

## RESEARCH ARTICLE

# A comparison of electrospray ionization, atmospheric pressure chemical ionization, and atmospheric pressure photoionization for the liquid chromatography/tandem mass spectrometric analysis of bisphenols. Application to bisphenols in thermal paper receipts and U.S. currency notes

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**Rationale:** Human health concerns have arisen for common bisphenols (BPA and BPS) as well as new structural analogs. While native sulfone bisphenols and sulfone-derivatized bisphenols are amenable to electrospray ionization (ESI), alternative ionization methods such as atmospheric pressure chemical ionization (APCI) and APPI were investigated to analyze non-derivatized, non-sulfone-containing bisphenols.

**Methods:** Ionization of bisphenols using negative ion APPI was compared to negative ion ESI and negative ion APCI for their relative abilities to produce  $[M-H]^-$  precursor ions for subsequent collision-induced dissociation (CID) in a triple quadrupole mass analyzer. Multiple reaction monitoring (MRM) transitions were optimized using the most sensitive ion transitions and coupled with high-performance liquid chromatographic (HPLC) separation to detect and quantify BPA, BPB, BPF, BPZ, BPAP, BPS, and BPSIP.

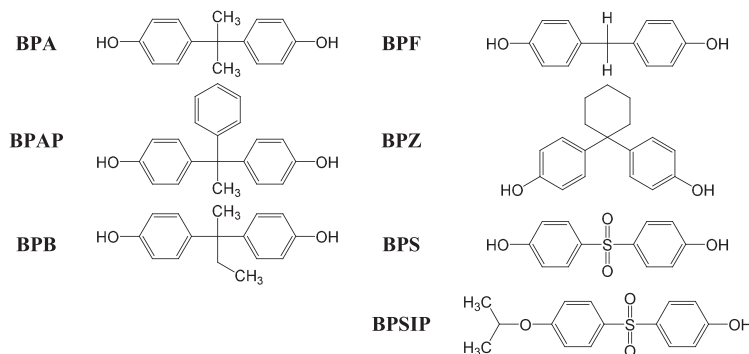
**Results:** APPI provides a more universal sensitivity over ESI toward the classes of bisphenols studied with detection limits of 20–50 pg on-column. The LC/APPI-MS/MS method was used to examine the levels of these seven bisphenols in thermal paper receipts and in U.S. paper currency. In both receipts and currency, BPA and BPS were the dominant bisphenols found in the paper.

**Conclusions:** The measurement of BPA and bisphenol analogs in thermal paper receipts and transfer of bisphenols from receipts to currency notes is of increasing importance to assess human dermal exposure routes to this class of compounds. Equivalent sensitivity between sulfone- and non-sulfone-containing bisphenols is achievable through the use of alternate ionization sources such as APCI and APPI that circumvents tedious and time-consuming derivatization procedures to render analytical sensitivity by ESI.

## 1 | INTRODUCTION

Bisphenol A (BPA, Figure 1) is a high volume chemical with annual production volumes of over six billion pounds and over 100 tons released into the global environment per year.<sup>1</sup> BPA is primarily used to make polycarbonate plastic and epoxy resins that are used as an internal coating for food and beverage cans. Additionally, BPA is found in polycarbonate toys, water pipes, drinking containers, eyeglass lenses, sports safety equipment, dental sealants, medical equipment and tubing, and consumer electronics.<sup>1</sup> As a result of the extensive use of

BPAs in consumer products, concerns have arisen given its classification as an endocrine disruptor (ED).<sup>1,2</sup> Moreover, the appearance of BPAs in every U.S. National Health and Nutrition Examination Survey (NHANES) cycle since 2003/2004 suggests a ubiquitous human exposure.<sup>3</sup> Detailed information on the general use, production, and human exposure levels of BPA was summarized in 2008 by the EU<sup>4,5</sup> the National Toxicology Program, Center for the Evaluation of Risks to Human Reproduction (NTP-CERHR),<sup>6</sup> as well as a 2013 literature review.<sup>7</sup> Health agencies generally agree that oral ingestion from BPA leaching from dental composites into saliva and BPA leaching



