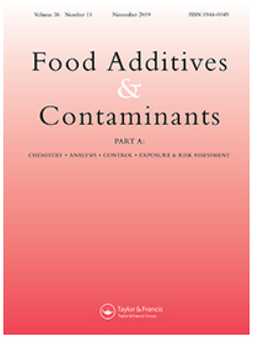

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LC-MS/MS analysis of bisphenol S and five other bisphenols in total diet food samples

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ABSTRACT

It is already known that bisphenol S (BPS) has been used as a substitute for BPA in thermal papers in recent years. It is not clear, however, if BPS has also been used to replace BPA in can coatings as currently being speculated due to a lack of credible studies on migration of BPS from can coatings and occurrence data of BPS in foods. In this study, an LC-MS/MS method was developed for the analysis of BPS, along with several other bisphenols, and method detection limits for BPS varied from 0.0017 to 3.1 ng/g depending on the type of sample matrix and the amount of sample analysed. This method was used to analyse 159 different food composite samples from a recent Canadian total diet study. Bisphenol E (BPE), bisphenol B (BPB), and bisphenol AF (BPAF) were not detected in any of the 159 food composite samples, bisphenol F (BPF) was detected in only three samples (25–2360 ng/g), and bisphenol A (BPA) was detected in 10 samples (5.3–41 ng/g) which were all prepared from canned foods. BPS was not detected in any of the canned food composite samples but was detected in nine food composite samples prepared from meat and meat products (1.2–35 ng/g), indicating sources for BPS other than can coatings may be possible, which will be investigated in future studies.

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Bisphenol A; bisphenol S; food; total diet; LC-MS/MS

Introduction

Bisphenol A (BPA) is an industrial chemical used in food packaging and other products such as thermal papers. One of the major applications of BPA in food packaging is in the production of epoxy resins which are frequently used in the internal coating for food and beverage cans to protect the contents from direct contact with metal. Residues of BPA in these coatings can migrate into foods, especially at elevated temperatures. Due to consumer concerns regarding the health effects of BPA, industries have been seeking alternatives to replace BPA and already have abandoned the use of BPA-containing packaging for some foods such as liquid infant formula products (Health Canada 2014) and canned soups (Campbell Soup Company 2016). Among the alternatives to replace BPA are the other bisphenol analogues, such as bisphenol S (BPS), bisphenol F (BPF), bisphenol B (BPB), and bisphenol AF (BPAF). The estrogenicity of tetramethyl bisphenol F (TMBPF) has also been assessed recently and its potential as an alternative for BPA in a new food-contact coating was demonstrated (Soto et al. 2017). It is already known that BPS has been used as a substitute for BPA in thermal papers in recent years, and thermal register receipts were found to contain high levels of BPS (as high as 22 mg/g or 2.2%) but had low or non-detectable levels of BPA in the same samples (Liao et al. 2012). However, it is not known if BPS has also been used as a substitute for BPA in can coatings as currently being speculated. There have been no credible studies demonstrating the migration of BPS from can coatings into foods. There is also a lack of occurrence data for BPS in foods, in general, relative to BPA, and concentrations of BPS in foods were also low in the available credible-published results (e.g. Liao and Kannan

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2013, 2014; Yang et al. 2014; Regueiro and Wenzl 2015a, 2015b).

BPA and other bisphenols structurally very similar to BPA (e.g. BPB, BPE, BPF) can be analysed by both liquid chromatography (LC) and gas chromatography (GC) coupled to mass spectrometry (MS) or tandem mass spectrometry (MS/MS). Compared to LC methods, the GC methods are more tedious due to the necessary derivatisation step but may offer better sensitivity. Since BPS is more polar than the other bisphenols due to its sulfonyl group, even after derivatisation of the hydroxyl groups, LC methods are more commonly used (Gallart-Ayala et al. 2011; Liao and Kannan 2013, 2014; Yang et al. 2014; Regueiro and Wenzl 2015a, 2015b). There may be some issues with the GC analysis of BPS but were rarely addressed in the relatively few available GC methods for BPS (Deceuninck et al. 2015; Česen et al. 2016; Jurek and Leitner 2017). In this work, analysis of BPS using a GC method was investigated, and an LC-MS/MS method was developed for simultaneous analysis of several bisphenols with BPS being the focus. This method was evaluated and used for the analysis of BPS and other bisphenols in various food samples from a recent Canadian Total Diet Study, providing information for the first time on dietary exposure of the Canadian populations to BPS.

