ATOMIC ABSORPTION INVESTIGATION OF HEAVY METALS CONTENT IN PLASTIC, PAPER AND BOARD FOOD CONTACT MATERIALS PRODUCED IN ROMANIA

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Abstract
Heavy metals, especially lead (Pb), cadmium (Cd) and chromium (Cr), are environmental contaminants which can be found in most foods in the food chain. These metals are also present in food contact materials, and, through them, can reach the human body. In the human body, these heavy metals are transported into body cells and tissues binding to proteins, nucleic acids destroying these macromolecules and disrupting their cellular functions. As such, heavy metal toxicity can have several consequences in the human body, such as affecting the central nervous function, damaging the blood constituents or vital organs, promoting several disease conditions.
Within this study, several food contact materials (plastic, paper and board) were selected from different Romanian producers and evaluated in terms of heavy metals content. Analysis was performed in order to evaluate the compliance with the limits imposed by the legislation in force, using atomic absorption spectrometry as analysis technique. All the analyzed materials were compliant. Heavy metals content of paper and board samples were higher than all plastic samples.

Keywords: heavy metals, food contact materials, food packaging, AAS, plastic, paper and board

Received: 30.12.2019 Reviewed: 26.02.2020 Accepted: 02.03.2020

INTRODUCTION

Because metals are found both in the environment and in some food products, human exposure to these contaminants can be by ingestion or inhalation. In small quantities, ones metals can help maintain a good health, but as these levels increase, they become toxic or even carcinogenic in the event of repeated long-term exposure (Jaishankar et al, 2014), because they cannot be metabolized by the body due to higher density than water (Khan and Khan, 2015).

Heavy metals contamination of food products can be achieved from the raw material stages as a result of the environment contamination where the culture grows, during the transportation of food or raw materials (Rather et al, 2017), from water used in processing, from equipment used in the technological flow, but also from the food contact materials used to pack and store the product (Bakircioglu et al, 2011). In the food industry a large variety of packaging materials can be found, the most used being plastic, paper and board. During storage and distribution until the consumption, it is expected that no migration of different chemical contaminants can lead from packaging material to food product (Mertoglu–Elmas and Cinar, 2018).

The metal components present in the packaging materials can migrate into the food product, then can achieve the human body (Kim et al, 2008; Khan and Khan, 2015). This process is influenced by several factors such as sunlight, pH of the stored product, temperature, contact time (Khan and Khan, 2015).

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

MATERIALS AND METHODS

Sample collection

47 samples of food contact materials (36 plastic and 11 paper/board) were purchased from

different Romanian producers. A full description is provided in Table 1.

Table 1. Samples description

Code	Material	Description
P1	PET film	220 µ transparent rigid PET film
P2	PET film	300 µ transparent rigid PET film
P3	PET film	350 µ transparent rigid PET film
P4	PET film	350 µ transparent rigid PET film
P5	PET film	400 µ transparent rigid PET film
P6	PET film	400 µ white rigid PET film
P7	PET film	450 µ transparent rigid PET film
P8	PET film	500 µ transparent rigid PET film
P9	PET film	550 µ transparent rigid PET film
P10	PET film	600 µ transparent rigid PET film
P11	PET film	650 µ transparent rigid PET film
P12	PET/PE film	515/35 µ transparent rigid PET/PE film
P13	PET/PE film	565/35 µ transparent rigid PET/PE film
P14	PET/PE film	665/35 µ transparent rigid PET/PE film
P15	PET/PE film	765/35 µ transparent rigid PET/PE film
P16	PET/PE film	515/35 µ transparent rigid PET/PE film
P17	PET/PE film	565/35 µ transparent rigid PET/PE film
P18	Bag-in-box	LLDPE/EVOH/LLDPE transparent bag-in-box
P19	HDPE film	Transparent HDPE film
P20	LDPE film	Transparent LDPE film
P21	CAST/BOPP wrapping film	Transparent CAST/transparent BOPP film, printed
P22	PE/PE wrapping film	White PE/transparent PE film, printed
P23	PE/BOPP wrapping film	White PE/mat BOPP film, printed
P24	BOPP/BOPP wrapping film	Pearl BOPP/mat BOPP film, printed
P25	HDPE closure	HDPE green closure
P26	HDPE closure	HDPE blue closure
P27	HDPE closure	HDPE yellow closure
P28	HDPE closure	HDPE white closure
P29	HDPE closure	HDPE red closure
P30	HDPE closure	HDPE gold closure
P31	HDPE closure	HDPE black closure
P32	HDPE closure	HDPE pink closure
P33	PET bottle	Blue water PET bottle
P34	PET bottle	Transparent PET bottle
P35	HDPE bottle	White HDPE milk bottle
P36	PS cup	White PS (GPPS and HIPS) yogurt cup
P37	Paper bag	Brown kraft paper bag
P38	PE/paper bag	White kraft paper bag, laminated with PE bag
P39	PP/paper bag	White kraft paper bag, laminated with PP bag
P40	BOPP/paper bag	Brown kraft paper bag with BOPP window
P41	BOPP/paper bag	White kraft paper bag with BOPP window
P42	PE/paper bag	Brown kraft paper bag, laminated with PE film
P43	PE/board box	White board cake box, laminated with PE film, printed
P44	PE/board trays	Brown board trays laminated with gold/silver PE film
P45	Board box	Coated white burger board box
P46	Board box	Printed board egg box
P47	Board box	Whitened and printed board pizza box