**FIGURE 1** Structures of the seven bisphenols studied

into food or beverages from the protective internal epoxy resin coatings of canned foods are the two most common exposure routes for oral ingestion of BPA.<sup>8</sup> Additional BPA human ingestion routes include direct mouthing of polycarbonates as well as secondary transfer from consumer products such as polycarbonate tableware, food storage containers, water bottles, and baby bottles.<sup>9</sup> Residual, unreacted monomers of BPA in polycarbonate, but also free BPA released by these polymers under alkaline pH conditions or during microwave heating<sup>10</sup> can migrate into beverages and foods,<sup>11</sup> partially explaining human exposure routes.<sup>12</sup> In the U.S., a 2008 NTP-CERHR monograph<sup>6</sup> concluded that BPA causes developmental toxicity, and in 2016 the California Office of Environmental Health Hazard Assessment (OEHHA) added BPA to the list of chemicals known to cause female reproductive toxicity.

Recently, concerns have arisen over dermal exposure to BPA through contact with thermal receipt paper.<sup>13–18</sup> BPA has been used since the 1970s as a color developer in lightweight printing devices relying on the thermal paper transfer technology which continues worldwide in cash registers and credit card terminals. In thermal printing methods, a powdery layer of BPA coats one side of the paper and protonates a thermochromic dye upon heating.<sup>19</sup> In addition to cashiers, consumers handle thermal receipt paper on a daily basis establishing concerns that thermal paper presents a route for dermal exposure to BPA. Elevated levels of BPA and its metabolites were found in the urine of occupationally exposed cashiers,<sup>20</sup> with the highest levels in pregnant women cashiers,<sup>21</sup> supporting gender differences in BPA absorption, metabolism, and/or excretion with a longer residence time in women than men.<sup>1</sup> Using viable human skin explants, BPA was dermally absorbed in short-term cultures and was largely metabolized to BPA mono-glucuronide and BPA monosulfate, unequivocally demonstrating that BPA is readily absorbed and metabolized by the skin.<sup>22</sup>

With increasing BPA regulation worldwide, bisphenol S (BPS, Figure 1), as well as unregulated, structural bisphenol analogs, are increasingly being employed as BPA alternatives in thermal printer paper.<sup>23</sup> The structural similarity of BPS to BPA has elicited similar concerns regarding its potential for human toxicity.<sup>23</sup> Not only can direct handling of thermal paper result in dermal exposure to bisphenols, but subsequent consumption of food with unwashed hands,<sup>16</sup> transfer to currency,<sup>25</sup> and thermal paper used in recycled paper products<sup>2</sup> are alternate human exposure pathways originating with thermal paper receipts.

Given the importance of detecting and quantifying ED chemicals such as bisphenols in the environment and biological samples, sensitive and selective methods for analysis of bisphenol by liquid chromatography/tandem mass spectrometry (LC/MS/MS) have been developed for both native bisphenols and derivatized bisphenols.<sup>26,27</sup> In the work reported herein, ionization of native bisphenols using negative ion atmospheric pressure photoionization (APPI) is compared with negative ion electrospray ionization (ESI) and negative ion atmospheric pressure chemical ionization (APCI) for their relative abilities to produce  $[M-H]^-$  precursor ions for subsequent collision-induced dissociation (CID) in a triple quadrupole mass analyzer. Multiple reaction monitoring (MRM) transitions were optimized using the most sensitive ion transitions and coupled with high-performance liquid chromatographic (HPLC) separation to detect and quantify BPA and BPS as well as five additional structural analogs to BPA and BPS. The LC/APPI-MS/MS method was applied to examine the levels of these seven bisphenols in thermal paper receipts and in U.S. paper currency.