Materials and methods

Materials and reagents

Acetonitrile (HPLC grade) and methanol (HPLC grade) were purchased from J.T. Baker (Phillipsburg, N.J.). Individual solutions of unlabelled bisphenols (A, AF, B, E, F and S) in acetonitrile (100 µg/mL) and individual solutions of ring-$^{13}C_{12}$ labelled (99%) bisphenols (A, AF, B, and F) in acetonitrile (100 µg/mL) were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). Ring-$^{13}C_{12}$ labelled (99%) bisphenol S (BPS-$^{13}C_{12}$) and 2,4′-bisphenol S (2,4′-BPS-$^{13}C_{12}$) were purchased from Toronto Research Chemicals Inc. (Toronto, ON). Solid phase extraction cartridges (Strata-X, 500 mg/6 mL) were purchased from Phenomenex (Torrance, CA).

Separate composite solutions of labelled and unlabelled bisphenols were prepared in acetonitrile. A standard solution of BPS-$^{13}C_{12}$ was prepared in acetonitrile (0.5 µg/mL). Calibration standard solutions (1, 5, 10, 25, 50, 100, 200 ng/mL) of bisphenols were prepared by combining appropriate volumes of composite bisphenol standard solutions (2.5 ng/µL), with a solution of BPS-$^{13}C_{12}$ and composite labelled bisphenol standard solutions (2.5 ng/µL) to 2 mL vials containing water and acetonitrile (3:2).

Sample collection

Food samples were collected from four different stores in Quebec City, Canada, over a five-week period in 2016. The foods were prepared as for consumption according to the established procedures (Dabeka and Cao 2013), and the individual samples of each type of food were combined into a total of 159 different food composites. Composites for foods that can be consumed both raw and cooked (e.g. cauliflower, carrots, broccoli, tomatoes, spinach) were prepared as a mixture of the raw and cooked (1:1). The food composites covered a variety of food categories including dairy products, meat, poultry, fish, cereal, vegetable, fruit, beverages and other miscellaneous foods. Stainless steel or glass vessels were used for all processing. Food composites were stored frozen in 250 mL glass jars at −20°C until analysis.

Sample extraction and analysis

Approximately 1 g of sample was weighed into a 15-mL polypropylene centrifuge tube. The sample was spiked with internal standards of ring-$^{13}C_{12}$ labelled bisphenols and then mixed. Six mL of acetonitrile was added, and the sample was shaken for 30 s and vortexed for 30 s. The sample was then centrifuged at 4000 rpm or 3220 rcf for 15 min. The liquid was decanted in a 60 mL glass tube and 40 mL of water was added to each tube. The tube was capped and the contents were mixed.

The Strata-X 500 mg/6 mL SPE cartridge was conditioned with 10 mL of acetonitrile followed by 10 mL of 20% acetonitrile in water. The aqueous extract was poured into a reservoir fitted on top of the cartridge, and the sample passed through the cartridge by gravity. The cartridge was rinsed with

10 mL of 20% acetonitrile in water, and eluted with 10 mL of methanol. The eluate was evaporated to dryness using an N_2 evaporator, reconstituted with 0.6 mL of water and 0.35 mL of acetonitrile and mixed well, and spiked with 50 µL of 2,4′-BPS-$^{13}C_{12}$ performance standard (0.5 ng/µL) for LC-MS/MS analysis.

