

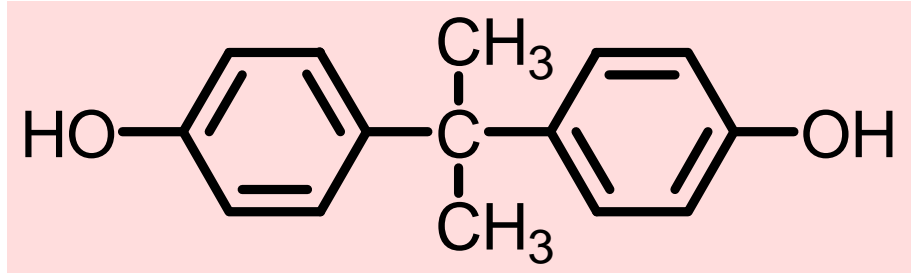


Bisphenol A in Japanese Canned Foods

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Bisphenol A (BPA)

- **Bisphenol A (BPA):**
2,2-bis(4-hydroxy phenyl) propane

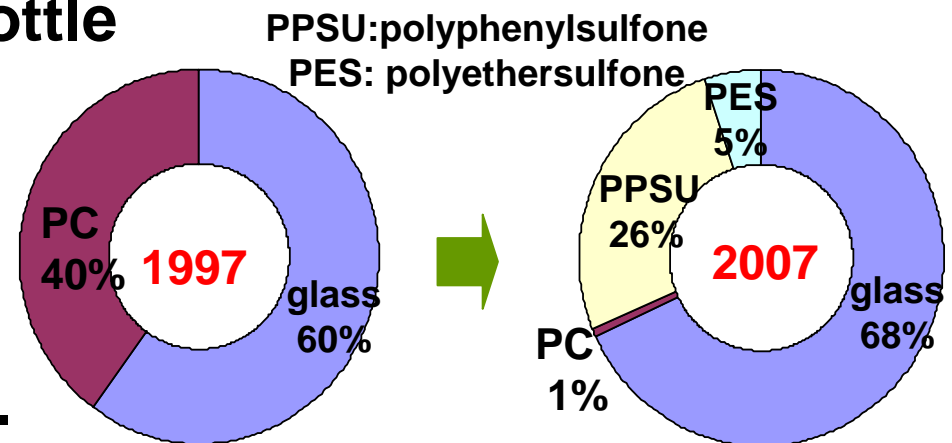


- A suspected **endocrine disrupter** producing estrogenic effects
- Mainly used as a monomer for **polycarbonate** and **epoxy resin**.
- Food contact articles made from polycarbonate or epoxy resin usually contain free BPA which **tends to migrate into foods**.

Polycarbonate

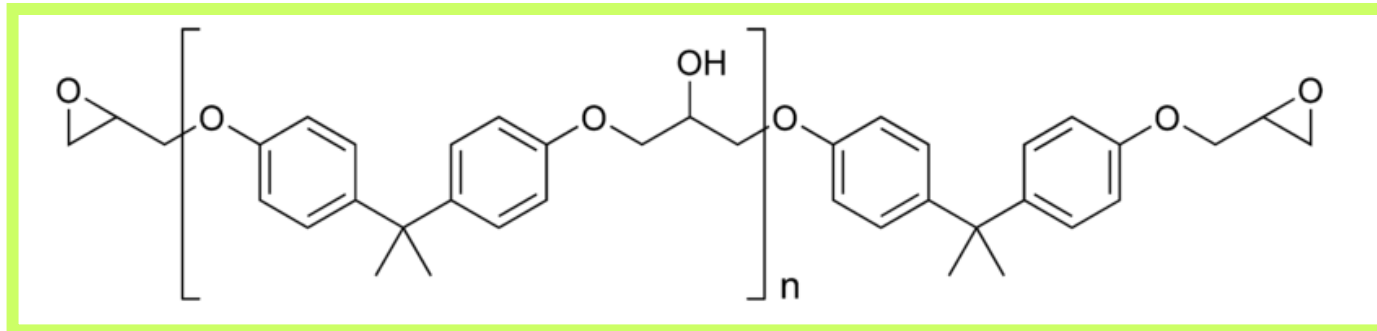
- Polycarbonate (PC) contain BPA as **an unreacted monomer** and **a degradation product of PC**.
- BPA residues were found to be 5-80 ppm in baby dishes and 18-37 ppm in nursing bottles, though their migration level was mainly less than 5 ppb.
- Japanese consumers then refused to buy PC tableware and nursing bottles, and **manufacturers stopped their production** in about 2000.

- The share of PC nursing bottle was about 1% on the Japanese market in 2007. Polyphenylsulfone and polyethersulfone became substitutes for PC.



