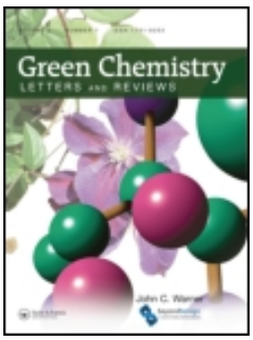

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RESEARCH LETTER

Concentration of bisphenol A in thermal paper

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Bisphenol A (BPA) is widely used as a color developer in thermal paper. Thermal paper is ubiquitous in daily life due to its use in cash register receipts, so opportunities for human contact abound. For this study, 10 blank cash register receipts were obtained from businesses in suburban Boston. BPA was extracted and analysis of concentration was performed using gas chromatograph/flame ionization detector. In some receipts, BPA was not detected but in others it was as high as 19 mg for a 12-inch long receipt, which is in line with concentrations indicated in patents. This study is intended to highlight the potential for human exposure to BPA as well as the ease with which exposure may be reduced through the use of BPA-free thermal paper.

Keywords: bisphenol A; thermal paper; thermochromism; analysis; endocrine disruptors

Introduction

Bisphenol A (BPA) is a common industrial chemical widely used in the production of polycarbonates and epoxy resins (Figure 1). Worldwide, BPA is one of the highest volume chemicals manufactured: it is produced at a rate of about six billion pounds per year (*1*). In 2004, approximately 2.3 billion pounds of BPA was prepared in USA alone (*2*).

In recent years, BPA has gained significant public attention as an environmental pollutant. Both the European Union (EU) (*3*) and the US National Toxicology Program (NTP) (*2*) have recently released lengthy reports devoted to BPA which reference hundreds of studies on BPA's hazard potential and exposure routes. Adverse effects associated with exposure to BPA have been reported in a wide range of vertebrate species from fish (*4*) to rodents (reviewed in *5*) to primates (*6*) and humans (*7–10*). These effects suggest but do not prove that BPA is implicated in a wide array of human health conditions, including heart disease (*7,8*), Type 2 diabetes (*7*), breast cancer (*11*), prostate cancer (*12*), infertility (*13*), and neurodevelopmental disorders, including attention deficit hyperactivity disorder (*14*).

Several distinct mechanisms have been identified as involved in BPA toxicity (reviewed in *10*). Most research has focused on BPA's ability to bind with the nuclear estrogen receptor and modify gene expression under the control of estrogen. Via this pathway, BPA is relatively weak compared to the native hormone 17β-estradiol. BPA also interacts with a cell membrane located receptor, through which it alters multiple physiological pathways. Via this mechanism, it is equipotent with 17β-estradiol (*10*). These multiple BPA mechanisms along with conflicting findings within the published literature have generated an ongoing debate about BPA safety (*15–17*).

In 2008, the European Food Safety Authority concluded that current BPA regulations protect human health (*18*). Yet that same year in an assessment that considered only reproductive and developmental effects, the US NTP concluded it had "some concern" for neurodevelopmental endpoints and for prostate development (*2*). The US Food and Drug Administration issued a statement similar to the NTP's in 2010 (*19*). Differing perspectives about BPA safety appear to arise out of disagreements over criteria for selecting studies/data to be used in risk assessments, as well as the nature of the dose-response curve (*16,20*).

BPA safety and source determination is critical in light of evidence that suggests significant BPA exposure and accumulation are occurring in the general population. In a recent review of human exposure to BPA (*21*), multiple studies showed measurable levels of BPA in human fluids and tissues. A Center for Disease Control study reported BPA in 95% of the urine samples taken from a population of 394 American adults. In a study of 23 healthy women, all breast milk samples registered positive for BPA. Of particular concern is the finding of especially high

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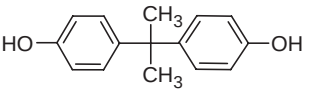

Figure 1. Bisphenol A (BPA).

levels of BPA in early term amniotic fluid. This was attributed to the reduced ability of the fetus to metabolize BPA, thus leading to significant accumulation (*21*).

While polycarbonate resins, particularly in food containers, have long been considered the main source of this human BPA exposure, more recent studies have given strong indications of additional BPA contamination sources. In a 2005 study, BPA levels were measured for fasting participants at times assumed to be long enough for complete BPA metabolism. BPA concentrations leveled off, but did not disappear as would be expected if polycarbonate food packaging sources were the only pathway for significant BPA exposure (*22*). These data can best be explained by the assumption that BPA is more ubiquitous in the environment then originally understood. (However, it is also acknowledged that this data could be explained by the pharmokinetics of BPA involving a longer half-life than previously expected (*22*).) Findings such as the detection of BPA in medical devices (*23*) and dental sealants (*24*) indicate sources of BPA unrelated to food containers. In this paper, we present evidence of an additional source of potential BPA exposure to the general public in the form of widely used thermal paper.