LC-MS/MS analysis

A Waters Acquity Ultra Performance Liquid Chromatography (UPLC) system (Milford, MA, USA) coupled to a Waters Quattro Premier XE mass spectrometer (Milford, MA, USA) operated in electrospray ionisation (ESI) negative mode was used for analyses. Chromatographic separation of target bisphenol analytes was achieved at 22°C on an Acquity UPLC BEH Phenyl column from Waters (1.7 µm, 2.1 mm x 100 mm) attached to a Waters Van Guard BEH phenyl pre-column (1.7 µm, 2.1 × 5 mm). The mobile phase consisted of (A): Water and (B): Acetonitrile. The gradient programming was as follows: initial gradient 40% (B) (held for 2 min) to 90% (B) in 8 min, hold for 1 min and go back to 40% (B) in 1 min, hold for additional 1 min to equilibrate. The injection volume was 10 µL and the flow rate set at 0.20 mL/min.

The MS/MS was operated in electrospray negative ionisation multiple reaction monitoring (MRM) mode. Source temperature, desolvation temperature, and desolvation gas flow were 120°C, 350°C, and 1000 L/hour, respectively. Extractor and capillary voltages were set at 4 V and 3 kV, respectively. Nitrogen was used as cone and desolvation gas and argon was used as collision gas with a flow of 0.20 mL/min.

The calculation of concentrations of bisphenols in samples was based on the isotope dilution methodology, BPF-$^{13}C_{12}$ was used as the internal standard for BPE due to lack of its labelled standard. In the course of method development, matrix effect was observed and 2,4′-BPS- $^{13}C_{12}$ was used as a performance standard to account for this, as well as for the uncertainty associated with injection reproducibility. The performance standard was added to the samples and calibration standards immediately prior to injection.

Results and discussion

Method performance

In order to investigate the occurrence of BPS, BPA and other bisphenols in foods, we initially focused on expanding our existing GC-MS method originally developed for the analysis of BPA in foods (Cao et al. 2008, 2011). This approach was taken since the GC analysis of BPS was demonstrated in a few studies (Deceuninck et al. 2015; Česen et al. 2016) with reasonable performance and no issues were reported. This expanded method worked well for the analysis of bisphenols structurally very similar to BPA, such as BPAF, BPB, BPE, and BPF (Cao and Popovic 2015, 2018), but it was not suitable for the analysis of BPS due to its sulfonyl group. BPS, after derivatisation, can be analysed by GC and comparable responses to the other bisphenols are observed in the initial injection using a brand-new GC column (Cao 2019). The BPS responses, however, could not be sustained and decreased considerably in the subsequent injections. This is due to BPS, after derivatisation, being still polar due to the sulfonyl group. Jurek and Leitner (2017) also observed a higher activity of BPS in the GC system, which resulted in peak tailing and decreased BPS sensitivity over time. Thus, GC-based methods cannot be used for the accurate analysis of BPS, especially in a large number of samples.

The multiple reaction monitoring (MRM) acquisition conditions for LC-MS/MS analysis of BPS and the other bisphenols were optimised in electrospray negative ionisation mode, and the MRM transitions, cone voltages and collision energies are summarised in Table 1. Two MS/MS ion transitions were monitored for each bisphenol, with the more abundant transition as the quantifier and the other as the qualifier for confirmation. The typical MRM chromatograms from a standard solution of the bisphenols are shown in Figure 1. The linearity of the instrument and the method were demonstrated using five standard solutions, with R^2 better than 0.99 for all bisphenols.

The sample extraction and clean-up procedure developed previously for BPA (Cao et al. 2008, 2011) was also investigated for the extraction of BPS and other bisphenols from foods. This procedure works well for the extraction of these

Table 1. MRM transitions (*m/z*), cone voltages (CV), and collision energies (CE) of target analytes under ES-ionisation mode.

