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HEAVY METALS CONTAMINATION OF FOOD CONTACT MATERIALS IN ROMANIA

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Abstract

Exposure of consumers to heavy metals is an important issue and many researches has focused on this topic in the last decades. These metals can reach the human body through food contact materials. The aim of this study is to analyze the heavy metals content (Pb, Cd, Cr) or heavy metals migration from different food contact materials (plastic, paper, board, glass, ceramic etc.) available on the Romanian market and to establish the compliance with the imposed limit. The influence of printing inks and dyes on the metals level in food contact materials was also studied. Heavy metals analysis was performed by atomic absorption spectrometry, after wet digestion of the samples.

Key words*: food contact materials, heavy metals, packages, spectrometry.*

INTRODUCTION

Food packaging is the main way of storing, transporting and protecting food products by external factors (Ahmadkhanika & Rastkari, 2017), but these packages may have some degree of chemical contamination.

This process of contamination occurs as a result of the direct or indirect contact between the food and the packing material, resulting in the transfer of substances between the two components, a process called migration (Rather et al., 2017). Thus, packaging made from virgin materials or recycled materials can be an important source of contamination of the environment with heavy metals, through heavy metal catalysts used for polymerization processes (Whitt et al., 2012), or through additives added to improve the properties of packaging materials, such as stabilizers, antioxidants, plasticizers, slipping agents (Rather et al., 2017, Constantinescu et al., 2019). Heavy metals resulting from the migration process reach the body where they can affect the proper functioning of biological systems by accumulating them in the body where they can promote the appearance of diseases, even at low concentrations (Sood & Sharma, 2019).

The aim of this study was to analyze the content of heavy metals (lead, cadmium and total chromium) in different types of food contact materials (plastic, paper and board), but also the levels of heavy metals that can migrate from different types of packaging materials (plastic, paper and board, glass) from Romanian producers, to evaluate their compliance with the limits imposed by the legislation in force.

MATERIALS AND METHODS

Sample collection

55 samples of food contact materials (32 plastic, 19 paper/board and 4 glass) were purchased from different Romanian producers. A full description is provided in Tables 1 and 2.

Reagents

Nitric acid (HNO_3) and Hydrogen peroxide (H_2O_2) were purchased from Merck. Calibration curves were obtained using Lead standard solution 1000 mg/l Pb for AA ($Pb(NO_3)_2$ in HNO_3 2%), Cadmium standard solution 1000 mg/l Cd for AA ($Cd(NO_3)_2$ in HNO_3 2%), Chromium standard solution 1000 mg/l Cr for AA ($Cr(NO_3)_3$ in HNO_3 2%) purchased from Scharlau, and a Multielement Standard Solution 6 for ICP purchased from Sigma Aldrich. Dilutions were performed using ultrapure water (18.2 MΩ.cm). All glassware used was cleaned and decontaminated with 10% HNO_3.

Table 1. Samples description analyzed for heavy metals content

Code	Material	Description
P1	PE film	200 µ transparent and printed PE film
P2	PE bottle	Red PE bottle
P3	HDPE bag	Transparent and printed HDPE bag
P4	HDPE closure	Green HDPE closure
P5	LDPE bag	Transparent and printed LDPE bag
P6	PP film	Transparent and printed PP film
P7	PP bottle	Red PP bottle
P8	PP fabric	White PP fabric, laminated
P9	PP trays	500 CC PP trays, color black
P10	BOPP film	Transparent BOPP film
P11	BOPP bag	Transparent BOPP bag, unprinted
P12	CPP bag	Transparent CPP bag, unprinted
P13	PP cup	White PP yoghurt cup
P14	PET bottle	2500 ml green beer PET bottle
P15	PET casseroles	250 CC transparent PET casseroles
P16	PE/EVOH/PE/ PET AF wrapping film	Transparent PE/EVOH/PE/ PET AF film, unprinted
P17	PE/PA wrapping film	Transparent PE/PA film, unprinted
P18	Stretch film	Transparent stretch film
P19	Cutlery PS	Transparent PS (GPPS and HIPS) cutlery
P20	Paper bag	Brown kraft paper bag
P21	Baking paper	Natural baking paper
P22	Juice labels	Paper juice labels
P23	Beer labels	Paper beer labels
P24	Paper towels	White paper towels, printed
P25	Cardboard type III	Natural cardboard
P26	Cardboard trays	White cardboard trays
P27	Cardboard casseroles	White cardboard casseroles
P28	Corrugated board	Natural corrugated board, printed
P29	Salt packages	Printed cardboard for salt packages
P30	Cardboard inserts	Promotional cardboard inserts for chip bags
P31	Egg box	Printed egg box
P32	Fruit box	Natural fruit box, unprinted

