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Determination of Bisphenol A in Thermal Paper Receipts

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Abstract: Bisphenol A (BPA) is a chemical substance which is produced in great quantities globally and of which serious negative effects on endocrine system are suspected. It is a commonly used color developer in thermal papers. BPA used for this purpose is in free, unbound form and is one of the potential sources for BPA exposure of humans. In this study, 12 thermal paper receipt samples were collected from various workplaces selected randomly and analyzed. BPA was determined in all samples. Average value of high BPA concentrations obtained from 10 samples was found as 13.83±0.69 mg BPA/g paper. At the same time, low values being 0.40±0.11 mg BPA/g paper and 0.11±0.05 mg BPA/g paper respectively were found in two samples as compared to others.

Keywords: Bisphenol A, BPA, Thermal paper, Human exposure.

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INTRODUCTION

Bisphenol A (BPA, 2,2-bis(4-hydroxyphenyl) propane) (Figure 1) is one of the chemical substances produced mostly in the world. It has generally been used in great quantities in manufacturing polycarbonate plastic, epoxy resin, dental materials as well as paper industry [1].

BPA is the subject of hot debates regarding "low dose" toxicological effects, *i.e.,* effects at doses clearly below the present tolerable daily intake (TDI) of 0.05 μg/kg body weight [2-4]. A great number of studies where BPA's effects on human health and especially on its destructive side effects are investigated were made and have continued to be made [5, 6]. BPA exposure of humans is basically through food and beverage. This is because epoxy resin used in producing containers where food and beverage are packed contains BPA. In addition, air, dust, and water are other sources of exposure. Furthermore, manual contact with thermal paper receipts received at the end of shopping is another source for BPA exposure [7, 8].

Thermal papers have been used as shopping mall receipts, public transportation tickets, lottery tickets, cinema tickets, airline tickets, *etc.* [9]. European Union's risk assessment report of BPA states that 168.000 tons of thermal paper is used per year in European Community and these papers contain 1890 tons of BPA [10]. BPA acts as a color developer in thermal papers [11]. It is present in its free, non-polymerized form and is thus easily available for uptake [12]. If a person who comes in contact with thermal paper receipts mentioned above in his-her daily life takes nourishment by direct contact of unwashed hands or by dermal contact, he/she has the BPA exposure. Furthermore, reusing these papers which were sent to recycling after usage in producing food and beverage containers by processing again has caused BPA contamination [13, 14].

In this study, BPA quantities of thermal paper receipts collected from different shops were determined and compared with other international studies.

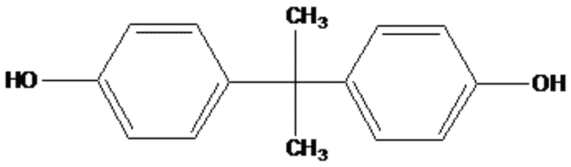

Figure 1: Molecular structure of BPA.

MATERIALS and METHODS

12 thermal paper receipt samples used in this study were collected from various workplaces randomly. We collected a fax paper, a bank account receipt, a bank card receipt, an ATM receipt, a lottery ticket, a gift store receipt, a gas station receipt, a restaurant receipt, and four shopping mall receipts (Table 1). Thermal printing paper was identified by its ability to darken upon heating. The samples were analyzed as soon as they were collected. The average BPA levels of samples were calculated by three parallel studies. The chemical substances were used of high purity.

20 mg of thermal paper receipt samples were cut into small pieces and extracted for 60 minutes in 50 mL of pure water in room temperature. After this extraction process, the BPA quantity passed into water was analyzed through high performance liquid chromatography (HPLC). All the HPLC analyses were carried out on a Agilent 1200 Series HPLC system equipped with an Supelco C_{18} column (100 x 2.1 mm, particle size 2.7 µm) using a mobile phase composed of water/acetonitrile (60:40, v/v) at a flow rate of 0.4 mL/min; the column temperature was 30 °C. Fluorescence excitation and emission wavelengths for BPA detection were 225 and 310 nm, respectively. Calibration line was formed between 25 and 200 µg BPA/L (R^2=0,999). Detection limit was calculated as 3.3 µg/L and relative standard deviations 1.1% for 6 measurements made in 30 µg/L.

RESULTS and DISCUSSION

The results of 12 thermal paper samples where BPA concentration was determined are shown in Table 1. BPA was found in all thermal paper receipts which were analyzed.