Compound	Quantifier	CV (V)	CE (eV)	Qualifier	CV (V)	CE (eV)
BPS	249 → 108	35	25	249 → 92	35	33
2,4′-BPS-$^{13}C_{12}$*	261 → 161	35	14	261 → 114	37	27
4,4′-BPS-$^{13}C_{12}$	261 → 114	37	27	261 → 98	37	45
BPF	199 → 93	35	25	199 → 105	35	20
BPF-$^{13}C_{12}$	211 → 99	35	23	211 → 111	35	22
BPE	213 → 198	40	16	213 → 118	40	29
BPA	227 → 212	40	18	227 → 133	40	20
BPA-$^{13}C_{12}$	239 → 224	40	17	239 → 139	40	31
BPB	241 → 212	37	20	241 → 226	37	20
BPB-$^{13}C_{12}$	253 → 224	37	19	253 → 238	37	15
BPAF	335 → 265	40	32	335 → 245	40	33
BPAF-$^{13}C_{12}$	347 → 277	40	22	347 → 257	40	31

*2,4′-BPS-$^{13}C_{12}$ was used as a performance standard.

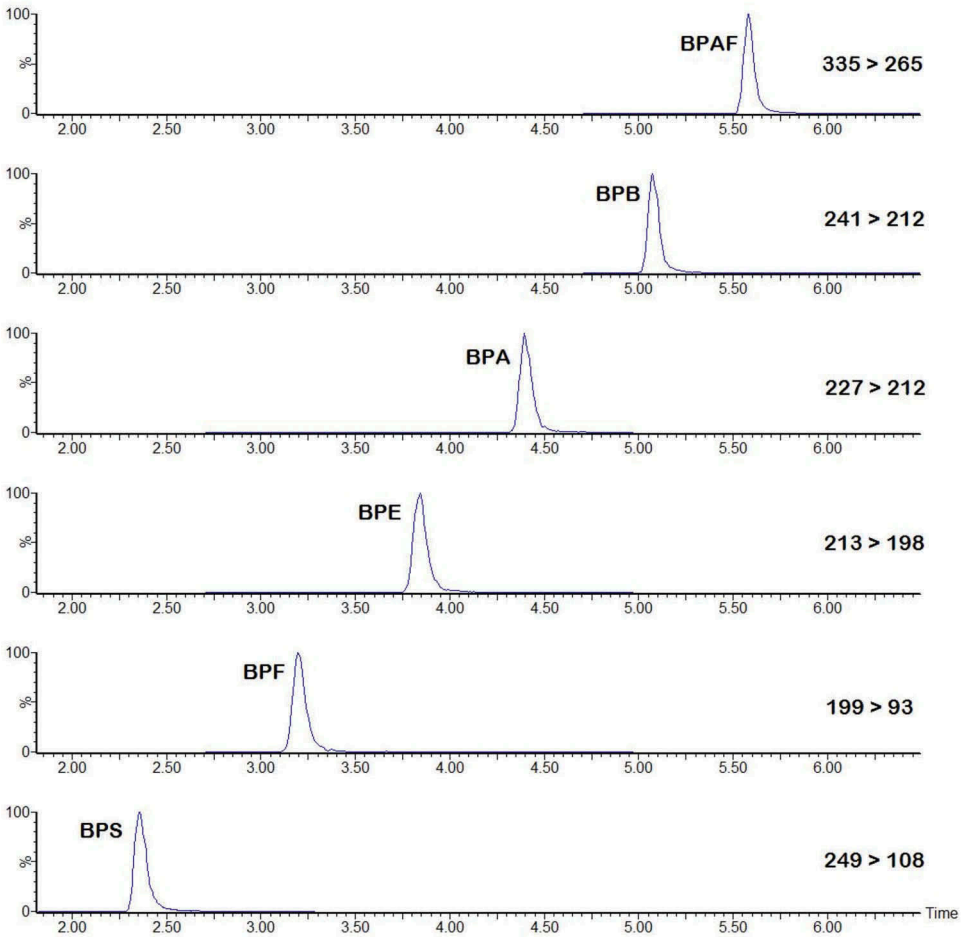

Figure 1. Typical LC-MS/MS chromatograms of bisphenols.

bisphenols structurally very similar to BPA, such as BPE, BPB, BPF, and BPAF (Cao and Popovis 2015, 2018), but recoveries were low for BPS, consistent with reports of other researchers (Yang et al. 2014). Owing to the polar structure of BPS due to its sulfonyl group it cannot be retained well on the C18 SPE cartridge during extraction.