## 2 | EXPERIMENTAL

### 2.1 | Chemicals

HPLC grade methanol (99.93%, Sigma-Aldrich, St Louis, MO, USA) and distilled-deionized water ( $>18$  M $\Omega$  cm) from a Direct-Q water purification system (Millipore, Billerica, MA) were used as LC mobile phase solvents. HRGC/HPLC-trace grade toluene (Pharmco, Brookfield, CT, USA) was used as a photospray dopant. HPLC grade methanol was used as a PLE solvent and Ottawa ignition sand (EMD Chemicals, Gibbstown, NJ, USA) was used as a PLE dispersant matrix. Analytical standards of 4,4'-( $\alpha$ -methylbenzylidene)bisphenol (BPAP, TCI America, 1571-75-1,  $>98.0\%$ ), 4,4'-dihydroxydiphenylmethane (BPF, TCI America; 6210-92-8,  $>99.0\%$ ), 1,1-bis(4-hydroxyphenyl) cyclohexane (BPZ, TCI America, 43-55-0,  $>98.0\%$ ), 2,2-bis(4-hydroxyphenyl)butane (BPB, TCI America, 77-40-7  $>98\%$ ), 4-hydroxy-4'-isopropoxydiphenylsulfone (BPSIP, Combi-Blocks, 95235-30-6, 97%), bis(4-hydroxyphenyl) sulfone (BPS, Sigma-Aldrich, 80-09-1, 98%), and 2,2-bis(4-hydroxyphenyl)propane (BPA, Sigma-Aldrich, 80-06-7,  $>99\%$ ) were obtained for direct infusion and preparation of analytical standards in HPLC grade methanol. Thermal paper receipts were obtained from local merchants and circulating U.S. currency was obtained from a local bank.

## 2.2 | MS/MS optimization

A mixture of the seven bisphenols shown in Figure 1 was prepared in methanol for infusion into the ionization source of a SCIEX 3200 QTRAP. The bisphenol solution was infused between 5–20  $\mu\text{L min}^{-1}$  into a flowing mobile phase to better mimic the ionization chemistry under typical source conditions following HPLC elution from an analytical column. For all ionization sources, a mobile phase flow rate of 1.0  $\text{mL min}^{-1}$ , an entrance potential (EP) of  $-10\text{ V}$ , and a collision exit potential (CXP) of  $-4\text{ V}$  were used. The source-dependent conditions used for comparison of the three ionization sources are provided in Table 1. Target precursor ion counts were approximately  $10^6$  to  $10^7$  counts, which were controlled by adjusting the flow rate of the bisphenol mixture from the direct infusion syringe. For each bisphenol, the source declustering potential (DP) was adjusted to maximize the intensity of the  $[\text{M}-\text{H}]^-$  precursor ion. The most abundant product ions were identified and the collision energy (CE) for each MRM transition was optimized (Figure S1, supporting information). Ion counts for each MRM transition were measured and scaled to take into account the flow rate of the infusion syringe. For each bisphenol, the ion counts of each MRM transition were normalized to the most intense ESI fragment so that comparison between inter-source MRMs and intra-source MRMs could be established. The results of the normalized comparison of ionization source sensitivity for the bisphenols studied and the optimized MRM voltages are provided in Table 2.

## 2.3 | LC/APPI-MS/MS method

A Prominence HPLC system consisting of binary LC-20AD pumps and a SIL-20A autosampler (Shimadzu, Columbia, MD, USA) was used under Analyst 1.6.2 software control (SCIEX, Framingham, MA, USA). Separation was achieved using an Eclipse XDB-C18 column (150 mm  $\times$  4.6 mm, 5  $\mu\text{m}$  particle size; Agilent) with an Eclipse XDB-C18 guard cartridge (12.5 mm  $\times$  4.6 mm, 5  $\mu\text{m}$  particle size; Agilent). A methanol/water (v/v) gradient program of 70:30 (0.5 min hold), ramped to 95:5 (over 4.5 min with 1 min hold) at a total column flow of 1.0  $\text{mL min}^{-1}$  afforded LC separation of the seven bisphenols studied in under 5 min.

## 2.4 | Analysis of bisphenols in thermal paper

Receipts on thermal paper were obtained from local stores to assess the identity and content of bisphenols in the receipts. Receipts were stored in the dark prior to analysis. Two 6.35 mm circular punches from

**TABLE 1** Source-dependent conditions used for comparison of the three ionization sources

	–ESI	–APCI	–APPI
Needle voltage (IS)	–4500 V	N/A	N/A
Needle current (IC)	N/A	–5	N/A
Repeller voltage (IS)	N/A	N/A	–900 V
Temperature (TEM)	550°C	350°C	350°C
Nebulizer gas (GAS1)	60	70	70
Auxiliary gas (GAS2)	60	30	30
Mobile phase	MeOH/H <sub>2</sub> O (75:25 v/v) (0.1% formic acid)	MeOH/H <sub>2</sub> O (75:25 v/v)	MeOH/H <sub>2</sub> O (75:25 v/v)

**TABLE 2** Normalized comparison of ionization source sensitivity for the bisphenols studied with the optimized collision energy (CE) for each product ion (PI)

