

Release of Bisphenol A from Food Can Lining upon Heating

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Nine different food cans, packed with water, were heat-treated for 30 min at 80 or 100°C in order to elucidate the trends associated with the leaching of bisphenol A (BPA) from internal coatings. Low levels of BPA were detected in water from all unheated cans, rising to 0.06 to 32 ng/cm² after heating at 100°C. Reducing the heat-treatment temperature to 80°C was found to reduce the BPA concentration in the contained water by up to two-thirds. The cans that recorded the highest BPA concentrations in water after heating were found to have components (lid, bottom or body) with high available BPA contents.

Key words — bisphenol A, food can, epoxy resin, heat treatment

INTRODUCTION

Bisphenol A, 2,2-bis(4-hydroxyphenyl)-propane or BPA, has been extensively used to date as a raw material for epoxy resin and polycarbonate plastic, and is produced in large quantities all over the world. Non-negligible levels of BPA, a suspected hormone-disrupting chemical,^{1–8)} have been detected in waterways and seawater around the world^{9–12)} and may pose a concern to ecosystems and humans.

BPA is widely used as a major component of the epoxy resin used to line food cans, and is stable in acid and at high temperature, important for the long-term storage of food. However, there is a possibility that trace amounts of non-polymerized BPA may

leach from the lining into the food packaged in the can. BPA is also added as a stabilizer or antioxidant for inner coatings other than epoxy resin.

In general, canned foods are shipped after sterilization by heating. It is thought that this heating may promote the migration of BPA from the lining into the food, and that the type of food packaged in the can may affect the amount of BPA leached.

Many researchers have reported BPA in canned food.^{13–17)} However, the amounts reported were highly variable due to the different situations and other factors. The purpose of this work is to investigate the relationship between the amount of BPA leached and the BPA content of the can lining, the heating temperature, and the lining material. For this purpose, nine different cans packaged with water were prepared. The BPA concentrations in the water were measured after heat treatment under constant conditions. It was expected that this analysis could clarify the relationship between the migration of BPA from can linings and heating temperatures without the influence of the can's contents.

MATERIALS AND METHODS

Preparation of Cans — Nine different cans and lids, each of different size, shape and material, were prepared for the experiment. All cans were filled with bottled spring water and sealed with a seamer. The cans were then heated for 30 min in an oil bath (10 l) maintained at either 80°C or 100°C using an immersion heater and a mixing rod, and then quenched in cool water. The cans were heated for sterilization before shipping as can foods. For example, the actual temperatures and times for sterilization of some of the cans were at 95°C for 10 min, at 88°C for 25 min, at 83°C for 7 min, and at 80°C for 20 min. **BPA Analysis** — Unheated and heated samples were opened and the 180-ml water samples were taken, from more than one can if necessary, for analysis. To these samples, 1 µg of BPA-d₁₆ (Kanto Chemical Co., INC., Tokyo, Japan) was added as an internal standard. The samples were passed through a solid-phase extraction cartridge (Sep-Pak plus PS-2, Waters Ltd., U.S.A.), which was cleaned with solvents in advance, at a rate of 5 ml/min using an automatic pump (Concentrator, Waters Co., U.S.A.). After extraction, the cartridge was centrifuged to remove water remaining therein. BPA and BPA-d₁₆ in the cartridge were eluted with 9 ml of dichloromethane at 1 ml/min. At the same time, a

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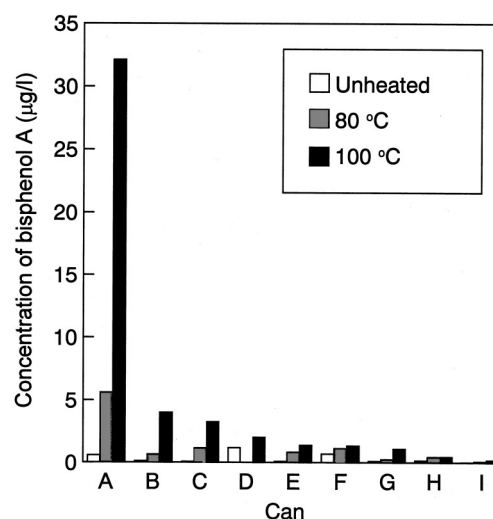
Table 1. Volumes, Structures and Inner Coating Materials of the Prepared Cans