Epoxy

- **Epoxy:** Thermosetting copolymer formed from the reaction of an epoxide “resin” with a polyamide “hardener”.
- The most common epoxy resin is **diglycidylether of BPA** produced from **BPA** and epichlorhydrin.



- Epoxy has a wide range of applications including paints, coating and adhesives.
- For food contact purposes, it is used as **a coating of tableware and metal cans**, and as **an adhesive for laminate films**.

Epoxy Can Coating



- There are many kinds of canned foods.
- **Metal cans** for food contact use are commonly coated on their surface by **epoxy** or others in order to protect both the cans and foods.
- Epoxy resin is very stable under its glass transfer temperature (ca.105°C)
 - ➡ But over 105°C, it begins to release BPA.
- Food is packed in a can and heated for cooking and/or sterilization over 105°C
 - ➡ BPA will easily migrate into the food.
- **The main source of BPA exposure on humans is canned foods**



Reports of BPA in Canned Foods

Japan past (ca. 2000):

- 1) Y. Kawamura *et. al.*, J. Food Hyg. Soc. Japan, 40, 158 (1999)
- 2) A. Takino *et. al.*, J. Food Hyg. Soc. Japan, 40, 325 (1999)
- 3) S. Horie *et. al.*, Bunseki Kagaku, 48, 579 (1999)
- 4) T. Yoshida *et. al.*, Food Add. Cont., 18, 69 (2001)
- 5) M. Imanaka *et. al.*, J. Food Hyg. Soc. Japan, 42, 71 (2001)

U.K. : A. Goodson *et. al.*, Food Add. Cont., 19, 796 (2002)

New Zealand: B. M. Thomson *et. al.*, Food Add. Cont., 22, 65 (2005)

Canada: X. Cao *et. al.*, J. Food Prot., 73, 1085 (2010)

Belgium: T. Geens *et. al.*, Food Add. Cont., 27, 1627 (2010)

U.S.A.: G. O. Noonan *et. al.*, J. Agric. Food Chem., 59, 7178 (2011)

Reported BPA Contents in Canned Foods

Canned food group	Japan (ca.2000)		UK (2002)		New Zealand (2005)		Canada (2010)		Belgium (2010)		USA (2011)	
	Max. ng/g	Ave. ng/g	Max. ng/g	Ave. ng/g	Max. ng/g	Ave. ng/g	Max. ng/g	Ave. ng/g	Max. ng/g	Ave. ng/g	Max. ng/g	Ave. ng/g
Fish	97	36	44	21	109	28	534	137	169	75	22	12
Meat	602	139	422	108	98	28	-	-	27	27	-	-
Vegetable	95	32	48	27	24	13	92	20	116	42	730	88
Fruit	7	1.6	41	29	< 10	0	-	-	20	12	19	5.1
Other food	86	33	41	12	21	8	189	68	73	35	790	72
Coffee/tea	213	26	-	-	-	-	-	-	0.9	0.7	-	-
Other drink	<2	0	<7	0	< 10	0	-	-	8	1	-	-
All	602	27	422	27	109	14	534	72	169	16	790	60

- The maximum content is 790 ng/g in refried beans in USA.
- Fish, meat, vegetable and other foods sometimes contain high BPA. Japanese coffee and teas also showed high contents.
- The averages of BPA are between 14 and 72 ng/g.
- BPA contents in Canada and USA look like higher than others.

Purpose of Present Survey

- Latter 1990s, the Japanese can manufacturers tried to develop “**BPA reduced cans**”, which are coated with **low-BPA epoxy** or covered with a PET film that replaced the epoxy coating.
- Based on the self regulation of “The Can Manufactureres Institute of Japan” the **migration limit of BPA is 10 ppb for food cans** and **5 ppb for drink cans** into simulants at 121°C for 30 min.
- Our present survey was performed to determine **the BPA contents in the domestic and imported canned foods in Japan** and to verify the effect of “**BPA reduced cans**”.

Samples

- Domestic and imported canned foods were purchased in Tokyo from 2011 to 2012.



Food group	Food (examples)	Sample number	
		Domestic	Imported
Fish	tuna in oil, oil sardine, boiled clam, boiled salmon, mackerel with miso	19	10
Meat	corned beef, sausage, luncheon meat	12	10
Vegetable	sweet corn, green peas, asparagus	13	18
Fruit	orange, peach, apple in syrup	8	10
Other food	onion soup, meat sauce, beef stew	12	12
Coffee/tea	coffee, tea with milk, green tea	21	-*
Other drink	soda, juice, beer, cocktail, rice wine	15	-*
Total		100	60

*: The imported drink cans are very small portion in Japanese market.