	PI (m/z)	CE (V)	ESI	APCI	APPI
BPA	211.1	–38	0.47	30.9	34.4
precursor 227.1 m/z	<b>133.2</b>	<b>–35</b>	<b>1.00</b>	<b>61.9</b>	<b>72.2</b>
BPAP	<b>274.2</b>	<b>–26</b>	<b>1.00</b>	<b>103</b>	<b>112</b>
precursor 289.3 m/z	211.2	–34	0.09	10.7	11.4
	195.1	–35	0.10	11.0	11.0
BPB	<b>212.1</b>	<b>–24</b>	<b>1.00</b>	<b>56.8</b>	<b>65.6</b>
precursor 241.1 m/z	147.2	–33	0.08	5.05	6.82
	93.2	–64	0.08	4.67	3.79
BPF	105	–31	0.68	26.0	30.4
precursor 199.0 m/z	<b>93.0</b>	<b>–30</b>	<b>1.00</b>	<b>36.9</b>	<b>41.2</b>
	77.1	–36	0.37	18.2	18.9
BPS	184.2	–32	0.06	0.13	0.13
precursor 249.1 m/z	156.1	–30	0.03	0.68	0.72
	<b>108.1</b>	<b>–36</b>	<b>1.00</b>	<b>1.80</b>	<b>1.92</b>
	92.0	–48	0.72	1.36	0.96
BPSIP	<b>248.2</b>	<b>–29</b>	<b>1.00</b>	<b>4.94</b>	<b>5.29</b>
precursor 291.1 m/z	184.2	–40	0.29	2.35	2.12
	156.0	–44	0.09	0.81	0.74
	108.1	–56	0.15	1.00	1.18
BPZ	223.2	–42	0.69	57.3	68.2
precursor 267.1 m/z	198.1	–46	0.15	13.1	15.0
	<b>173.3</b>	<b>–36</b>	<b>1.00</b>	<b>95.5</b>	<b>112</b>
	145.2	–50	0.85	84.6	98.2

For comparative purposes, all ion counts are normalized to the ESI counts of the product ion with the highest sensitivity for each compound.

The MRM transition with the highest sensitivity is indicated in bold.

the receipt were massed and added to 1.5 mL methanol in a microcentrifuge tube. Receipt punches were extracted for 24 h on an orbital shaker table at room temperature. A volume of 2  $\mu\text{L}$  of the extract was analyzed by LC/APPI-MS/MS. Extraction efficiency was evaluated by subjecting the previously used receipt punches to a second, 24 h extraction in methanol.

## 2.5 | Analysis of bisphenols in currency

Bisphenols in paper currency were analyzed by pressurized liquid extraction (PLE) using an ASE-200 extractor (Dionex, Sunnyvale, CA, USA). The mass of the paper currency note was determined before and after extraction. PLE was accomplished by placing a cellulose filter at the exit of a 22 mL cell, folding the currency accordion-style along the short side of the note and inserting the folded note into the 22-mL cell. The remaining volume of the cell was filled with Ottawa ignition sand. Methane at 100 °C and 1500 psi was used as an extraction solvent in three 7-min static cycles with a 20% cell flush between cycles. Approximately 40 mL of methanol was collected in a pre-weighed extraction vial and the final volume of methanol was determined gravimetrically. The final extract was filtered through a 0.2  $\mu\text{m}$  PTFE membrane syringe filter (VWR Scientific, West Chester, PA, USA) for LC/APPI-MS/MS analysis. PLE blanks ( $n = 3$ ) were measured using the procedure above using only sand.