Reagents

Nitric acid (HNO_3) 65% and Hydrogen peroxide (H_2O_2)30% 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%) and Chromium standard solution 1000 mg/l Cr for AA ($Cr(NO_3)_3$ in HNO_3 2%) purchased from Scharlau. Dilutions were performed using ultrapure water (18.2 MΩ.cm). All glassware used was cleaned and decontaminated with 10% HNO_3.

Equipment

Heavy metals analysis was performed using an AAnalyst 600 graphite furnace atomic absorption spectrometer system (Perkin Elmer) provided with a Transversely Heated Graphite Atomizer (THGA) furnace assembly and longitudinal Zeeman-effect background correction.

Sample preparation

Samples were prepared by wet digestion using anMWS-2 microwave system (Berghof). Samples were weighted and then treated with 4 ml of HNO_3 65% and 1 ml of H_2O_2 using the program presented in Table 2.

Calibration

Calibration curve for each element was performed using reagents described above. Characteristics of each calibration curve are presented in Table 3.

Table 2. Microwave heating program

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

Table 3. Calibration curves characteristics

Analyte	Wavelength (nm)	Domain	Number of calibration points	Regression coefficient	LOD (µg/L)	LOQ (µg/L)
Pb	283.3	10 - 50 µg/l	5	0.997491	2.0	6.0
Cd	228.8	1 - 5 µg/l	5	0.999696	0.2	0.6
Cr	357.9	10 - 50 µg/l	5	0.998030	1.3	3.9

RESULTS AND DISCUSSIONS

According to European Directive 94/62/EC on packaging and packaging waste (consolidated version 2018) which aims to harmonize national measures concerning the management of packaging and packaging waste in order to prevent any impact thereof on the environment, the sum of concentration levels of lead, cadmium, hexavalent chromium and mercury present in packaging or packaging components shall not exceed 100 mg/kg. The aforementioned directive is transposed into the Romanian legislation by Law 249/2015 on the management of packaging and packaging waste.

Considering the mentioned aspects, from the analysis of the results presented in Fig. 1 it can be observed that they fall within the limits imposed by the legislation in force. The values for plastic materials are considerably lower than for paper and board. Contamination from the surface and printing ink colors of paper-based food packaging is a major source of toxic metals (EPA/310-R-02-002, 2002).

In the case of PET films (P1-P11), the results showed no significant difference between samples, meaning that film thickness does not have major influence on the heavy metals content (Pb: values between < 0.002 and0.053 mg/kg; Cd: values between < 0.0002 and 0.122 mg/kg; Cr: values between 0.090 and 0.291).

When films structure consists of PET/PE (P12-P17), the heavy metals content does not change very much; there are also no significant difference between samples (Pb: values between < 0.002 and 0.145 mg/kg; Cd: < 0.0002 mg/kg; Cr: values between < 0.0013 and 0.426).