Bisphenol A (BPA) in thermal paper

Direct thermal printing is the preferred technology for a wide variety of commercial applications including point of sale receipts, luggage tags, faxes, and labels. In the direct thermal printing process, a printed image is produced by selectively heating specific areas of coated thermal paper as it is passed over a thermal print head. The coating undergoes a color change in the areas where it is heated, producing an image. This temperature-induced color change is termed as thermochromism (*25*).

The thermochromic paper used in this process typically consists of two layers: the base paper and the thermal sensitive layer (Figure 2). The base paper is typically a standard paper formulation and the thermal sensitive layer typically consists of three components: the thermochromic dye, a weakly acidic color developer (traditionally BPA), and a solvent. The solvent is generally a long-chain aliphatic compound (fatty acid, amide, alcohol, etc.) with a melting point in the range of 45–65°C. The active components

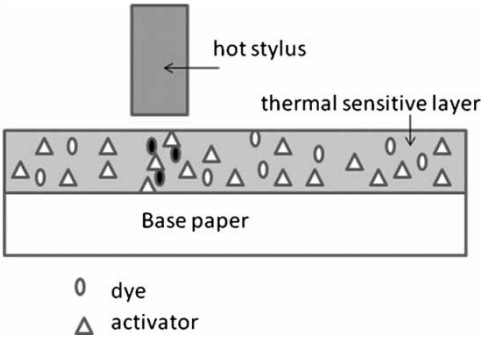

Figure 2. Schematic of thermal paper and thermal sensitizing process (*27*).

are dissolved within the solvent and upon heating regions of the coating with a printer stylus, the solvent acts as a medium in which the developer and dye are able to interact, resulting in the dye coloring (*26*).

Many of the thermochromic dyes are spirolactones, one of the most common being crystal violet lactone (CVL). In its ground state at ambient temperature, CVL is colorless. When the dye/solvent/developer system is heated above the melting point of the solvent by a printing stylus, BPA (the developer) interacts with CVL, donating protons which open the rings of the lactone and increase the conjugation of the system, resulting in a blue color (Figure 3).

In spite of the volume of research in existence indicating the potential hazards of BPA, it remains a widely used developer in thermal printing, due to its efficacy, availability, and low cost (*27*). Alternatives to BPA include other phenol derivatives and aromatic carboxylic acids (*28*).

Bisphenol A (BPA) exposure routes

Exposure to BPA related to its use in thermal paper can occur in manufacturing, during consumer use, and after recycling. In manufacturing, the primary concern is worker exposure during batching of BPA, for which the worst case inhalation exposure was estimated at 100 μg/kg bw/day (*2*). The NTP expressed "some concern" based on effects in laboratory animals administered 10 μg/kg bw/day, but identified 5 μg/kg bw/day as the recommended no observed adverse effect level (NOAEL; *29*). More recently, however, the FDA published a 2010 statement concluding that using traditional approaches to risk assessment they are unable to establish a safe level without additional data. The FDA is now working with the National Institutes of Environmental Health and Safety (NIEHS) to gather the needed data (*19*).

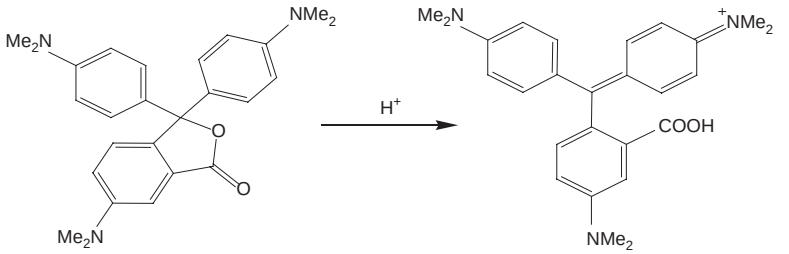

Figure 3. Tautomers of crystal violet lactone, left: ring-closed, colorless form; right: ring-opened, colored state (*26*).

The potential for exposure to BPA by consumers and workers handling thermal paper exists because BPA developer is present in a free or unbound state within the solvent, which is not designed to offer significant resistance to abrasion. Thermal paper with protective layers is available but is more costly (*30*).