### 3 | RESULTS AND DISCUSSION

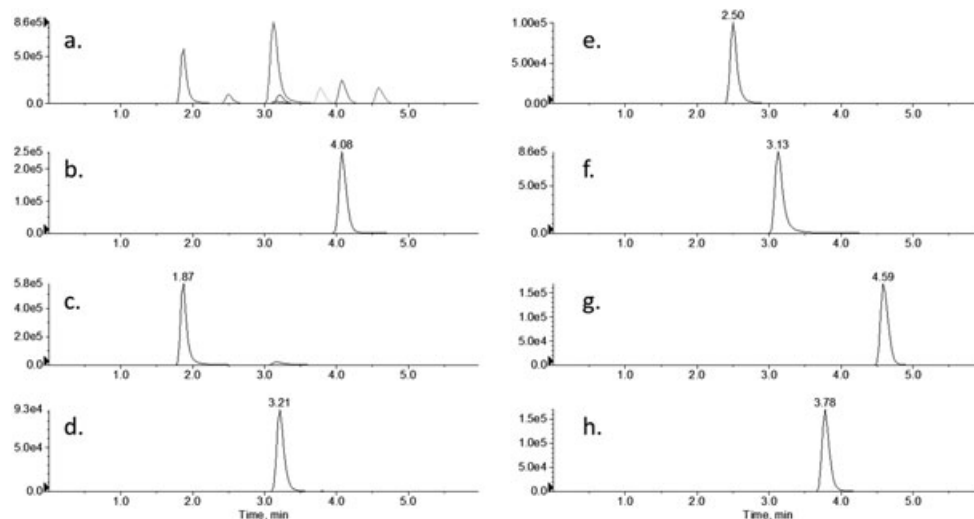
#### 3.1 | Ionization source comparison for LC/MS/MS

The relative intensities of the MRM transitions for the bisphenols are shown in Table 2 as a function of the ionization source used. With the exception of BPSIP, Zhao et al.<sup>28</sup> have identified productions of the remaining six bisphenols using high-resolution Orbitrap MS. While the intent of this work is to identify the most prominent and abundant fragments for use in MRM method development, the fragments reported herein are consistent with those of Zhao et al displaying the 93 *m/z* phenoxide ion at higher CE, and the loss of a phenol group  $[M-H-C_6H_6O]^-$  for bisphenols not containing a sulfonyl group. This loss of a phenol group provides the most sensitive MRM transition for BPA and BPZ while the phenoxide product ion provides the most sensitive MRM transition for BPF. Loss of the bridging methyl group in BPAP  $[M-H-CH_3]^-$  and loss of the bridging ethyl group in BPB  $[M-H-C_2H_5]^-$  provides the most sensitive MRM transitions. Considering the sulfone-containing bisphenols, the most sensitive MRM transition for BPS is  $[M-H-C_6H_5O-SO]^-$  and, while this ion is observed for BPSIP, the highest sensitivity MRM transition in BPSIP is the loss of an isopropyl group  $[M-H-CH(CH_3)_2]^-$ . A dramatic difference can be seen in the MRM sensitivity with the choice of ionization source for the negative ion mode precursor ion. Overall, the highest MRM sensitivity is seen with APPI and the lowest sensitivity is seen with ESI. APCI provides lower MRM sensitivity than APPI but generally has much higher MRM sensitivity than ESI. It is readily apparent that the BPS and BPSIP sulfone-containing bisphenols investigated show very similar sensitivities in all three ionization modes, suggesting that these are readily analyzed by standard ionization methods such as ESI. Indeed, the derivatization with pyridine-3-sulfonyl chloride will result in higher polarity and acidity and leads to sensitive detection by positive mode ESI as non-sulfone bisphenol pKa values are in the 9.8–10.4 range and are neutral compounds under typical acidic or neutral conditions used in the LC separation.<sup>29</sup> In contrast, BPS has a higher polarity and a pKa range

of 7.4–8.0 that is likely to facilitate ionization by ESI. The ionization of the remaining five, alkyl-bridged bisphenols are dramatically enhanced through APPI and APCI modes of ionization suggesting that proton abstraction in the gas phase occurs more readily. Deprotonation of the analyte by APPI and APCI is possible for compounds that have higher gas-phase acidity than the reactant molecules in the ion source, or if the proton affinity (PA) of the deprotonated analyte is lower than that of the reactant anion which is presumably  $O_2$ .<sup>30</sup> From the intra-source comparison results, it is apparent that alternative sources such as APCI and APPI can provide large gains in sensitivity for alkyl-bridged bisphenols that cannot be achieved short of sample derivatization procedures. The chromatogram shown in Figure 2 combines a fast LC separation with APPI-MRM ion selectivity to illustrate that extracted ion chromatograms can provide adequate compound resolution for the seven bisphenols studied.