Outline of Testing Method

Sample 10 g (drink 50 g)

Added a surrogate (BPA-d₁₆) and methanol

Homogenized and centrifuged

Defatted and purified if needed

Ethylated with Et₂SO₄ and 1 mol/L KOH/EtOH

Dried, then added 1 mL acetone

GC/MS with an internal standard (pyrene-d₁₀)

Column: Inertcap17ms (0.25mmX30m,0.25µm)

Temperature: 100°C (1min)-20°C/min-250°C-
10°C/min-290°C (5.5min)

Detection ion (*m/z*): 269* & 284 (BPA), 280* &
298 (BPA-d₁₆), 212* (pyrene-d₁₀)

(*: for quantification)

Results - High BPA samples (Top 10)

Domestic Can			Imported Can			
Group	Food	BPA (ng/g)	Group	Food	BPA (ng/g)	Country
Other	Hashed beef stew	30	Other	Demiglace sauce	390	N.Z.
Fish	Boiled scalloper	21	Other	White sauce	340	N.Z.
Meat	Corned beef	18	Other	Gratin sauce	320	N.Z.
Fish	Sardine with miso	17	Fish	Blue crab	320	Thai
Fish	Bonito with bean	16	Other	Tomato soup	240	U.S.A
Fish	Tuna in oil	13	Fruit	Coconut milk	200	Thai
Fish	Boiled salmon	12	Fish	Oil sardine	150	Spain
Meat	Cooked chicken	12	Other	Onion gratin soup	150	U.S.A
Meat	Grilled chicken	12	Fish	Tuna in oil	120	V.N.
Vege.	Boiled asparagus	11	Other	Minestrone soup	110	U.S.A

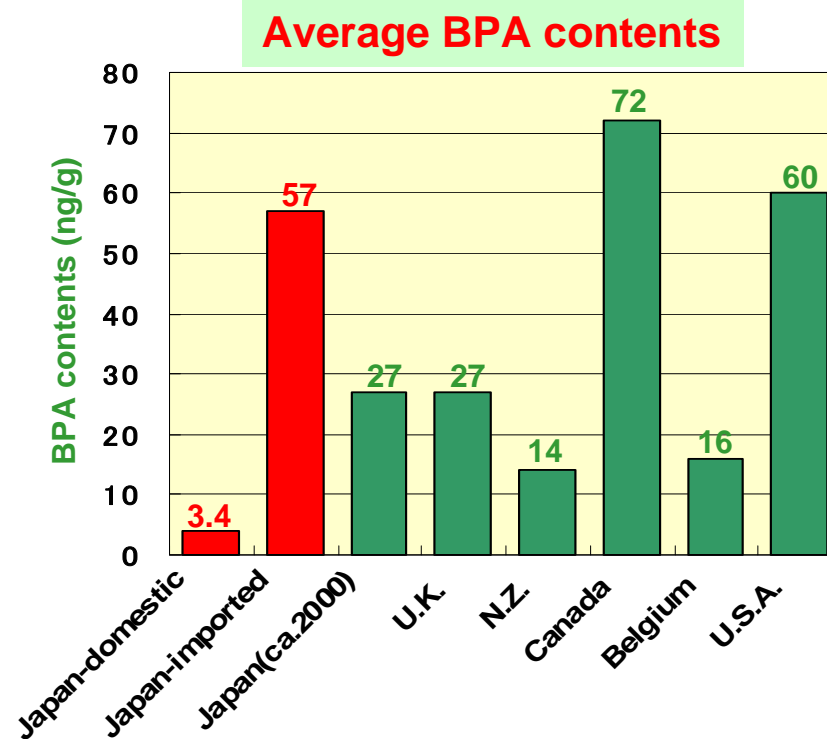
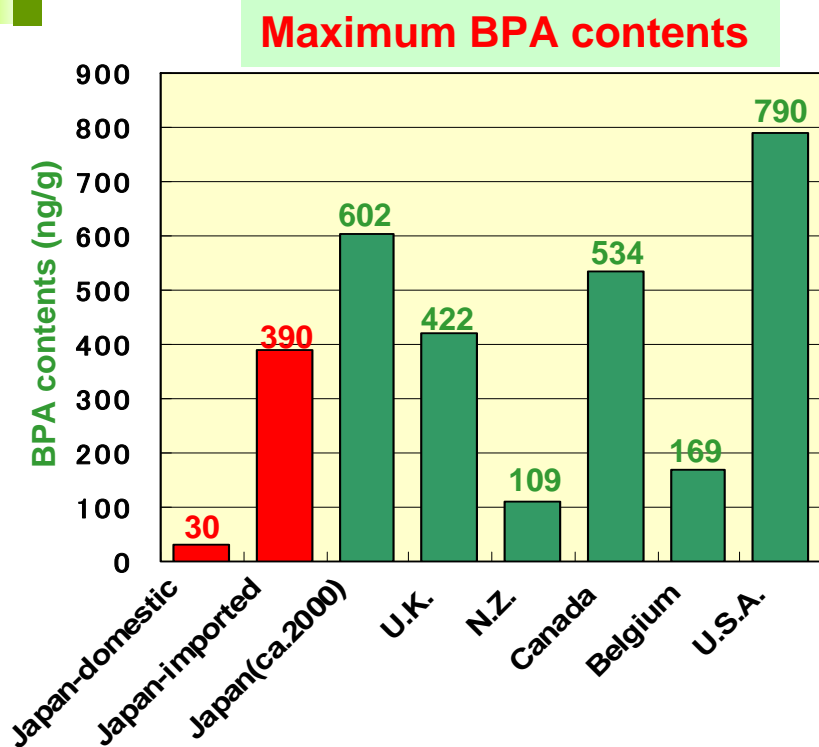
Vege.: Vegetable, N.Z.: New Zealand, V.N.: Viet Narm