Volume /ml	Can structure	Inner coating material			
		Body	Lid	Bottom	
A	92	3-piece	None	Phenolic-epoxy	Phenolic-epoxy
B	162	3-piece	Phenolic-acrylic epoxy	Vinyl-organosole	Phenolic-acrylic epoxy
C	204	3-piece	Epoxy and vinyl	Epoxy and vinyl	Epoxy and vinyl
D	319	3-piece	Phenolic-epoxy	Epoxy-phenol	Phenolic-epoxy
E	200	3-piece	Epoxy-urea and vinyl	Epoxy-urea and vinyl	Epoxy-urea and vinyl
F	450	3-piece	Epoxy-urea	Phenolic-epoxy	Phenolic-epoxy
G	196	3-piece	Phenolic-acrylic epoxy and acrylic-epoxy	Phenolic-epoxy and acrylic- epoxy	Phenolic-acrylic epoxy
H	448	3-piece	Non	Phenolic-epoxy	Phenolic-epoxy
I	202	seamless	Polyethyleneterephthalate	Vinyl-organosole	Polyethyleneterephthalate

trace amount of water was dehydrated with the other cartridge, which was filled with anhydrous sodium sulfate (Sep-Pak Dry, Waters Co.), mounted on the rear. The eluate was evaporated down to approximately 0.5 ml under high-purity nitrogen gas flow, and 200 μ l of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA; SUPELCO, Inc., Bellefonte, Pennsylvania, U.S.A.) was added to the eluate for the silylation^{18,19} of BPA and BPA-d₁₆. The resultant sample was sealed and left to stand at room temperature for 1 hr to allow the reaction to proceed.

An ion-trap mass detector and gas chromatogram (GC3800/Saturn200, Varian Inc., U.S.A.) with a capillary column of cross-linked 5%-phenylmethylsiloxane (DB-5, J&W Scientific Inc., U.S.A.) was used for BPA analysis. Separation was performed in splitless mode under the following conditions: injector pressure 10.0 psi, linear velocity 38 cm/sec, split ratio 10, split vent opening time 1 min after injection, injection port temperature 280°C. The oven temperature program was as follows: initial temperature 50°C, hold for 1 min, increase at 10°C/min to 280°C, hold for 7 min. Mass spectra were measured in full scan mode.

The total peak area of the $m/z = 357$ and 358 peaks was used for quantification of trimethylsilylated BPA (BPA-TMS), and the 368 and 369 peaks were used for quantification of BPA-d₁₆-TMS. The amount of BPA in the water was calculated from the ratio between these 2 values. The detectable limit in this work was estimated to be about 0.05 ppb (0.05 μ g/l) based on a linear calibration line and blank tests.

**Fig. 1** Bisphenol A Concentrations in Water Packed in Food Cans after Heat Treatment for 30 min

All of the cans were filled with bottled spring water and sealed. The cans were heated for 30 min at either 80°C or 100°C, and then quenched in cool water. The concentrations of bisphenol A leached from internal coatings were analyzed by GC/MS.

RESULTS AND DISCUSSION

Table 1 lists the volumes, structures and inner coating materials of the cans prepared in this work. All the cans were fabricated for packaging fruit or juice, and only 2 cans (E and C) were composed of the same material for the body lid and bottom. Can I (seamless) is the only can that did not have an epoxy coating.

Figure 1 shows the BPA concentrations in water from the unheated and heated cans. It was found that all samples contained BPA even before heating irrespective of the type of can. The BPA concentration then increased upon heating in all cases. Measurements were carried out with due consideration for