Table 2. Samples description analyzed for heavy metals migration

Code	Material	Description
P1	PET bottle	900 ml white PET bottle for milk
P2	PET bottle	1000 ml transparent PET bottle for water
P3	PET bottle	2500 ml green PET bottle for beer
P4	PET jars	Transparent PET jars
P5	HDPE bag	Transparent and printed HDPE bag
P6	HDPE closure	HDPE closure for water bottle, color blue
P7	LDPE bag	Transparent and printed LDPE bags
P8	LDPE bottle	Red LDPE bottle for ketchup
P9	PP trays	500 ml black PP trays
P10	PP cup	200 ml PP yoghurt cup, color white
P11	BOPP bags	Transparent BOPP bags
P12	PS cup	White PS (GPPS and HIPS) yoghurt cup
P13	EPS bowl	500 CC White EPS bowl
P14	Silicone baking paper	*baking paper* coated with *silicone*
P15	Paper muffins	*White and brown paper muffins*
P16	Chocolate	White chocolate box, printed
P17	Coffee cup	White paperboard coffee cups, printed
P18	Silver cardboard trays	silver cardboard trays for cakes
P19	Pizza	Brown pizza box, upper surface printed
P20	Jar glass	Transparent jar glass
P21	Glass bottle	Uvag glass bottle for beers
P22	Glass bottle	Flint glass bottle for water
P23	Glass containers for salt	Transparent glass containers for salt

Equipment's

Lead, cadmium and chromium content were performed using an AAnalyst 600 graphite furnace atomic absorption spectrometer system (Perkin Elmer) provided with a Transversely Heated Graphite Atomizer (THGA) assembly and longitudinal Zeeman-effect background correction. Specific migration of metals was performed using a NexION 300Q Inductively Coupled Plasma Mass Spectrometer (Perkin Elmer).

Sample preparation

For heavy metals content analysis, samples were prepared by wet digestion in microwave system (MWS-2, Berghoff) using HNO_3 65% and H_2O_2 according to the program presented in Table 3.

Table 3. Microwave heating program

Step	Temperature (°C)	Duration (min)	Power (%)
1	160	5	80
2	220	40	90
3	Cooling	20	0

For the analysis of heavy metals that can migrate from the packing materials, the samples were subjected to certain test conditions. Thus, the plastics were exposed 10 days to 40 degrees (OM2), using as a food simulant 3% (v/v) acetic acid, for paper and cardboard a cold aqueous extract was obtained (24 hours at room temperature) which was stabilized with HNO_3 65%, and the glass packaging materials were tested 24 hours at room temperature, using as food simulant 4% (v/v) acetic acid.

Calibration

Calibration curve for each element was performed using reagents described above. 5 calibration points were used for each calibration curve. The correlation coefficient of each calibration curve was higher than 0.995.

RESULTS AND DISCUSSIONS

Heavy metals content

According to European Directive 94/62/EC on the management of packaging and packaging waste to prevent their impact on the environment (consolidated version 2018), transposed into Romanian legislation by Law 249/2015 on the management of packaging and packaging waste, the sum of concentrations of lead, cadmium, hexavalent chromium and mercury present in packaging or packaging components must not exceed 100 mg/kg.

From the results presented in Table 4, it can be observed that they fall within the limits imposed by the legislation in force. The values obtained for plastic materials (P1-P19) are considerably lower than for paper and cardboard packaging (P20-P32).

For plastic materials, lead levels ranged between < 0.002 and 5.997 mg/kg, < 0.0002 and 0.059 mg/kg for cadmium and between < 0.013 and 0.638 mg/kg for chromium. In the case of paper and cardboard samples higher levels were obtained for the three determined metals, so that for lead the levels ranged between < 0.002 and 14.650 mg/kg, for cadmium between < 0.0002 and 0.490 mg/kg, and for chromium between < 0.013 and 25,800 mg/kg.

