

Chemical contaminants migration from food contact materials into aqueous extracts

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Abstract. Cardboard packaging is widely used in the food industry, especially as secondary or tertiary packaging, or as transport packaging. In most cases, these packs may contain certain chemical contaminants that can be accidentally transferred to packaged foods. These contaminants include Bisphenol A (BPA) and Formaldehyde, which can cause significant adverse effects, especially to vulnerable persons. For this reason, the purpose of this study was to analyze by a UV - VIS spectrophotometric method the content of BPA and Formaldehyde from 17 corrugated board samples from Romanian producers. BPA concentrations varied between 0.044 mg/dm² and 0.090 mg/dm², while Formaldehyde concentrations were lower than 0.048 mg/dm². The results were compared with the legislation in force to establish their compliance for contact with food.

1 Introduction

Nowadays, there has been an increase in the production of packaging materials for all industries. This is due to the fact that each product is sold in a package. Packaging has a vital importance especially in the food industry where they are used as food contact materials (FCM), whose role is to preserve, to protect, to promote the food products throughout the food chain [1].

According to EU Regulation no. 1935/2004 [2], FCM must not release chemicals that may endanger consumers health, affect product sensory or nutritional properties, or alter food composition [3].

These chemicals, called food contact chemicals (FCC), are chemical constituents from food contact materials that are added to these packaging, and which, under certain conditions, can migrate into the packaged food product [4].

The main types of FCM used in the food industry are represented by plastics, glass, paper and cardboard, metallic materials [5]. These products must be safe for food contact. Their compliance with regulations in force, depending on the type of material is necessary to be tested [1].

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The widespread use of paper and cardboard packaging, as primary, secondary or tertiary packaging, is due to the low price, reduced weight, availability on the packaging market, ease of storage, but also good mechanical properties [5].

In connection with substances that can migrate from this type of packaging, their number is quite large. Formaldehyde and Bisphenol A (BPA) are two chemical compounds (Figure 1) which can cause adverse effects on the consumers health. Most of the chemical contaminants that can migrate, including formaldehyde and BPA, come either from the printing inks, or from the adhesives used in the process of obtaining the packaging [1].

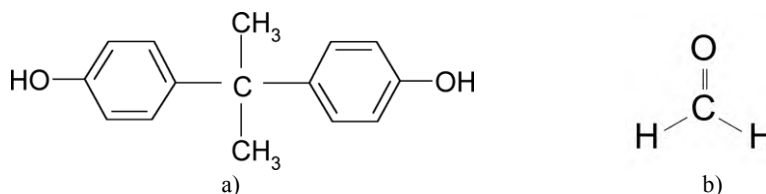


Fig. 1. BPA (a) and Formaldehyde (b) chemical formulas.

These compounds can migrate from the packaging into the product under certain conditions, being influenced by direct or indirect contact with the food, their chemical properties, their initial concentration, contact time and temperature [1].

The aim of this study was to assess the possible contamination with BPA and Formaldehyde of several types of cardboard from different Romanian producers, in order to evaluate the compliance with the legislation in force.

2 Material and method

2.1 Sample description

A total of 17 samples of corrugated cardboard (CB) were used in this study. These samples, presented in Table 1 were collected from different Romanians producers.

Table 1. Characteristics of the analyzed samples.

Sample no.	Sample description
1	CB type 3 (TL-W-TL), natural, E flute
2	CB type 3 (K-W-TL), natural, E flute
3	CB type 3 (TA-W-CO), natural, E flute
4	CB type 3 (TL-W-TL), natural, E flute
5	CB type 3 (K-W-TL), natural, B flute
6	CB type 3 (TA-W-TL), white, B flute
7	CB type 3 (TL-W-CO), natural, C flute
8	CB type 3 (TL-W-TL), natural, C flute
9	CB type 3 (TA-W-TL), white, C flute
10	CB type 5 (TA-W-TL-W-TL), white, BC flute
11	CB type 3 (TL-W-TL), natural, E flute
12	CB type 3, natural, E flute
13	CB type 3, natural, B flute
14	CB type 3, natural, C flute
15	CB type 3, natural, C flute
16	CB type 3, white, E flute
17	CB type 5, natural, BC flute

