased from the spaghetti bolognese, baby food and soup was opened and a duplicate sub-sample taken for analysis. The remaining food in the can was then heated as before and a further duplicate sub-sample taken for analysis. The before and after results are given in table 7.

A small increase (8.7% and 14.6%, respectively) in BPA concentration was indicated in the soup and baby food. A decrease (17.9%) was apparent for the spaghetti bolognese. However, this latter foodstuff was not homogenous in the can and it was very difficult to take a representative sample for analysis prior to heating, whereas the soup and baby foods were homogenous. Homogenization of the spaghetti in the can was not considered as it could change the properties of the food. Although the result for spaghetti bolognese was inconclusive, this approach was considered promising for the other foodstuffs.

Table 7. Retail food cans—results from same can before and after heating.

	Result BPA $\mu g\,kg^{-1}$	
Canned food	Not heated	Heated in can
Soup (425 g)	21.6, 21.9 $m = 21.8$	24.2, 23.1 $m = 23.7$
Baby food dessert (128 g)	43.4, 38.5 $m = 41.0$	46.0, 48.0 $m = 47.0$
Spaghetti bolognese (425 g)	101.4, 91.6 $m = 96.5$	74.8, 83.5 $m = 79.2$

Follow-up experiments on heating food in the can. A minimum of eight replicates of three further canned food samples with the same batch number were purchased and again the contents analysed for BPA, with sub-samples taken from the same can before and after heating. The foods that were chosen were two different varieties of baby food desserts and a rice pudding; these were judged to be foods that could be heated in the can in some situations and were already reasonably homogenous so that representative sub-samples could be taken after mixing. The final temperatures of the foods measured in the cans were measured as 69°C for the baby food and 71°C for the rice pudding. The results are given in table 8.

To assess whether there was evidence for a difference in the BPA results obtained on heating the foodstuffs in the cans, a significance test (Miller and Miller 1993) was conducted with the null hypothesis being that the mean results obtained for not-heated and heated foodstuff were equal. To achieve this, the standard deviations calculated from the duplicate unheated and quadruplicate heated food analyses were pooled to obtain the combined standard deviation (CSD) with 4° of freedom. This value was substituted into the equation $t = (m_1 - m_2)/\mathrm{CSD}\ \sqrt{(1/n_1 + 1/n_2)}$, where m_1 and m_2 are the mean values being compared and n_1 and n_2 are the number of replicates. The test value (t) was then compared against the critical value of t (2.78 for 4° of freedom and a confidence level of 95%).

In all but one of the 19 experiments, the calculated test values were less than the critical value for t,

Table 8. Retail food cans—further results from same can before and after heating.

		Undamaged cans				Damaged cans			
		Mean BPA level $\mu g\,kg^{-1}$ (ppb)				Mean BPA level $\mu g\,kg^{-1}$ (ppb)			
Canned food		Not heated ($n = 2$)	Heated ($n = 4$)	CSD	t-Test value	Not heated ($n = 2$)	Heated ($n = 4$)	CSD	t-Test value
Baby food 1 (128 g)	1st can	19.6	21.1	0.66	2.62	30.4	34	1.51	2.75
	2nd can	31.3	33.7	2.35	1.18	20	20.8	1.92	0.48
	3rd can	18.9	19.6	0.34	2.38	32.1	34.5	0.88	3.15
Baby food 2 (128 g)	1st can	34.6	34.8	0.88	0.11	37.6	38.5	2.51	0.41
	2nd can	36.5	40.4	2.97	1.52	30.5	33	1.99	1.45
	3rd can	35.3	35.1	1.58	0.15				
	4th can	41.5	40.7	1.42	0.65				
	5th can	44	46.7	2.08	1.50				
Rice Pudding (213 g)	1st can	24.5	25	1.06	0.55	23.5	25	0.97	1.79
	2nd can	27.1	28.1	2.21	0.52	21.3	19.8	2.08	0.83
	3rd can	21.2	20.6	0.61	1.14	18.5	19	1.33	0.44

CSD = combined standard deviation.

Table 9. Remaining BPA levels in cans from table 8.

