Available online at www.sciencedirect.com
ScienceDirect
Food Research International 41 (2008) 411–418
FOOD RESEARCH INTERNATIONAL
www.elsevier.com/locate/foodres

Levels of heavy metals in candy packages and candies likely to be consumed by small children

Ki-Cheol Kim *, Yong-Bae Park, Myung-Jin Lee, Jung-Beom Kim, Jeong-Weon Huh, Dae-Hwan Kim, Jung-Bok Lee, Jong-Chan Kim

Gyeonggi-do Institute of Health and Environment, 324-1 Pajang-dong, Jangan-gu, Suwon, Gyeonggi-do 440-290, Republic of Korea

Received 14 January 2008; accepted 28 January 2008

Abstract

Ninety two samples of child-consumed candies and candy packages were analyzed for seven heavy metals. Lead (Pb) was detected at concentrations of 110.3–6394.1 mg kg^{-1} in ten of 92 candy packages. The directive factor of Pb contamination had originated in the lead-based ink of the outer cover. Particularly, Pb was detected at high concentrations in case of green- or yellow-colored packages. Chromium (Cr) was detected at high concentrations in cases where Pb was also detected at high concentrations, and the Cr levels ranged from 136.9 mg kg^{-1} to 1429.3 mg kg^{-1} in seven of the 92 candy packages. Hexavalent chromium [Cr(VI)] was detected at 87–105.0% of the total Cr in polypropylene-coated wrappers with printed outer covers. The migration of Cr(VI) increased with elution time up to 0.20 μg $(cm^2)^{-1}$ for 30 days in basic (pH 10.0) solution; however, there were no migrations in acidic (pH 4.0) and neutral (pH 7.0) solutions. The migration of Pb increased with elution time up to 0.65 μg $(cm^2)^{-1}$ and 0.28 μg $(cm^2)^{-1}$ in basic (pH 10.0) and acidic (pH 4.0) solutions, respectively. However, any migration was hardly observed in neutral (pH 7.0) solution.

Keywords: Heavy metals; Candy and candy packages; Migration; Lead; Hexavalent chromium [Cr(VI)]

1. Introduction

The word "package" refers to a container that provides a means of protecting, marketing, or handling a product, and it includes a unit package, an intermediate package, and a shipping container. In many countries, various plastic materials are used in food packaging, and most of them are printed by color inks on the outer cover. Importantly, food products such as candies that are likely to be consumed frequently by small children are wrapped in colorful packages in order to induce them to purchase the products. Heavy metals, such as lead, chromium, and copper, can be put onto the children's hands that hold candies. Due to their frequent hand-to-mouth behavior, children are likely to be posed by ingesting these heavy metals. There is a general understanding that the package surface in contact with the food should be free of printing ink, that is, the package itself should form an effective barrier between the printed surface and the food, and the unintentional transfer of components of printing inks from the outer printed surface onto the food contact surfaces should be avoided. Use of printing inks only on the outer surface of the package does not ensure that it will not contaminate the food, although the inner surface of the package is coated with films such as polyethylene or polypropylene. There are 4 mechanisms by which substances used in printing inks can migrate from the printed surface to the food contact surface: blocking, rubbing, peeling, and diffusion (Bradley et al., 2005). There are several scientific studies on migration of contaminants from packages into food (Castle, Jickells, Gibert, & Harrison, 1990; Parry & Aston, 2004; Summerfield & Cooper, 2001; Thompson, Parry, & Benzing, 1997). Moreover, there has been considerable scientific progress in understanding and modeling the migration of adventitious substances with hazardous potential from packages into

* Corresponding author. Tel.: +82 31 250 2527; fax: +82 31 250 2617.
E-mail address: kkcphm@daum.net (K.-C. Kim).

0963-9969/$ - see front matter
doi:10.1016/j.foodres.2008.01.004

foodstuffs that are in direct or indirect contact with the packages (Duffy, Hearty, Gilsenan, & Gibney, 2006; Franz, Huber, & Piringer, 1994; Johns, Hickells, Read, Framshaw, & Castle, 1996; Laoubi & Vergnaud, 1996).