2.2 Reagents

All chemicals used in this study were of analytical reagent grade. Bisphenol A (2,2 – Bis(4-hydroxyphenyl) propane), Nitric Acid (HNO₃ 65%), Formaldehyde solution (370 g/L), Anhydrous Ammonium Acetate, Acetic Acid (99%) and 2,4-Pentandione were purchased from Merck. All dilutions were performed using ultrapure water (18.2 MΩ.cm). All glassware used was cleaned and decontaminated with 10% HNO₃.

2.3 Equipment

BPA and Formaldehyde analysis was performed by UV/VIS molecular spectroscopy, using a Jasco v550 UV/VIS Spectrophotometer, provided with a deuterium lamp and a wavelength range between 190 nm and 900 nm. A GFL type water bath (Burgwedel, Germany) for preparing the solutions and an OHAUS analytical balance for weighing the samples were also used.

2.4 Preparation of water extract

Sampling, preparation and extraction of samples were performed according to SR EN 645: 1997 standard [6]. For the preparation of the extract, 10 grams (± 0.1 g) of each sample were used. Samples were cut into small pieces, were immersed in 200 mL water, and after 24 hours at 23°C (± 2 °C), the extract is filtered, brought to a 250 mL volumetric flask and then analyzed.

2.5 Preparation of standard solutions

For BPA calibration curve, 0.1 g of BPA was weighted in a volumetric flask and then filled up to 100 ml with ethanol. The solution was diluted 100 times with ultrapure water for obtaining solution B. The standard solutions were prepared, from solution B, according to Table 2.

Table 2. Preparation of standard solutions for BPA calibration curve.

Solution B (mL)	1	2	3	4	5	6	7	8	9
Ultrapure water (mL)	9	8	7	6	5	4	3	2	1

Calibration curve for formaldehyde was performed according to SR EN 1541: 2003 [7]: 5 mL of formaldehyde solution are diluted up to 1000 mL in a volumetric flask (Solution I) with ultrapure water. Then, another 20 times dilution is performed for obtaining Solution II, which, finally is diluted 100 times to obtain Solution III. 1 mL of the final solution contains approximately 0.001 mg of formaldehyde. The calibration solutions were prepared, from solution III, as presented in Table 3.

Table 3. Preparation of Formaldehyde calibration solutions.

Solution III (mL)	1	5	10	15	20	25
2,4-Pentandione reagent (mL)	5	5	5	5	5	5

2.6 Calibration

Calibration curve for each element was performed using reagents described above. The calibration curve for BPA and Formaldehyde reveal a good linearity over the whole range

of concentrations. Also, for both chemical contaminants a recovery of over 95% and a regression coefficient higher than 0.995 was obtained. The limits of detection and quantification for the analyzed contaminants were 0.01 mg/L, respectively 0.03 mg/L for BPA and 0.004 mg/L and 0.012 mg/L for Formaldehyde.

2.7 Sample preparation

10 ml of extract were acidified with HNO₃ 65% and boiled for 25 minutes. After cooling, 1 ml of KOH 50% was added in order to complete reaction. If BPA is present the solution is turning yellow. The solution is then measured at 430 nm. The control solution was prepared in the same way, except for the 10 ml which were of ultrapure water.

Formaldehyde reacts with 2,4-Pentandione, in the presence of ammonium acetate, forming 3,5-diacetyl-1,4-dihydrolutidine. The extract is then measured at 410 nm wavelength. Preparation of calibration solutions and samples was performed according to SR EN 1541:2003 [7].

2.8 Calculation of results

BPA concentration calculation was performed using Equation (1).

$$C = (C_s - C_c) \times 1000 / V_0 \quad (1)$$

C is BPA concentration (in mg/L), C_s is the BPA concentration of the sample (mg/10 ml extract), C_c is the BPA concentration of the control (mg/10 ml standard solution), V₀ is the volume of extract used (10 mL).