#### 3.2 | Method limits of detection (LODs)

Six calibration mixtures in methanol were prepared containing the seven bisphenols ranging in concentration from 50 to 1250 ng mL<sup>-1</sup>. A calibration plot was made using 2  $\mu$ L injections of the standard solutions. Linear regression using peak areas as a function of the prepared concentration in ng mL<sup>-1</sup> was calculated with 1/x weighting to calculate the response factor for each compound by LC/APPI-MS/MS. The intercept term of the regression equation was not significant within the standard error of the regression and thus the linear regression equation was forced through zero. The LODs listed in Table 3 were calculated at a signal-to-noise (*S/N*) = 3. Inter-day and intra-day relative precisions of the method were 4.8% and 5.4% (*n* = 5), respectively. Through the use of the APPI (or APCI) ionization source, it is apparent from the LOD values in Table 3 that APPI can provide an equivalent order of magnitude sensitivity for all bisphenols studied, while similar LOD values using ESI are preferential to the sulfonated bisphenols. Thus, the use of APPI circumvents the need to derivatize non-sulfonated bisphenols to obtain an appropriate sensitivity.



**FIGURE 2** Chromatographic separation of the seven bisphenols using the LC/APPI-MS/MS method: a, all MRM transitions; b, 289/274 MRM for BPAP; c, 249/108 MRM for BPS; d, 227/133 MRM for BPA; e, 199/93 MRM for BPF; f, 291/248 MRM for BPSIP; g, 267/173 MRM for BPZ; and h, 241/212 MRM for BPB

**TABLE 3** Optimized compound potentials for the bisphenol MRM transitions and on-column limits of detection (LODs) using LC/APPI-MS/MS

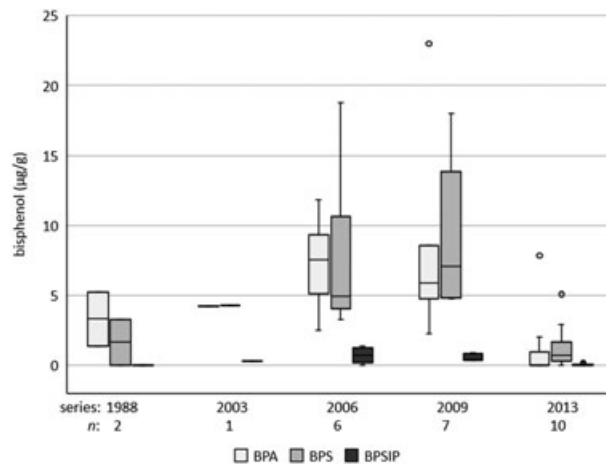
	$t_R$ (min)	Precursor ( $m/z$ )	Fragment ion ( $m/z$ )	DP (V)	CE (V)	LOD ( $\mu\text{g}$ )
BPS	1.87	249	108	[M-H-C <sub>6</sub> H <sub>5</sub> O-SO] <sup>-</sup>	-58 -36	23.6
BPF	2.50	199	93	[M-H-C <sub>7</sub> H <sub>6</sub> O] <sup>-</sup>	-50 -30	47.9
BPSIP	3.13	291	248	[M-H-CH(CH <sub>3</sub> ) <sub>2</sub> ] <sup>-</sup>	-55 -29	27.1
BPA	3.21	227	133	[M-H-C <sub>6</sub> H <sub>6</sub> O] <sup>-</sup>	-46 -35	39.4
BPB	3.78	241	212	[M-H-CH <sub>2</sub> CH <sub>3</sub> ] <sup>-</sup>	-46 -24	39.2
BPAP	4.08	289	274	[M-H-CH <sub>3</sub> ] <sup>-</sup>	-54 -26	21.2
BPZ	4.59	267	173	[M-H-C <sub>6</sub> H <sub>6</sub> O] <sup>-</sup>	-61 -36	51.3