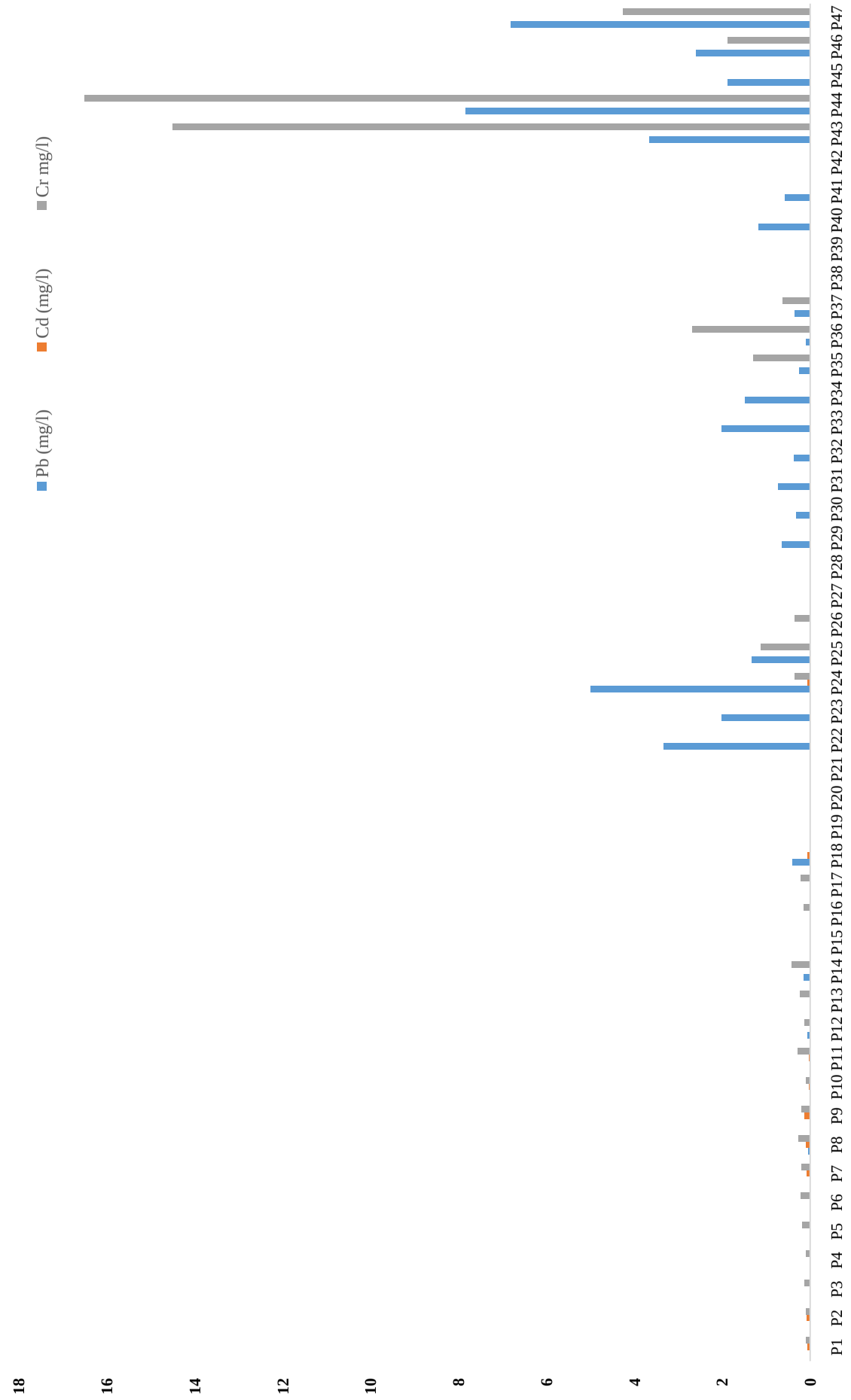

Figure 1. Heavy metals content in food contact materials

Samples of wrapping films having different structures (P22-P24) had the highest Pb content of plastic samples (between 2.011 and 4.989 mg/kg).
Analyzing HDPE closures samples (P25-P32) a significant influence of dye nature on lead content can be observed. The values ranged from < 0.002 mg/kg for white closure to 0.737 mg/kg for black closure and 1.331 mg/kg for green closure. Values for cadmium were below LOD (0.0002 mg/kg) for all the samples, while the values for chromium were bellow LOD (0.0013 mg/kg) for 6 out of 8 samples.
Significant differences for lead and chromium content were also observed for the plastic bottles samples: while white HDPE bottle sample had the highest chromium content (1.290 mg/kg) and the lowest lead content (0.254 mg/kg), the PET bottles had higher values for lead content when adding blue dye.
Samples of paper and board (P37-P47) had higher contents of heavy metals, reaching values of 7 mg/kg (lead) and 16 mg/kg (chromium). There is a remarkable difference among the levels of heavy metals depending on the procedure of sample pretreatment (Conti and Botre, 1997).

CONCLUSIONS

Atomic absorption spectrometry with graphite furnace technique (GF-AAS) was used to evaluate the heavy metals content (Pb, Cd and Cr) in 47 samples of plastic, paper and board food contact materials produced in Romania. For mentioned heavy metals, European Directive 94/62/EC on packaging and packaging waste states the maximum allowed limit for the sum of concentration levels of lead, cadmium, hexavalent chromium and mercury present in packaging materials to 100 mg/kg. The highest values obtained for analyzed samples were in case of paper and board, but they did not exceed 20 mg/kg value for the sum of lead, cadmium and total chromium. In case of plastic, the highest obtained value for the sum of the 3 mentioned metals did not exceed 5.5 mg/kg. All tested samples are in accordance with the legislation in force (European Directive 94/62/EC and Romanian Law 249/2015).

ACKNOWLEDGEMENTS

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

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