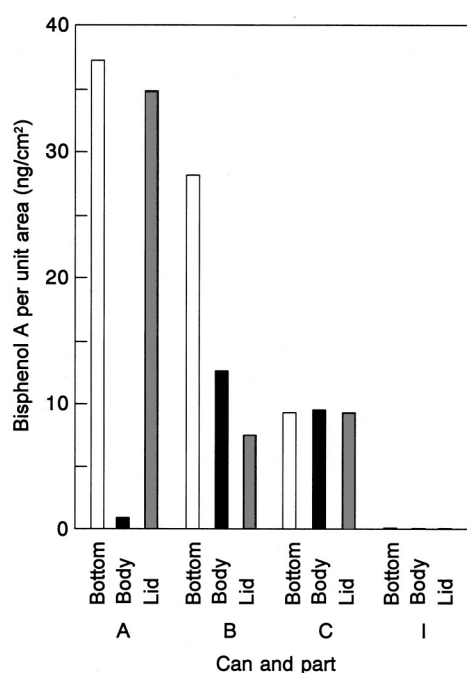


Fig. 2 Amount of Bisphenol A Extracted from Can Parts with Acetone for 20 hr

Square pieces (about 1×1 cm) were cut from all 3 parts of some of the cans, and the outer label was peeled off. The amounts of bisphenol A, which were extracted with acetone from these pieces over 20 hr, were analyzed by GC/MS.

contamination control because the BPA level was relatively low. The present measurement technique was confirmed to be sufficiently sensitive to detect these low levels of BPA.

The BPA concentrations in the cans heated to 80°C were 1.6 to 16.7 times higher (average 6.0 times) than that for unheated cans, and the cans heated at 100°C exhibited BPA concentrations of 1.7 to 55.4 times (average 18.2 times) the unheated concentration. The BPA concentration in the cans heated to 100°C was up to 6.1 times (average 3.0 times) higher than that for 80°C , indicating that it is desirable from the point of view of minimizing BPA leaching to reduce the temperature of sterilization as much as possible considering other safety factors. Based on the present results, reducing the sterilization temperature from 100°C to 80°C could reduce the BPA concentration by as much as two-thirds.

The BPA concentrations obtained were widely variable, and no correlation was seen between the type of can or lining material in this study. Even for cans with apparently identical linings (A and H), the results were quite different. This suggests that BPA migration may depend on the state of BPA in the polymer, such as the degree of polymerization of

the resin or whether the BPA was used as a primary material or an additive.

Figure 2 shows the amounts of BPA extracted with acetone from square pieces. There is no clear relationship with the results shown in Fig. 1, however it can be seen that the cans producing higher BPA concentrations have components with high leachable BPA content. Most notably, the bottom and lid of can A, lined with the same phenolic epoxy, exhibited the highest available BPA content, whereas the body contained very little BPA. In this case, the BPA in the water leached from the lid and bottom, not the body. In the case of can C, all components were of the same composition, epoxy and vinyl, and the BPA content was the same for all components. However, although the bottom and lid of can B were the same, the BPA contents differed. As expected for can I, which produced the lowest BPA concentration in the packaged water, very little BPA was dissolved from any of the components. These results suggested that it was difficult to predict a leaching amount of BPA from the coating composition. It was therefore considered that leaching test was needed for examination of leaching BPA.

REFERENCES

- 1) Gaido, K. W., Leonard, L. S., Gould, J. C., Babai, D., Portier, C. J. and McDonnell, D. P. (1997) Evaluation of chemicals with endocrine modulating activity in a yeast-based steroid hormone receptor gene transcription assay. *Toxicol. Appl. Pharmacol.*, **143**, 205–212.
- 2) Vom Saal, F. S., Cooke, P. S., Buchanan, D. L., Palanza, P., Thayer, K. A., Nagel, S. C., Parmigiane, S. and Welshons, W. V. (1998) A physiologically based approach to the study of bisphenol A and other estrogenic chemicals on the size of reproductive organs, daily sperm production, and behavior. *Toxicol. Ind. Health*, **14**, 239–260.
- 3) Welshons, W. V., Nagel, S. C., Thayer, K. A., Judy, B. M. and Vom Saal, F. S. (1999) Low-dose bioactivity of xenoestrogens in animals: fetal exposure to low doses of methoxychlor and other xenoestrogens increases adult prostate size in mice. *Toxicol. Ind. Health*, **15**, 12–25.
- 4) Lutz, I. and Kloas, W. (1999) Amphibians as a model to study endocrine disruptors: I. Environmental pollution and estrogen receptor binding. *Sci. Total Environ.*, **225**, 49–57.
- 5) Laws, S. C., Carey, S. A., Ferrell, J. M., Bodman, G. J. and Cooper, R. L. (2000) Estrogenic activity

