Evaluation of Metal Concentrations in Food Packaging Materials: Relation to Human Health

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ABSTRACT

The determination of iron, cobalt, nickel, manganese, cadmium, chromium, lead, and copper in 39 different food packaging materials from Turkey was performed by flame atomic absorption spectrometry (FAAS). The contents of the investigated packaging materials included cheeses, fast-foods, meats, candy, desserts, fish, milk-containing sweets, fresh pasta, mixed nuts, bagels, goodies, olives, cheesecake bars, pudding, coffee, patty, sausage, and pizza.

The packaging samples (7.48-134.4 g m^{-2}) were immersed in 3% (v/v) acetic acid for 24 hours at 40 ºC to allow for migration prior to the determination of the metal concentrations. Good accuracy was obtained as verified by the analysis of certified reference material (CRM) NIST-SRM 1570a Trace Elements in Spinach Leaves.

The analyte concentrations in the packaging material samples were found to range from 0.13-221.2, 0.32-11.1, 0.05-33.2, 0.05-101.9, 0.04-3.09, 0.23-4.10, 0.42-22.1, and 0.03-58.2 μg g^{-1} for Fe, Co, Ni, Mn, Cd, Cr, Pb, and Cu, respectively.

INTRODUCTION

The extensive employment of novel food packaging materials has caused an increase in the migration of hazardous metals from these products into the packaged foods. Various materials are widely used and paper and paper derivatives are indeed one of the primary sources (1). Catalysts, thermal stabilizers, adhesives, lubricants, antioxidants, pigments, bleaching agents, printing inks, and different chemicals are used during the production processes (2) and can migrate from the printed surface to the food contact surface (3). The different types of papers are produced by pulping, bleaching, and treatment processes. Recycled paper and paperboard products are produced from sources such as newspapers, magazines, and cartons which are pulped with water and cleaned and de-inked with surfactants (4-6).

Legislation in the area of food contact materials and articles is very complex and constantly in progress. In the United States, the Food and Drug Administration (FDA) has published its own food ingredients and packaging guidelines for the industry (7-8). In Europe, the concern about the examination of packaging materials with regard to the content of toxic substances has substantially grown after introduction of the EC Directive (94/62/EC), which limits the level of the toxic heavy metals in packaging materials (2, 9-11). The "maximum permitted quantity of the residual substance in the material or article expressed as mg per dm^2 of the surface in contact with foodstuffs" (QM) restriction limits were established for Cd, Pb, and Hg by the Council of Europe Resolution AP (9) for paper, paperboard materials, and articles intended to come into contact with foodstuffs. The QM restriction quality limits (mg dm^{-2} paper and paperboard) are 0.002 mg dm^{-2} for Cd, 0.003 mg dm^{-2} for Pb, and 0.002 mg dm^{-2} for Hg (9).

Due to the negative and positive influences and the importance of trace elements in the human body (12-17), many scientific studies have been published about the migration of contaminants from paper packaging materials to foods and evaluation of these products for direct or indirect food contact applications (18-25).

This paper describes the determination of Fe, Co, Ni, Mn, Cd, Cr, Pb, and Cu in various food packaging materials by the application of migration studies. Cheeses, fast foods, meats, candy, desserts, fish, milk-containing sweets, fresh pasta, mixed nuts, bagels, goodies, olives, cheesecake bars, pudding, coffee, patty, sausages, and pizza are the foods studied with regard to their contact with packaging materials. The migration study proposed here is similar to official methods reported in the literature (26-29).

EXPERIMENTAL

Instrumentation

A Model 3110 flame atomic absorption spectrometer (PerkinElmer, Inc., Shelton, CT, USA) was used. All measurements were done in an air-acetylene flame. The instrumental operating conditions are listed in Table I. The parameters were set as recommended by the manufacturer. The detection limits for analyte elements for flame atomic absorption spectrometric determinations are given in Table II.

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Standard Solutions and Reagents

All reagents were of analytical reagent grade unless otherwise stated. The standard solutions of the analytes for calibration were prepared by diluting a stock solution of 1000 mg L^{-1} of the analyzed element (E. Merck, Darmstadt, Germany). Acetic acid used for the migration tests was also from E. Merck. The standard reference material (SRM) used to compare the accuracy of the method was NIST SRM 1570a Trace Elements in Spinach Leaves (National Institute of Science and Technology, Gaithersburg, MD, USA).