Formaldehyde concentration calculation was performed using Equation (2).

$$C_f = C \times (V_0 / V_1) \times (b / 100) \times (1 / G) \quad (2)$$

C_f is Formaldehyde concentration (in mg/dm²), C is formaldehyde concentration from calibration curve (in mg), V₀ is the total volume of the extract (250 mL), V₁ is the volume taken for testing (25 mL), b is sample weight (in g/m²) and G is the mass of the sample (in grams).

3 Results and discussion

BPA analysis method is based on the reaction between BPA and HNO₃ with the formation of aromatic compounds (ortho-phenols) of yellow color. Analyzing the results presented in Figure 2, the BPA concentrations varied between 0.044 mg/dm² and 0.090 mg/dm².

According to CEPI Guide, 2012 [8], the maximum allowed limit for BPA in paper and cardboard intended for food contact is 0.1 mg/dm². All values obtained are below the limit.

Regarding formaldehyde, according to the EC Resolution ResAP version 3/2007 [9], the maximum allowed limit is 2.5 mg/dm². As can be observed analyzing the results in Table 4, all values are much lower than the limit.

The highest values for both BPA and Formaldehyde were found in sample 13, which is a 3-layer corrugated board. However, the values obtained are higher than in the case of samples 10 and 17 which are cardboard samples consisting of 5 layers. This may be due to the raw material (paper) from which the layers were obtained.

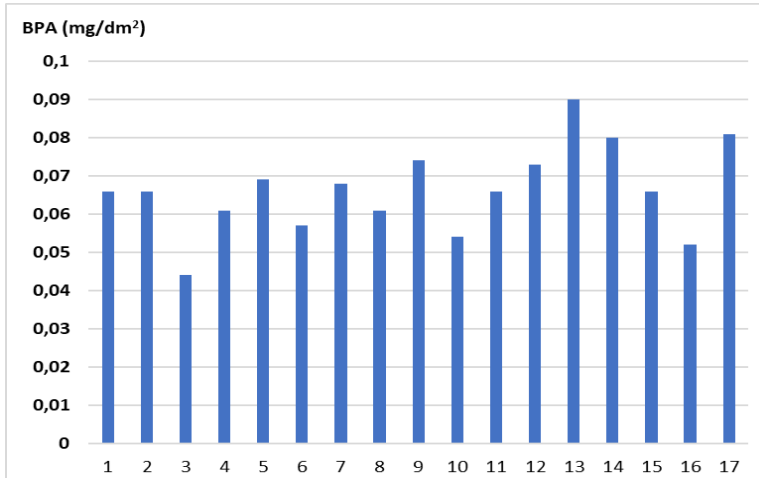


Fig. 2. BPA analysis results.

Table 4. Formaldehyde concentration in analyzed samples.

Sample no.	Formaldehyde concentration (mg/dm ²)
1	0.017
2	0.008
3	< 0.004
4	< 0.004
5	0.022
6	< 0.004
7	< 0.004
8	0.033
9	< 0.004
10	< 0.004
11	< 0.004
12	0.04
13	0.048
14	0.032
15	0.028
16	0.014
17	0.014

4 Conclusions

In this article a simple and rapid method was used for BPA and Formaldehyde analysis in corrugated cardboard used as FCM.

All the results obtained are below the maximum allowed limits, for both BPA and Formaldehyde. Regarding the BPA content, the concentrations found were higher than those in the literature [10, 11]. The differences may occur due to the analytical methods used.

In the case of formaldehyde, the values obtained are comparable with some results from the literature [12]. One reason could be that the UV-VIS method is the standardized method for determining the formaldehyde in paper and board used for contact with food. The

differences that may occur may be due to the experimental conditions and the heterogeneity of the samples.

Taking into account the obtained results, all the samples can be used in contact with food. Further, much more detailed studies are needed to demonstrate this.

This work was supported by a grant of the Romanian Ministry of Education and Research, through Sectorial Plan, contract no. 3PS/2019.

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