### 3.3 | Bisphenols in thermal paper

The optimized LC/APPI-MS/MS method was applied to the analysis of 28 thermal paper receipts obtained from local merchants around Villanova, Pennsylvania (Table S1, supporting information). Receipts were obtained from large chain stores ranging in merchandise from groceries, building supplies, food, and entertainment. Four receipts were obtained from smaller local merchants. Exhaustive extraction was achieved on the first sample preparation as analysis of the second extract did not measure any level of bisphenols in the extract. This is perhaps to be expected as the bisphenol developer is applied as a thin surface coating on the paper and not integrated into the papermaking process. BPS was the most prevalent bisphenol detected in the thermal paper receipts with mean levels of  $20.6 \pm 2.6 \text{ mg g}^{-1}$  and a range of  $15.7\text{--}26.0 \text{ mg g}^{-1}$ ; however, four receipts contained BPA with mean levels of  $19.8 \pm 9.8 \text{ mg g}^{-1}$  and a range of  $10.5\text{--}30.2 \text{ mg g}^{-1}$ . The remaining five bisphenols were not detected in any of the 26 receipts. Two receipts, one from an independent restaurant and one from an organic market that was specifically labeled as 'BPA and BPS free', did not contain any of the seven bisphenols. The bisphenol levels in these thermal paper receipts analyzed by LC/APPI-MS/MS are comparable to a 2012 analysis by Geens et al<sup>14</sup> using derivatization GC/MS where 32 of 44 Brazilian thermal receipts contained BPA ranging between 9 and  $21 \text{ mg g}^{-1}$ .

### 3.4 | Bisphenols in U.S. currency

The optimized LC/APPI-MS/MS method was applied to the analysis of 26 U.S. paper currency notes in circulation using a PLE method (Table S2, supporting information). ASTM Standard Test Method D7858-13 relies on PLE using ethyl acetate for the determination of BPA in soil, sludge and biosolids.<sup>31</sup> Ethyl acetate is an appropriate solvent for trace analysis as it permits evaporative concentration and reconstitution of the residue in a small volume of methanol. As trace levels of BPA in U.S. currency were not expected, an evaporative concentration step was not necessary and a methanol PLE was adopted followed by direct analysis of the extract. Results indicated exhaustive extraction was achieved on the first methanol PLE extraction as bisphenols in a second PLE extract were undetectable. Bisphenols were not detected in PLE sand blanks as an assessment of laboratory or procedural contamination. Figure 3 depicts the levels of

**FIGURE 3** Boxplot of the bisphenol concentrations measured in the 26 U.S. currency notes analyzed by LC/APPI-MS/MS grouped by the note series

the three detected bisphenols in U.S. currency as a function of the note series. The median BPA and BPS concentration decreases with increasing note series suggesting there is an increased frequency of contact with thermal paper receipts with increased circulation of the currency. BPS was found in 24 of the paper notes with mean levels of  $5.33 \pm 5.13 \text{ } \mu\text{g g}^{-1}$  and a range of  $0.13\text{--}18.75 \text{ } \mu\text{g g}^{-1}$ . BPA was found in 19 paper notes with mean levels of  $6.39 \pm 4.94 \text{ } \mu\text{g g}^{-1}$  and a range of  $0.58\text{--}22.99 \text{ } \mu\text{g g}^{-1}$ . Unlike the thermal paper receipt data, a single alternative bisphenol, BPSIP, was detected in 15 of the currency notes. The levels and ranges of BPA and BPS in the low  $\mu\text{g g}^{-1}$  measured in this work are similar to the levels measured by Liao et al<sup>24,32</sup> in U.S. and world currencies by LC/ESI-MS/MS and could be indicative of bisphenol transfer from thermal paper receipts that are placed in purses or wallets in contact with currency. BPSIP was detected at lower levels ( $0.59 \pm 0.36 \text{ } \mu\text{g g}^{-1}$ , range  $0.19\text{--}1.37 \text{ } \mu\text{g g}^{-1}$ ) than BPA and BPS; however, it is noteworthy that with an expanded number of MRM targets, the presence of BPS substitutes such as BPSIP are being detected on U.S. bank notes in circulation which presumably reflects the increasing use of BPA and BPS alternatives in thermal paper receipts.<sup>23</sup>

The measurement of BPA and bisphenol analogs in thermal paper receipts and transfer of bisphenols from receipts to currency notes is of increasing importance to assess human dermal exposure routes to this class of compounds. In specialized occupational populations, such as cashiers, risk of dermal absorption is likely to be of greater concern. Mass spectrometric analytical methods can provide both specificity and sensitivity; however, the sensitivity of alkyl-bridged bisphenols is inherently less due to polarity and ionization potentials. Equivalent sensitivity between sulfone- and non-sulfone-containing bisphenols is achievable through the use of alternate ionization sources such as APCI and APPI that circumvent tedious and time-consuming derivatization procedures.

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## SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

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