Results-Frequency and Content of BPA

Group	LOQ (ng/g)	Domestic Can			Imported Can		
		Freq. (%)	Max. (ng/g)	Ave. (ng/g)	Freq. (%)	Max. (ng/g)	Ave. (ng/g)
Fish	5	68	21	7.9	80	320	76
Meat	5	58	18	6.8	100	25	14
Vegetable	5	38	11	4.1	89	85	35
Fruit	5	0	< 5	0	10	200	20
Other food	5	8	30	2.5	100	390	139
Coffee/tea	1	43	4	1.1	-	-	-
Other drink	1	0	<1	0	-	-	-
All	-	35	30	3.4	78	390	57

LOQ: Limit of quantification; Freq.= % of detected/total sample numbers
 When the average was calculated, ND (under LOQ) was assumed as 1/2
 LOQ (Freq.≥ 20%) or as “0” (Freq.< 20%).

Comparison of BPA Contents in All Surveys



- The maximum and average **BPA contents in the domestic canned foods** are **significantly lower** than those in the imported canned foods and in the other survey results.
- This drastic reduction in Japanese domestic canned foods should be due to the **“BPA reduced cans”** which Japanese can manufacturers have developed.

Estimated BPA Intake in Japan-1

- The estimated BPA intake from canned foods in Japan was calculated for **the domestic and imported canned foods**, then, both were added to the total intake.
- **BPA intake** = Σ (canned food intake x average of BPA contents in each food group)
- **The canned food intake** was calculated based on the annual production, export and import amount of canned foods (in 2010 for the present and that in 2001 for the past) / population (128×10^6 in 2010 and 127×10^6 in 2001) / 365 days.

<For example>

Domestic canned food intake in each group

= (annual production- export amount) / 128×10^6 / 365

Estimated BPA Intake in Japan-2

Food type	Present (2011-12)					Past (ca.2000)	
	Domestic Can		Imported Can		Total	Total Can	
	Food intake (g/p/d)	BPA intake (ng/p/d)	Food intake (g/p/d)	BPA intake (ng/p/d)	BPA intake (ng/p/d)	Food intake (g/p/d)	BPA intake (ng/p/d)
Fish	2.2	17	0.9	68	85	3.1	112
Meat	0.2	1	1.4	20	21	1.2	167
Vegetable	1.1	5	6.3	221	226	8.6	275
Fruit	0.8	0	5.3	106	106	7.6	12
Other foods	1.0	3	1.0*	139	142	3.5*	116
Coffee, tea	58.1	64	0	0	64	77.4	2012
Other drinks	- **	0	- **	0	0	- **	0
All samples	63.4	90	14.9	554	644	101.4	2694

p: person, d: day, *: Imported amount of “other foods” can was not available, thus it was presumed as same as that of domestic can, **: annual production, export and import amount of alcoholic drinks was not available.

- BPA intake **from the domestic cans** was only 90 ng/person/day.
- But the estimated BPA intake from total cans became 644 ng/person /day, because **the imported cans were strongly pushed it up.**

Conclusion

- **The BPA contents in Japanese domestic canned foods were significantly reduced** when compared to the imported canned foods and the past Japan or other countries.
- This drastic reduction in the BPA contents should be due to the **“BPA reduced cans”** which Japanese can manufacturers have developed since later 1990s.
- The estimated BPA intake from the domestic cans was **90 ng/person/day**. But the intake from the imported can was 554 ng/person/day and total intake became **644 ng/person/day**.
- These results indicate that **the BPA intake from canned foods can be reduced by the can manufacturing techniques**.