Strata-X is a polymeric reversed-phase SPE sorbent with a modified pyrrolidone ligand. It offers multiple modes of retention including hydrophobic, π-π interactions as well as hydrogen bonding. Additionally, it is known to retain polar analytes more tightly than the traditional C18 sorbents (Phenomenex 2010). Its performance for the extraction of BPS and other bisphenols from

various food matrices was investigated at three spiking levels (5, 25, and 50 ng), with five replicates at each level, and the results are shown in Table 2.

Given that a sensitive GC-MS method for analysis of BPA and other bisphenols (BPE, BPB, BPF, and BPAF) in foods has been established in our lab (Cao and Popovis 2015, 2018), the focus of this work was to develop a method for BPS. The other bisphenols (BPA, BPE, BPB, BPF, and BPAF) will be analysed simultaneously only if possible under the optimised conditions for BPS. The method performed very well for both BPS and BPAF with similar sensitivities, recoveries were from 92.4% to 104% (98.8% average) with relative standard deviations from 0.40% to 9.6% (3.2% average) for BPS, and from 93.9% to 109% (102% average) with relative standard deviations from 0.40% to 8.9% (2.3% average) for BPAF (Table 2). The method detection limits (MDLs), measured as 10 times the signal-to-noise ratio for different food matrices (not pure standard), varied among different food types, and were as low as 0.060 ng/g for BPS in fruit, 0.036 ng/g for BPAF in vegetable, and even lower for simple matrix samples, especially when a large volume of the sample is processed for analysis, with 0.0017 ng/g and 0.0013 ng/g for BPS and BPAF in water (50 mL), respectively. However, the other bisphenols (BPF, BPE, BPA, BPB) were affected by the matrix effects and interferences; BPF and BPE simply cannot be measured in fruit and vegetable samples, MDLs were as high as 19, 20, 57, and 14 ng/g for BPF, BPE, BPA, and BPB in fish, respectively. The relative standard deviations varied from 1.8% to 21%, 1.7% to 22%, 0.80% to 23% and 0.46% to 25% for BPF, BPE, BPA and BPB, respectively.

Analysis of total diet samples

A total diet study consists of purchasing foods commonly consumed, processing them as for consumption, combining the foods into food composites, and homogenising them for analysis. The Canadian Total Diet Study (TDS) has been ongoing since 1969, monitoring various chemical contaminants in the Canadian food supply and playing an important role in generating data for human exposure assessment. The total diet samples collected since 2008 have been analysed for BPA to generate occurrence data for dietary exposure assessment updates and to observe temporal trends of BPA in foods and determination of changes in the use of BPA in food packaging (Cao et al. 2011, 2015). Food samples from the recent 2016 TDS were analysed in this study for BPS, BPA and other bisphenols (BPE, BPB, BPF, and BPAF) to investigate the occurrence of the other bisphenols currently being considered as alternatives to BPA in food packaging.

BPE, BPB and BPAF were not detected in any of the 159 food composite samples analysed; thus, it is unlikely these bisphenols have been used in food packaging, and more specifically, in food can coatings. Results of BPS, BPF, and BPA in the food composite samples are shown in Table 3. BPF was detected in only three food composite samples, at 25 ng/g in chicken burger, 231 ng/g in hamburger, and 2360 ng/g in condiments. The sample of condiments was prepared as a mixture of ketchup and mustard (2:1). It is known that BPF occurs naturally in mustard which forms as a reaction product from the breakdown of the glucosinolate glucosinalbin with 4-hydroxybenzyl alcohol as an intermediate (Zoller et al. 2016). The BPF observed in the sample of condiments is very likely from the mustard instead of the food packaging. The BPF detected in the chicken burger and hamburger samples is also very likely from the mustard present in these products when analyzed.