Average value of ten thermal paper receipts having high concentration ratios was calculated as 13.83 ± 0.69 mg BPA/g paper. This average value we obtained is compatible with the literature [15-20]. As seen in Table 1, the highest BPA concentration were determined in supermarket samples No: 2, 3, and 4. The results are 19.52 ± 0.71 mg BPA/g paper, 20.14 ± 1.23 mg BPA/g paper and 21.65 ± 0.83 mg BPA/g paper, respectively. When considering these results and excessiveness of customer circulation, supermarket cashiers may be the persons who have the highest risk of undergoing BPA exposure [21]. However, rather low values were determined as 0.40±0.11 mg BPA/g paper and 0.11±0.05 mg BPA/g paper respectively in one bank account receipt and one lottery receipt, comparing to other samples. In some thermal paper receipts, low BPA concentrations were determined also by Geens *et al*. (2012) (22). This situation can be described with the use of alternative chemical substances instead of BPA because of its bad name in recent years. Goldinger *et al.* (2015) (15) investigated some alternatives of BPA, namely bisphenol S (BPS), bisphenol F (BPF), Pergafast® 201 and D-8. Their study showed that D-8 and Pergafast® 201 could be good alternatives for the replacement of BPA. Recently some Swiss retailers announced stopping the use of thermal papers containing BPA. In addition, cross contamination can occur while BPA-free thermal papers are being processed along with high BPA content papers which are reprocessed in recycling plants [23]. In similar studies made with thermal paper samples in Belgium, Switzerland and U.S.A., the results of 15.00 mg BPA/g paper, 13.50 mg BPA/g paper and 12.50 mg BPA/g paper respectively were reported. However, the BPA values obtained in studies carried out in countries like Japan, Korea, and Vietnam were calculated between <LOD and 10.00 mg BPA/g paper. These values have been observed as low values when compared with other country's results. Reason of this situation may be tight control onto materials containing BPA applied by Japan [24].

CONCLUSION

According to the results we achieved, BPA concentration in 10 out of 12 thermal paper receipts analyzed is between 7.26 ± 0.58 and 21.65 ± 0.83 mg BPA/g paper. Similar results have also been reported in the literature. High BPA content ratio of thermal papers can cause contamination risk for "BPA-free" papers during reprocessing in recycling plants. Furthermore, waste waters containing BPA of these plants can give hazardous effects to environment. And the most important risk is thermal paper sourced BPA exposure of humans. According to Genns *et al.,* 2012; an estimation of human exposure through thermal paper results in a median intake of 445 ng BPA/day for the general population, which corresponds to an exposure of 6.4 ng/kg bw/day for a person of 70 kg. The exposure of those people who come occupationally in contact with thermal

paper can be much higher. Biomonitoring studies shall be required in the future so that influences of BPA on human health can be revealed completely.

Table 1.BPA concentrations in 12 thermal paper receipts according to the type of store (n=3).

Type of store	BPA (mg/g paper±SD)
Fax paper	7.26±0.58
Bank account receipt	0.40±0.11
Bank card receipt	14.96±0.54
ATM receipt	15.00±0.72
Lottery ticket	0.11±0.05
Gift store receipt	12.94±0.66
Gas station receipt	8.47±0.33
Restaurant receipt	10.78±0.67
Supermarket 1	7.59±0.61
Supermarket 2	19.52±0.71
Supermarket 3	20.14±1.23
Supermarket 4	21.65±0.83

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Türkçe Öz ve Anahtar Kelimeler

Termal Kâğıt Fişlerde Bisfenol A'nın Tayini

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Öz: Bisfenol A (BPA) dünya çapında büyük miktarlarda üretilen ve bağışıklık sistemine ciddi negatif etkide bulunduğundan şüphelenilen bir kimyasal maddedir. Bu madde termal kâğıtlarda renk geliştirici olarak yaygın şekilde kullanılmaktadır. Bu amaçla kullanılan BPA serbest ve bağlanmamış bir haldedir ve insanlardaki BPA maruziyetinin potansiyel kaynaklarından biridir. Bu çalışmada, 12 termal kâğıt örneği, rasgele seçilen çeşitli çalışma yerlerinden toplanmış ve analiz edilmiştir. BPA bütün örneklerde bulunmuştur. 10 örnekten elde edilen yüksek BPA derişimlerinin ortalama değeri 13,83±0,69 mg BPA/g kâğıt olarak tespit edilmiştir. Aynı zamanda, diğerleriyle karşılaştırıldığı zaman iki örnekte sırasıyla 0,40±0,11 mg BPA/g kâğıt ve 0,11±0,05 mg BPA/g kâğıt olarak düşük değerler bulunmuştur.

Anahtar kelimeler: Bisfenol A, BPA, Termal kâğıt, insanda maruziyet.

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