TABLE I
Instrumental Operating Conditions

Element	Wavelength (nm)	Slit Width	Lamp Current (mA)
Fe	248.3	0.2	30
Co	240.7	0.2	30
Ni	232.0	0.2	30
Mn	279.5	0.2	20
Cd	228.8	0.7	8
Cr	357.9	0.7	12
Pb	283.3	0.7	15
Cu	324.8	0.7	15

TABLE II
The Detection Limits for Analyte Elements for FAAS Detection

Element	(μg g^{-1})
Fe	1.0
Co	1.4
Ni	0.9
Mn	2.9
Cd	0.02
Cr	0.7
Pb	2.4
Cu	0.2

Samples of Packaging Materials

A total of 39 different food packaging materials were obtained from local dealers in Kayseri City, Turkey. Prior to the beginning of the migration tests, each sample was cut into squares (10x10 cm) and stored at 4 ºC for about 6 hours. Then they were put into weighing bottles, desiccated in an oven at 105 ºC for 2 hours until constant weight was reached. The food packaging materials along with their specific mass (7.48-134.4 g m^{-2}) values are listed in Table III.

Migration Procedure

Exactly 2 dm^2 of contact surface for each sample (the two sides of 1 dm^2 specimens) were cut into pieces and kept in 100 mL of a 3% (v/v) metal-free solution of acetic acid for 24 hours at 40 ºC. At the end of this treatment, the contact liquid solution was analyzed by flame AAS for determination of the analyte metals.

The data were subjected to a statistical analysis and correlation matrices were produced to examine the interrelationships between the trace metal concentrations. A Student's *t*-test was employed to estimate the significance of the values.

RESULTS AND DISCUSSION

The results of the migration test (3% v/v acetic acid) for Fe, Co, Ni, Mn, Cd, Cr, Pb, and Cu determination are listed in Table IV. The data are expressed both as μg of heavy metal per g of paper sample and also as μg of heavy metal per dm^2 of paper sample. The accuracy of the presented method was evaluated by means of trace element determination in the NIST SRM 1570a Trace Elements in Spinach Leaves. The results in Table V show that the values were within or near the certified values, indicating that there was good agreement. The relative standard deviations of the determinations were less than 10%. The Student's *t*-test was used in this study ($p<0.05$).

Pb Concentrations

Lead (Pb) is a widely distributed environmental poison and when used in the manufacture of packaging materials is a source of contamination of the food. Therefore, the monitoring of Pb concentration becomes essential. According to the Turkish Food Codex, the Pb content of any paper in direct contact with food may not exceed 20 μg g^{-1} (29). The concentrations of Pb in this study were in the 0.42–22.1 μg g^{-1} (0.41-11.8 μg dm^{-2}) range. Some of the investigated samples had values above the quality limit (3 μg dm^{-2}) established by the Council of Europe (9). However, the mean value for the 39 investigated samples was near this quality limit. Paperboard packaging for patty (sample No. 26) at 11.8 μg dm^{-2} had four times higher values than the European Council quality limit. This high concentration may originate from the lead-based colored ink on the paper.

Cd Concentrations

The Council of Europe proposed the maximum Cd limit for packaging paper and board as 0.002 mg dm^{-2} (9). In this study, the Cd content of all samples was below that limit. The values for Cd were in the 0.04–3.09 μg g^{-1} (0.03–0.64 μg dm^{-2}) range, with mean values of 0.81 μg g^{-1} and 0.31 μg dm^2.

Cr Concentrations

The recommended daily intake of Cr by the National Research Council, Food and Nutrition Board is 50–200 μg (30,31). The Cr levels found in the materials used for this study ranged from 0.23–4.10 μg g^{-1}, with a mean value 1.45 μg g^{-1}. These values are also lower than the surface guideline limits of 3.05 μg dm^{-2} provided by the Council of Europe (9).