Among the 159 food composite samples analysed, BPA was detected in only 10 food composite samples, ranging from 5.3 ng/g to 41 ng/g. These 10 samples were all prepared using canned foods, wholly or partly; thus, BPA in these samples is very likely from the can coatings. Compared to the results from previous years of the TDS (Cao et al. 2011, 2015), a further decrease in BPA concentration was observed in some of the samples, especially soups. This observation is consistent with the effort from industries to remove BPA from food packaging (Campbell Soup Company 2016). Slight increases in BPA concentrations were observed only in a few samples (e.g. beans, corn, and peas). It should be mentioned that the LC-MS/MS method used in this work is not as

Table 2. Method accuracy, precision, and method detection limit (MDL) for analysis of BPS and other bisphenols in various food matrices.

		BPS		BPF		BPE		BPA		BPB		BPAF	
Food	Spiking level, ng/g	Recovery (%), mean ± SD*	MDL (ng/g)	Recovery (%), mean ± SD*	MDL (ng/g)	Recovery (%), mean ± SD*	MDL (ng/g)	Recovery (%), mean ± SD*	MDL (ng/g)	Recovery (%), mean ± SD*	MDL (ng/g)	Recovery (%), mean ± SD*	MDL (ng/g)
Infant formula (1 g)	5	96.0 ± 2.4	0.10		6.2	104 ± 11	2.0	98.4 ± 3.0	1.0	99.2 ± 4.6	0.75	99.2 ± 1.8	0.16
	25	99.1 ± 1.2		105 ± 6.6		104 ± 8.8		99.9 ± 2.0		98.9 ± 0.91		101 ± 1.2	
	50	99.6 ± 0.79		109 ± 10		105 ± 11		101 ± 2.2		99.6 ± 1.3		101 ± 1.1	
Fish (1 g)	5	93.6 ± 7.8	3.1		19		20		57		14	99.6 ± 2.6	1.4
	25	101 ± 0.40				97.7 ± 21				101 ± 1.9		101 ± 1.0	
	50	103 ± 2.6		88.7 ± 18		107 ± 8.2		103 ± 1.3		101 ± 1.0		101 ± 1.7	
Meat (1 g)	5	92.4 ± 8.8	0.18	112 ± 21	4.4	109 ± 11	5.2	108 ± 25	4.9	84.3 ± 21	2.2	109 ± 8.9	0.061
	25	98.4 ± 2.4		84.6 ± 15		126 ± 5.0		111 ± 12		96.6 ± 18		109 ± 3.4	
	50	102 ± 8.1		117 ± 18		115 ± 12		108 ± 5.0		109 ± 12		108 ± 4.3	
Fruit (1 g)	5	93.6 ± 4.3	0.060					97.5 ± 2.5	0.64	98.8 ± 3.6	0.48	97.6 ± 1.7	0.063
	25	98.7 ± 2.3						104 ± 10		99.8 ± 0.46		100 ± 0.44	
	50	99.8 ± 0.64						99.1 ± 0.79		100 ± 1.5		99.9 ± 1.1	
Vegetable (1 g)	5	98.0 ± 4.9	0.078					102 ± 2.6	1.5	98.0 ± 2.4	1.00	101 ± 1.1	0.036
	25	98.7 ± 1.2						100 ± 2.4		98.9 ± 1.0		101 ± 0.52	
	50	99.1 ± 1.7						100 ± 1.3		99.9 ± 1.3		100 ± 0.87	
Soup (1 g)	5	102 ± 3.0	0.13	105 ± 6.2	3.0	81 ± 3.2	1.6	103 ± 10	2.7	101 ± 4.6	2.1	100 ± 3.8	0.069
	25	101 ± 1.6		107 ± 10		87.8 ± 5.9		105 ± 2.2		99.9 ± 2.1		101 ± 0.40	
	50	100 ± 1.3		102 ± 1.8		86.4 ± 2.4		102 ± 3.0		100 ± 1.9		101 ± 1.4	
Beverage (5 mL)	1	92.9 ± 2.6	0.016	105 ± 15	1.1	92.4 ± 6.2	0.42	105 ± 13	0.45	87.6 ± 6.5	0.38	93.9 ± 4.9	0.010
	5	104 ± 1.3		111 ± 13		111 ± 1.8		107 ± 1.8		98.4 ± 0.87		108 ± 1.5	
	10	103 ± 3.3		109 ± 5.9		119 ± 7.8		108 ± 3.7		105 ± 6.3		108 ± 3.6	
Water (50 mL)	0.01	101 ± 7.6	0.0017	98.4 ± 11	0.095	102 ± 15	0.039	109 ± 16	0.038	94.0 ± 6.5	0.040	101 ± 4.1	0.0013
	0.5	99.7 ± 2.2		107 ± 9.5		97.4 ± 5.3		102 ± 6.7		97.4 ± 2.2		99.0 ± 1.9	
	1	100 ± 1.6		102 ± 1.9		99.0 ± 7.3		100 ± 1.1		98.8 ± 2.6		99.5 ± 1.6	