A major source of BPA in the recycled paper pathway is thermal paper. The EU estimated that about 4 million pounds of BPA was used in the EU in 2005/2006 to prepare thermal paper. Of that thermal paper, 10% is trimmed and sent directly to the recycling plant and another 30% of the used paper eventually ends up in the paper recycling stream. In total, an estimated 1.5 million pounds of BPA will end up in paper recycling sites each year (*3*). Recycled paper used in household consumer products, such as paper towels, has been found to contain BPA (*31, 32*). In addition, the pulping of recycled thermal paper may introduce a chlorinated derivative BPA into effluent water streams (*33*). In a 2007 study, significant levels of BPA were found in recycled materials. In fact, the presence of BPA can be used to indicate the percent of recycled vs. virgin material used in a product (*34*).

The goal of this study was to determine whether BPA was present in receipts collected from local businesses, and if present to quantify the BPA concentrations analytically. This study did not investigate health impacts or exposure potential. Properties of thermal paper, such as abrasion resistance or leaching of BPA, were also not investigated in this work.

Results and discussion

Eight of the 10 receipts tested had quantifiable concentrations of BPA (Table 1). A few receipts had levels of BPA below the detection limit of the method.

The expected mass of BPA was calculated for a 12-inch receipt, which was estimated to be a typical length (all receipts were of equal width and thickness). Detectable BPA varied from 3 to 19 mg per 12-inch receipt.

The levels of BPA measured (in the samples in which BPA was detected) are consistent with those expected from thermal paper patent literature, where on a weight percentage basis there is an approximate 1:1 ratio between dye and developer (*35,36*) the dye content per area of thermal paper is in the range of 0.05–1 g/m^2 (*37*), so BPA content in the range of 1–24 mg for a 12-inch receipt is in line with patent information. It appears there are three grades of thermal paper: one with full BPA content (9–19 mg/12 inches), low BPA content (1–3 mg/12 inches), and BPA free (<limit of detection (LOD)).

Since BPA in thermal paper exists as free, unreacted molecules, there is the potential for mobility and therefore human exposure during handling of receipt paper. Therefore, to reduce the potential for BPA exposure among their customers and workers, businesses may consider purchasing thermal paper containing non-toxic alternative developers. Two of the receipt samples used in this study (Stores 6 and 10) appear to be BPA-free formulations.

Table 1

	BPA concentration in receipt, weight (%; g BPA/100 g receipt paper)[a]	Milligrams BPA in a 12-inch receipt (3 1/8" wide)
Store 1	1.54	17.3
Store 2	1.20	13.4
Store 3	0.83	9.3
Store 4	1.70	19.1
Store 5	1.63	18.3
Store 6	<LOD	<1.0
Store 7	1.09	12.2
Store 8	1.68	18.8
Store 9	0.30	3.4
Store 10	<LOD	<1.0
LOD	0.09	1.0
LOQ	0.26	2.9

[a]The relative standard error of the duplicate measurement is 6.8%.

Experimental

General

BPA, fluorinated bisphenol A (BPAF; 4,4'-(hexafluoroisopropylidene)diphenol), anhydrous ethanol, anhydrous pyridine, and 1-(trimethylsilyl)imidazole: pyridine 1:4 solution (TMSI:pyridine) were purchased from Sigma-Aldrich and used as received.

Sampling

A convenience sample of blank (unprinted) receipt paper from 10 local retail stores was obtained, one receipt per store. No effort was made to obtain a sample that was representative of the kind or size of business, nature of goods sold, geographical, or market sector distribution. Within store and within chain variation was not considered.

Extraction procedure

An effective extraction procedure was determined by extracting 200 mg portions of a single receipt known from prior analysis to be high in BPA content with 20 mL ethanol at 35°C for various times (1, 2, 4, 8, and 24 hours). Extraction was determined to be complete after 1 hour.

A 200 mg piece of each receipt sample was weighed and placed into Teflon capped vials. A 20 mL aliquot of anhydrous ethanol was added and the samples were stirred at 35°C for 1 hour. The ethanol was removed from the vials by Pasteur pipette and then the samples were washed with 2 aliquots of 2 mL of ethanol each. The ethanol extract and washes were combined in a round bottom flask and rotary evaporated. The residue was redissolved in anhydrous pyridine. Some samples turned dark upon heating and evaporation of the ethanol. Some thermal receipt formulations use a thermal and solvochromatic dye such as CVL to cause the color change upon printing; the color change we observed upon rotary evaporation is in accord with this color forming mechanism. Three 5 mL aliquots of pyridine were used to quantitatively transfer the residue after evaporation to a 25 mL volumetric flask. The pyridine aliquots were filtered via syringe equipped with 1 μm PTFE Acrodisc filter prior to in addition to the volumetric flask. Addition of the pyridine to the evaporated residue caused the dark color to turn clear in the samples in which it was observed. Each sample was then diluted to the appropriate volume.