TABLE III
Foods in Contact With Packaging Materials and Specific Mass Employed for Heavy Metals Determination by Flame AAS

Sample	Food	Mass (g m^{-2})
1	Cheese	37.6
2	Fast food	20.9
3	Meat	19.2
4	Candy	19.9
5	Fast food	17.8
6	Fast food	128.4
7	Dessert	17.0
8	Fast food	18.3
9	Fish	21.3
10	Milky sweet	37.0
11	Fresh pasta	36.5
12	Fast food	19.1
13	Mixed nuts	31.0
14	Mixed nuts	34.1
15	Fast food	29.7
16	Bagel	20.5
17	Fast food	27.4
18	Goodies	21.8
19	Olive	60.6
20	Fast food	15.9
21	Fast food	24.9
22	Cheesecake bars	28.1
23	Pudding	45.1
24	Fast food	26.0
25	Coffee	68.9
26	Patty	126.1
27	Sausage	43.8
28	Pizza	54.3
29	Cheese	22.2
30	Milky sweet	27.4
31	Dessert	17.8
32	Meat	47.9
33	Fast food	17.1
34	Milky sweet	58.5
35	Candy	7.48
36	Fast food	21.5
37	Fast food	134.4
38	Milky sweet	54.0
39	Coffee	14.8

TABLE IV
Results of Migration Test (3%, v/v, acetic acid)
All data are expressed both as µg of heavy metal per g of sample and also as µg of heavy metal per dm^2 of paper sample.

	Concentration							
Sample	Fe	Co	Ni	Mn	Cd	Cr	Pb	Cu
1	67.8	0.41	0.02	4.40	0.42	0.74	4.44	0.50
2	5.52	0.41	0.02	1.79	0.12	0.31	1.33	0.35
3	7.26	0.41	0.02	0.61	0.41	0.31	0.55	0.20
4	44.0	0.41	2.21	4.38	0.34	0.31	0.55	0.50
5	3.13	0.41	0.02	0.83	0.34	0.31	2.88	0.04
6	0.17	0.41	2.21	0.06	0.49	0.30	0.54	0.04
7	3.13	0.41	0.02	0.72	0.49	0.31	2.09	0.20
8	3.73	0.88	0.02	0.83	0.57	0.31	1.33	0.04
9	23.9	0.41	0.02	2.64	0.12	0.31	0.55	0.66
10	29.8	0.88	0.02	0.18	0.12	0.31	0.55	0.04
11	6.10	1.35	0.02	0.82	0.42	0.73	4.42	3.27
12	17.9	0.88	0.02	1.15	0.42	0.74	1.32	0.81
13	29.8	0.88	0.02	13.1	0.64	0.73	0.55	0.50
14	6.99	1.94	3.12	34.8	0.13	0.31	3.19	0.09
15	6.50	1.95	0.59	1.09	0.18	0.31	0.61	0.83
16	18.7	1.43	1.22	5.70	0.11	0.31	4.04	1.41
17	2.59	0.40	1.85	0.10	0.10	0.31	0.61	7.29
18	7.98	0.40	0.59	0.85	0.25	0.31	4.05	2.01
19	30.9	1.95	3.11	4.32	0.15	0.31	4.90	2.00
20	5.02	1.43	0.59	2.08	0.15	0.31	3.18	0.24
21	8.91	2.46	3.11	1.46	0.13	0.31	4.91	4.21
22	0.15	0.40	1.85	0.10	0.12	0.31	0.62	0.09
23	6.00	3.49	5.01	2.46	0.13	0.31	4.92	0.53
24	8.92	1.43	3.74	3.20	0.11	0.31	5.75	4.78
25	0.15	0.40	1.85	0.10	0.03	0.31	0.61	26.8
26	22.1	5.03	9.43	22.3	0.28	2.45	11.8	2.30
27	13.3	1.43	3.11	4.95	0.15	0.74	4.04	21.8
28	3.57	1.43	1.85	1.47	0.15	0.30	4.05	29.8
29	7.48	2.46	3.11	1.22	0.11	0.31	4.91	0.68
30	2.59	0.40	1.22	0.59	0.03	0.31	2.33	15.9
31	0.15	0.40	0.85	0.72	0.09	0.31	2.88	0.69
32	4.06	0.91	1.22	36.1	0.09	0.31	1.65	0.69
33	2.60	0.40	0.86	2.96	0.09	0.31	0.41	0.49
34	0.15	0.40	0.85	0.10	0.09	0.30	0.41	0.49
35	0.15	0.40	2.48	0.10	0.09	0.31	0.41	0.48
36	0.15	0.40	0.86	0.22	0.09	0.31	0.41	0.48
37	14.8	1.95	3.75	16.1	0.35	2.02	5.36	2.77
38	4.06	0.40	0.85	1.34	0.09	0.31	0.41	1.11
39	4.04	0.91	0.85	2.95	0.09	0.31	0.41	1.10