*n = 5

Table 3. Concentrations (ng/g) of BPS, BPF and BPA in the food composite samples from 2016 TDS.

	Concentration, ng/g		
Food composite	BPS	BPF	BPA
Beef, steak	18		
Beef, roast	7.1		
Beef, ground	35		
Pork, fresh	5.1		
Veal, cutlets	6.9		
Lamb	1.2		
Luncheon meats, cold cuts	2.7		
Organ meats	7.6		
Wieners & sausages	3.3		
Hamburger		231	
Chicken burger		25	
Condiments		2360	
Evaporated milk, canned			11
Soups, meat, canned			25
Soups, creamed, canned			41
Soups, broth, canned			23
Baked beans, canned			36
Beans, string, fresh + canned (1:1)			18
Beets, fresh + canned (1:1)			12
Corn, frozen + canned (1:2)			41
Peas, frozen + canned (1:1)			30
Tomatoes and tomato sauce, canned			5.3

sensitive as the GC-MS method used previously (Cao et al. 2011, 2015) for BPA analysis; thus, BPA was not detected in many samples where BPA was detected at lower levels previously.

BPS was not detected in any of the canned food composite samples but was detected in nine of the 159 food composite samples with concentrations from 1.2 ng/g to 35 ng/g. These nine food composite samples are all from the meat group (11 samples in total), and the canned luncheon meat and cured pork are the only two meat samples where BPS was not detected. This obviously does not support the current speculation that BPS has been used as a replacement for BPA in can coatings. However, since this is the first time total diet samples were analysed for BPS and these samples were from only one TDS year (2016), analysis of food samples from future years is in progress to continue the investigation of the presence of BPS in foods and the consistency of the results. A thorough-targeted survey of canned foods is also being planned to focus on BPS, since only a limited number of canned foods can be collected in a TDS.

BPS was detected in meat products in some early studies, but the levels were low, with an average of 0.609 ng/g (Liao and Kannan 2013) and 2.16 ng/g (Liao and Kannan 2014). The sources for BPS found in the meat samples in this study are not clear. These samples were generally packaged on polystyrene foam trays overwrapped with cling films, and they are not known to contain BPS or other bisphenols. Thus, sources other than food packaging, such as natural formation of BPS like BPF (Zoller et al. 2016), may be possible, and the presence of BPS in meat products will be further investigated.

In summary, since GC methods are not suitable for the accurate analysis of BPS due to its polarity with the sulfonyl group, an LC-MS/MS method was developed instead and used to analyse food samples from a recent Canadian Total Diet Study for BPS and other bisphenols. Among the six bisphenols analysed, BPE, BPB, and BPAF were not detected in any of the 159 food composite samples. BPF was detected in a few samples where mustard was used, and BPA was detected in some foods where canned foods were used. BPS was detected in only 9 of the 159 food composite samples, they were all samples of meat products, and none of them was prepared from canned foods. Thus, sources other than can coatings may be possible for BPS in foods and should be investigated in future studies.

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