Table 4. Heavy metals content in food packaging samples (mg/kg)

Sample	Pb	Cd	Cr
P1	1.507	< 0.0002	< 0.013
P2	0.024	< 0.0002	0.118
P3	1.228	< 0.0002	< 0.013
P4	0.267	< 0.0002	0.638
P5	1.066	< 0.0002	< 0.013
P6	0.937	< 0.0002	< 0.013
P7	1.577	< 0.0002	< 0.013
P8	0.423	< 0.0002	< 0.013
P9	1.618	< 0.0002	< 0.013
P10	0.813	0.059	< 0.013
P11	0.825	< 0.0002	< 0.013
P12	1.467	< 0.0002	< 0.013
P13	< 0.002	0.056	0.055
P14	< 0.002	< 0.0002	< 0.013
P15	5.977	< 0.0002	< 0.013
P16	< 0.002	< 0.0002	< 0.013
P17	< 0.002	< 0.0002	< 0.013
P18	< 0.002	< 0.0002	< 0.013
P19	0.477	< 0.0002	< 0.013
P20	5.737	< 0.0002	2.450
P21	< 0.002	< 0.0002	3.040
P22	4.301	0.005	6.722
P23	2.602	0.008	1.856
P24	< 0.002	< 0.0002	< 0.013
P25	3.674	< 0.0002	5.130
P26	14.650	0.025	25.800
P27	1.693	< 0.0002	< 0.013
P28	7.509	0.064	6.260
P29	4.703	0.490	1.402
P30	3.454	< 0.0002	4.740
P31	8.492	0.064	1.690
P32	13.177	0.301	2.000

The high levels of heavy metals in paper and board are due to the chemical additives used to process pulp and secondary fibers to obtain paper or cardboard (Mertoglu, 2017), additives such as adhesive chemicals, mineral products used to improve certain characteristics of paper (Conti, 2008; Mertoglu, 2017).

The metal levels in samples with high weight (corrugated cardboard - P25, P26, P27, P28, P31, P32) are higher compared to those with lower weight (baking paper, paper towels - P24, P21). These differences are also generated by

the presence of dyes and printing inks, which are a major source of toxic metals (Mertoglu, 2017).

Heavy metals migration

According to ResAP EC Resolution 3/2002, the maximum values of lead and cadmium that can migrate from paper and cardboard are 0.012 mg/l, respectively 0.018 mg/l.

From the results presented in Table 5, it can be observed that they fall within the limits imposed by the legislation in force and do not represent a source of contamination of food products.

Although there are no limits for the level of chromium that can migrate from this category of packaging, the obtained values were lower than the detection limit of this method.

Table 5. Heavy metals migration from paper and board materials (mg/l)

Sample	Pb	Cd	Cr
P14	< 0.002	< 0.0002	< 0.013
P15	< 0.002	< 0.0002	< 0.013
P16	0.003	< 0.0002	< 0.013
P17	0.0028	< 0.0002	< 0.013
P18	< 0.002	< 0.0002	< 0.013
P19	0.005	< 0.0002	< 0.013

For Pb and Cd migration in glass (Table 6), the results were compared with the limits presented in the standard ISO 7086-2/2000 Glass hollowware in contact with food - Release of lead and cadmium - Part 2: Permissible limits, which are 5.0 mg/l for Pb and 0.5 mg/l for Cd. The obtained values are very low, confirming the claim that glass is a very stable packaging material.

Table 6. Heavy metals migration from glass materials (mg/l)

Sample	Pb	Cd
P20	< 0.002	< 0.0002
P21	< 0.002	< 0.0002
P22	< 0.002	< 0.0002
P23	< 0.002	< 0.0002

According to the Regulation (EU) no. 10/2011 on plastic materials and articles intended to come into contact with food, plastic materials and articles shall not release substances in quantities exceeding the specific migration limits.

The values obtained are lower than maximum allowed limits for all metals (Table 7).