- of octylphenol, bisphenol A and methoxychlor in rats. *Toxicol. Sci.*, **54**, 154–167.
- 6) Kwak, H. I., Bae, M. O., Lee, M. H., Lee, Y. S., Lee, B. J., Kang, K. S., Chae, C. H., Sung, H. J., Kim, J. H., Mar, W. C., Sheen, Y. Y. and Cho, M. H. (2001) Effects of nonylphenol, bisphenol A, and their mixture on the viviparous swordtail fish (*Xiphophorus helleri*). *Environ. Toxicol. Chem.*, **20**, 787–795.
 - 7) Funabashi, T., Kawaguchi, M. and Kimura, F. (2001) The endocrine disrupters butyl benzyl phthalate and bisphenol A increase the expression of progesterone receptor messenger ribonucleic acid in the preoptic area of adult ovariectomized rats. *Neuroendocrinology*, **74**, 77–81.
 - 8) Gutendorf, B. and Westendorf, J. (2001) Comparison of an array of in vitro assays for the assessment of the estrogenic potential of natural and synthetic estrogens, phytoestrogens and xenoestrogens. *Toxicology*, **166**, 79–89.
 - 9) Motoyama, A., Suzuki, A., Shiota, O. and Namba, R. (1999) Direct determination of bisphenol A and nonylphenol in river water by column-switching semi-microcolumn liquid chromatography/electrospray mass spectrometry. *Rapid Commun. Mass Spectrom.*, **13**, 2204–2208.
 - 10) Khim, J. S., Lee, K. T., Kannan, K., Villeneuve, D. L., Giesy, J. P. and Koh, C. H. (2001) Trace organic contaminants in sediment and water from Ulsan Bay and its vicinity, Korea. *Arch. Environ. Contam. Toxicol.*, **40**, 141–150.
 - 11) Kuch, H. M. and Ballschmiter, K. (2001) Determination of endocrine-disrupting phenolic compounds and estrogens in surface and drinking water by HRGC-(NCl)-MS in the picogram per liter range. *Environ. Sci. Technol.*, **35**, 3201–3206.
 - 12) Petrovic, M. and Barcelo, D. (2001) Determination of phenolic xenoestrogens in environmental samples by liquid chromatography with mass spectrometric detection. *J. AOAC Int.*, **84**, 1074–1085.
 - 13) Howe, S. R. and Borodinsky, L. (1998) Potential exposure to bisphenol A from food-contact use of polycarbonate resins. *Food Addit. Contam.*, **15**, 370–375.
 - 14) Kawamura, Y., Inoue, K., Nakazawa, H., Yamada, T. and Maitani, T. (2001) Cause of bisphenol A migration from cans for drinks and assessment of improved cans. *Shokuhin Eiseigaku Zasshi*, **42**, 13–17.
 - 15) Imanaka, M., Sasaki, K., Nemoto, S., Ueda, E., Murakami, E., Miyata, D. and Tonogai, Y. (2001) Determination of bisphenol A in foods using GC/MS. *Shokuhin Eiseigaku Zasshi*, **42**, 71–78.
 - 16) D'Antuono, A., Dall'Orto, V. C., Lo Balbo, A., Sobral, S. and Rezzano, I. (2001) Determination of bisphenol A in food-simulating liquids using LCED with a chemically modified electrode. *J. Agric. Food Chem.*, **49**, 1098–1101.
 - 17) Yoshida, T., Horie, M., Hoshino, Y. and Nakazawa, H. (2001) Determination of bisphenol A in canned vegetables and fruit by high performance liquid chromatography. *Food Addit. Contam.*, **18**, 69–75.
 - 18) Li, D., Park, J. and Oh, J. R. (2001) Silyl derivatization of alkylphenols, chlorophenols, and bisphenol A for simultaneous GC/MS determination. *Anal. Chem.*, **73**, 3089–3095.
 - 19) Takao, Y., Lee, H. C. and Arizono, K. (1999) An attempt by solid-phase microextraction with on-column silylation for a rapid and highly sensitive determination of bisphenol A. *Bunseki Kagaku*, **48**, 589–593.