In addition to the receipt samples, a reagent blank was prepared. The reagent blank consisted of 20 mL of ethanol added to a Teflon capped vial without the addition of receipt paper which was carried through the entire extraction and analysis procedure. One of the receipt samples was extracted and analyzed in duplicate. A reagent spike was prepared from a third piece of the same receipt by adding 864 μg BPA in ethanol to the sample prior to extraction.

Calibration

Eight calibration standards were prepared by weighing 100 mg of BPA into a series of vials and diluting appropriately with pyridine, to produce a series of standards ranging from the blank, with no BPA added, to 50 μg/mL BPA (after derivatization). In addition to the calibration standards, a separate check standard was prepared by the same method.

Derivatization and internal standard

To 1 mL of each calibration and receipt sample was added 88.7 μg BPAF in pyridine solution as an internal standard. After mixing thoroughly, 100 μL of this solution was added to 100 μL of TMSI:pyridine solution (approximately 10 × molar excess of the amount required to derivatize the highest concentration calibration standard), mixed thoroughly, and then heated at 40°C for half an hour (*38*). Derivatized samples were then analyzed by gas chromatography (GC). Complete derivatization was confirmed using GC/mass spectroscopy by the absence of BPA and BPAF peaks and the presence of the appropriate trimethylsilyl derivatives.

Gas chromatograph/flame ionization detector (GC/FID) method

Analyses were performed using a VF-1 ms column (15 m length × 0.25 mm ID × 0.25 um film thickness; Varian, Inc.) on a CP-3800 GC (Varian, Inc.) equipped with CP-8400 autosampler, 1177 split/splitless injector, and FID. The injector was operated at 220°C and the split ratio was 1:10. The oven was program at 200°C isothermal for 10 minutes. The detector temperature was 300°C. The injection volume was 1 μL. Each sample and calibration standard was injected and analyzed in triplicate. Helium was used as the carrier gas.

Analysis

Peaks for the internal standard and BPA were identified and integrated by Galaxie chromatography software (Varian, Inc., version 1.9.3.2.). The trimethylsilyl derivatives of the internal standard and BPA eluted at 2.00 and 3.44 minutes, respectively. Statistical analyses were performed using the R environment by the R Foundation, version 2.10.0 (*39*) and package chemCal (version 0.1–26; (*40*)). The peak area of BPA for each injection was normalized

to the area of the internal standard. A calibration curve is shown in Figure 4. Receipt extracts that had concentrations of BPA higher than 50 μg/mL as injected (the highest point in the calibration curve) were diluted further until their concentrations were within the range of the calibration curve.

Data quality

The LOD and limit of quantitation (LOQ) were determined using the method of Mocak et al. (*41*). The LOD was 3.1 μg/mL and the LOQ was 9.4 μg/mL on the basis of the diluted samples injected in the GC. On a weight basis in the receipts, the LOD and LOQ were 860 and 2600 ppm, respectively. The amount of BPA observed in the reagent blank was below the LOD. The duplicate samples differed by 13%. Spike recovery was 96% of the expected value. Check standards varied from their actual value by no more than 11%.

Conclusions

The amount of BPA in thermal receipt paper obtained from suburban Boston businesses has been quantified using GC/FID. Several receipts contained no detectable BPA, but where quantified, BPA was found to vary from 3 to 19 mg per 12-inch receipt. This highlights a possible source of BPA exposure in the general population as well as the possibility for businesses to avoid this risk by using BPA-free receipt paper.

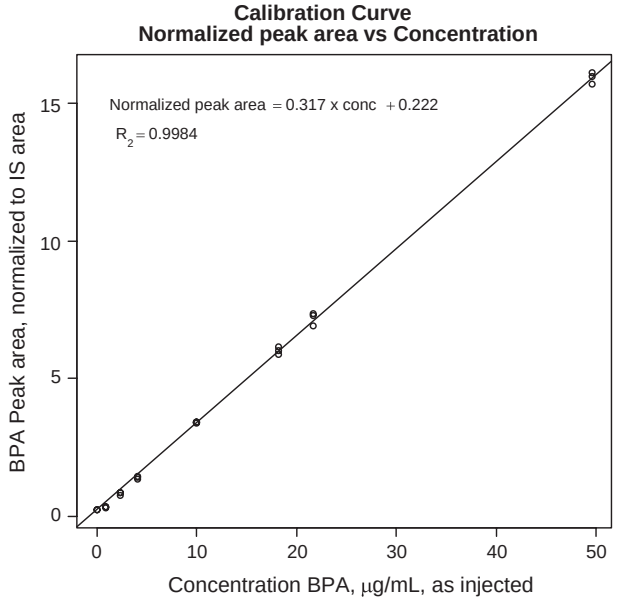

Figure 4. Calibration curve.

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