Table 7. Maximum allowed limits form metals according to Regulation (EU) no. 10/2011

Element	Maximum allowed limit (mg/kg)
Barium	1.0
Cobalt	0.05
Copper	5.0
Iron	48.0
Manganese	0.6
Nickel	0.02
Zinc	5.0

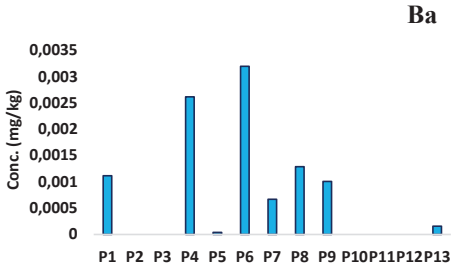

Figure 1. Barium migration from food contact materials

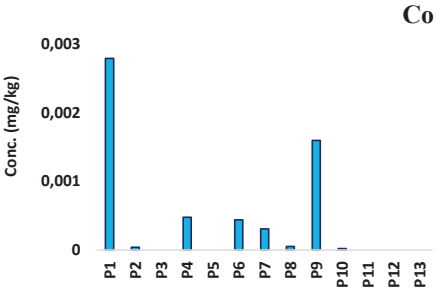

Figure 2. Cobalt migration from food contact materials

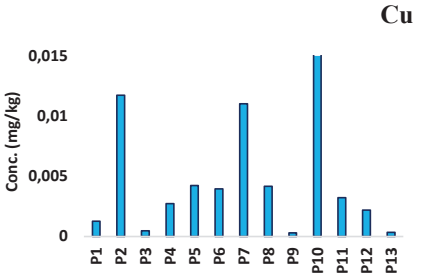

Figure 3. Copper migration from food contact materials

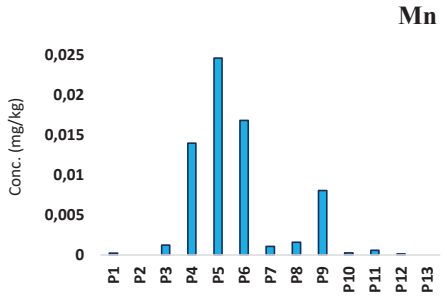

Figure 4. Manganese migration from food contact materials

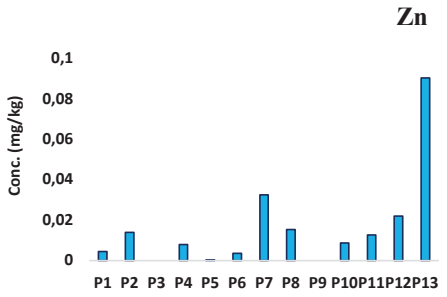

Figure 5. Zinc migration from food contact materials

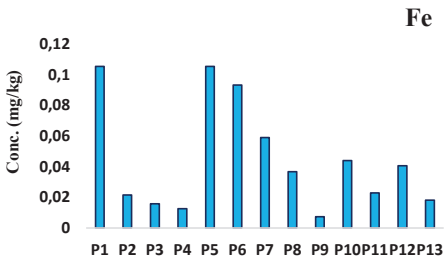

Figure 6. Iron migration from food contact materials

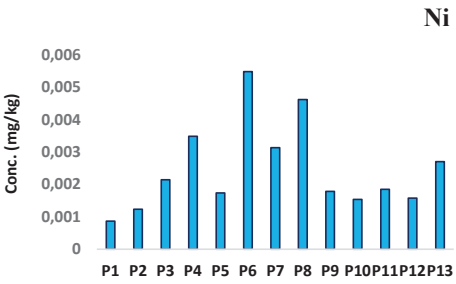

Figure 7. Nickel migration from food contact materials

Analyzing all the obtained results (Figures 1-7), it can be observed that the highest values were obtained for Fe and Zn, while the lowest values were obtained for Co.

CONCLUSIONS

Two versatile techniques, atomic absorption spectrometry with graphite furnace (GF-AAS) and inductively coupled plasma mass spectrometry (ICP-MS) were used to evaluate the heavy metals content and metals specific migration of several food contact materials (plastic, paper/board and glass).

The obtained results were compared with maximum allowed limits stated by the legislation in force: European Directive 94/62/EC on packaging and packaging waste and Romanian Law 249/2015 regarding management of food packaging and food packaging waste, Regulation (EU) no. 10/2011 on plastic materials and articles intended to come into contact with food or Resolution ResAP EC 3/2002 on paper and board materials and articles intended to come into contact with foodstuffs.

The values obtained are lower than maximum allowed limits for all metals analyzed. In terms of heavy metals content, the values obtained for paper and board are higher than for plastic.

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