	BPA remaining in coating and % migration			
	Not dented		Dented	
Canned food	$\mu g\,kg^{-1}$	% migration	$\mu g\,kg^{-1}$	% migration
Baby food 1 (dessert)	28	41	20	60
	22	59	19	51
	23	45	30	48
Baby food 2 (dessert)	30	53	28	58
	24	60	31	52
	20	64		
Rice Pudding	3	89	9	72
	7	79	4	84
	6	78	10	64

showing that there was no evidence of a difference in the results for the heated and unheated food. One experiment (baby food 1, 3rd can, dented) gave a test value of 3.15 that exceeded the critical value for t of 2.78. However, this single outlier could be expected with a confidence level of 95% and it is clear that the bulk of the data support the null hypothesis that there is no significant difference in BPA levels as a result of heating the foods in the cans.

Following the heating procedure, the cans were emptied, wiped clean and extracted with acetonitrile for 24 h at ambient temperature to estimate the levels of BPA remaining in the coating. Table 9 gives the remaining levels of BPA in the coating determined by acetonitrile extraction for the samples given in table 8 and the percentage migrating into food = migration into food $\times$ 100/(migration into food + acetonitrile ext.).

For the retail baby food cans in particular, it is evident that a smaller proportion (% migration) of BPA migrates into the food compared to the proportion of BPA migrating into foodstuffs from the 41P cans. This may be due to a number of factors such as less severe processing conditions or thicker coatings for these canned foods.

Discussion and conclusions

The data generated in the homogeneity studies demonstrated that there was a considerable variability in the BPA contents of the empty cans used for the storage experiments. There was also a noted variation in the levels of BPA found in some of the retail canned food samples purchased, even though the batch numbers were the same.

In order to investigate the effects of storage and damage, this apparent inhomogeneity was overcome by determining both the concentration of BPA in the food and that remaining in the coating after storage. This enabled the proportion of BPA migrating to food to be calculated. It was found that a high proportion (80–100%) of the BPA present in the can coating migrated into the food during the processing stage, typically 90 min at 121°C. It was also clear that BPA was stable in the four foods studied and in the food simulant 10% ethanol both during the high temperature processing of the cans and the 3 months storage at a temperature of 40°C, representing up to 3 years storage at ambient temperature.

The proportions of BPA migrating into the four foods and the food simulant were similar and did not significantly change on storage of the cans at ambient or refrigerator temperatures for up to 9 months and an accelerated test representing 3 years at ambient temperature. Owing to the heterogeneity of the cans, there was a significant spread of results expressed as BPA concentrations in the food, but overall the data for the four foods were similar. However, the data for 10% ethanol, expressed as ppb ($\mu g\,kg^{-1}$) BPA, were overall significantly higher compared to the foods. This can be demonstrated from the calculated mean concentrations of all of the BPA concentrations for each food regardless of damage and storage time;

- Minced beef $53.8 \pm 7.6\,\mu g\,kg^{-1}$
- Milk $49.8 \pm 10.9\,\mu g\,kg^{-1}$
- Carrots $47.2 \pm 5.1\,\mu g\,kg^{-1}$
- Soup $45.7 \pm 5.0\,\mu g\,kg^{-1}$
- 10% ethanol $68.3 \pm 9.0\,\mu g\,kg^{-1}$

With the large number of data points ($n = 34$–37) and the assumption that there are no significant effects of damage and storage time, the can coating heterogeneity variable will tend to average out, so any significant difference in the mean concentrations can be identified. In this case, the results for 10% ethanol are significantly higher than the other foods.

One explanation for this is that, during the can processing stage, 10% ethanol is interacting with the coating to release more free BPA than originally was present or that can be extracted with foods or acetonitrile. An analytical bias can be discounted based upon the reproducibly good recoveries found for the control samples.

Damage to the can, in the form of denting, did not have an appreciable effect on BPA migration. This was also supported by the data obtained on the retail baby food and rice pudding canned foods. Difficulties encountered with the heterogeneity of different retail food cans, in experiments to investigate the effects of heating the food in the can, were overcome by determining the levels of BPA in the food before and after heating the same can. Only results obtained from the same can were then compared using a significance test. It was concluded that there were no significant changes in BPA levels on heating the food in the can.

The results for the analysis of BPA in canned foodstuffs, found during this work, are of a similar order to those reported in an earlier survey on BPA in canned foods (Food Standards Agency 2001).

The results from this project demonstrated that there was no increase in BPA migration, associated with heating the food in the can, damage to the can or extended storage of food cans where the food is consumed at the end of its declared shelf life.

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