TABLE V
Results of Analysis with Migration Test for SRM NIST-SRM 1570a Trace Elements in Spinach Leaves (n=3)

Element	Certified Value ($\mu g\ g^{-1}$)	Our Value ($\mu g\ g^{-1}$)	Recovery (%)
Mn	75.9±1.9	71.3±1.6[a]	93
Co	0.39±0.05	N.D.[b]	-
Ni	2.14±0.10	2.1±0.2	98
Cd	2.89±0.07	2.66±0.2	92
Cu	12.2±0.6	11.7±0.5	95

[a] Average ± standard deviation.
[b] N.D. = Not determined.

Fe Concentrations

Exposure to excess Fe can lead to numerous pathological consequences such as colorectal cancer and heart disease (32). There is no suggested Fe limit for paper packaging materials. The average Fe content of the studied samples was 36.9 $\mu g\ g^{-1}$ and 13.9 $\mu g\ dm^{-2}$. The FAO/WHO set a limit for heavy metal intake based on body weight. For an average adult (60 kg body weight), the provisional tolerable daily intake (PTDI) is 214 µg Pb, 48 mg Fe, 3 mg Cu, and 60 mg Zn, respectively (33).

Ni Concentrations

The Ni concentrations in the samples were in the 0.05–33.2 $\mu g\ g^{-1}$ and 0.02–9.43 $\mu g\ dm^{-2}$ range. There is no information available in the literature for maximum allowable nickel levels. However, the WHO (World Health Organization) recommends a maximum daily intake of 100–300 µg Ni (34). Thus, the nickel levels found in the samples can be considered as not being a health risk.

Co Concentrations

In the literature, no information is available for safe cobalt levels in food packaging paper. The maximum concentration of Co for the cheese packaging material tested in this study was 2.46 $\mu g\ dm^{-2}$ (11.1 $\mu g\ g^{-1}$), indicating that there are no health safety concerns from the cobalt content of packing materials.

Mn Concentrations

The U.S. Institute of Medicine recommends that Mn intake from food, water, and dietary supplements should not exceed the tolerable daily upper limit of 11 $mg\ day^{-1}$ (30). In our study, the Mn levels were in the 0.05–101.9 $\mu g\ g^{-1}$ range with 4.61 $\mu g\ dm^{-2}$ as the mean surface value, indicating that there are no health safety concerns for this type of packaging material.

Cu Concentrations

The average daily dietary requirement for Cu in the adult human has been estimated to be 3 mg (33). The Cu values in our work were found to range from 0.03–58.2 $\mu g\ g^{-1}$, with a mean value for contact surface as 3.39 $\mu g\ dm^{-2}$, indicating that there are no health safety concerns.

CONCLUSION

The food industry and scientists are faced with great difficulties in the attempt to achieve migration control of toxic elements leaching into foods from their respective packaging materials. Only limited data are currently available for permissible maximum levels of toxic metals. Restriction limits have been established for cadmium, lead, and nickel by the Council of Europe for paper and paperboard materials and articles intended to come in contact with foodstuff. The Turkish Food Codex has a regulation for the lead content of packaging paper.

The samples investigated in this study show below maximum legal concentrations of Fe, Co, Ni, Mn, Cd, Cr, and Cu, except for Pb. Thus, in general, these packaging products pose no health risks with respect to maximum metal concentrations. However, routine or even daily controls with official methods should be made available and required for better accuracy, ease, and repeatability in food packaging materials analysis.

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