Many kinds of child-consumed candy products were sold at a low price at retail stores near elementary schools in South Korea. Most of the packaging is so poorly designed that the inner coating does not maintain structural integrity, allowing ink components in the outer package layer to migrate into the candy. Furthermore, candy contact surfaces of the packages have a potential for contamination because finished packaging films are frequently distributed to end users in reel form in which the outer printed surface and food contact surfaces of the packages are in contact with each other. There are many kinds of metal-based inorganic pigments. The metal components can migrate from the printed surface to the food contact surface if the package is poorly designed. In particular, heavy metals from the ink can migrate onto the candy if harmful lead (Pb)- or hexavalent chromium [Cr(VI)] – based inks are intentionally used in the food package. Migration can be severe if the surface of the candy is sticky.

For more than a century, Cr(VI) exposure has been known to be associated with cancer induction in humans, especially bronchial carcinoma and lung cancer (IARC, 1990; Léonard & Lauwerys, 1980; Levy & Vanitt, 1986; Newman, 1981). However, not all the Cr(VI) compounds are equally potent as carcinogens. In particular, the water-insoluble Cr(VI) compounds of particulate forms are more potent carcinogens than the water-soluble ones (HolmesAmie et al., 2005; Patierno, Banh, & Landolph, 1988). Most studies using particulate Cr(VI) have focused on lead chromate ($PbCrO_4$) as a model compound for particulate salts (Wise, Orenstein, & Patierno, 1993; Wise, Stearns, Wetterhahn, & Patierno, 1994). $PbCrO_4$ is an inorganic pigment used in paints, inks and plastics; however, most of the countries have prohibited the use of lead chromate in food packages because it is deleterious to health.

The aim of this study was to survey the presence of heavy metals in candies and candy packages from retail stores near elementary schools in South Korea. In addition, the effect of pH on the migration of heavy metals was investigated using food simulants.

2. Materials and methods

2.1. Chemicals and reagents

All the standard stock solutions of heavy metals were certified reference materials that were purchased from Wako Chemical Co. (Japan). The concentrations of the stock solution were as followed: Pb (999 ± 0.005), Cd (1002 ± 0.006), Cr (1006 ± 0.006), Cu (1002 ± 0.005), Zn (1004 ± 0.005), Co (1004 ± 0.006), and Mn (1004 ± 0.004) mg l^{-1}. HNO_3 and H_2O_2 were of heavy metal analysis grade and purchased from Wako Chemical Co. (Japan). Reagent water, toluene, and acetone were of analytical reagent grade and purchased from J.T. Baker (USA). $MgCl_2$, Na_2CO_3, NaOH, and diphenylcarbazide for Cr(VI) analysis were purchased from Fluka Chemicals (Switzerland). Buffer solution was prepared at pH 7.0 and used according to the US EPA (Environmental Protection Agency) method 3060A in the laboratory.

2.2. Digestion of candies and candy packages for heavy metal analysis

Candy samples were digested with microwave-assisted acid digestion. Samples were weighted to approximately 2.0 g in a vessel, to which 9.0 ml HNO_3 and 1.0 ml H_2O_2 were added. The temperature of the microwave instrument was increased from room temperature to 200 °C at 5 °C min^{-1} and held at this temperature for 15 min. After digesting, the solution was gently heated to remove HNO_3, and the residue was then diluted to 10–20 ml with 0.5 mol l^{-1} HNO_3. Sample blanks were performed with empty vessel, to which 9.0 ml HNO_3 and 1.0 ml H_2O_2 were added.

Candy packages were digested using the dry ash method (500 °C, 6 h). Samples were weighted to approximately 0.2 g in ceramic crucible and diluted to 10–100 ml with 0.5 mol l^{-1} HNO_3 after digesting. Sample blanks were also performed with empty ceramic crucible. Eight or nine Samples and their blank were simultaneously analyzed as a sample batch. All the solutions were assayed by ICP-OES (Perkin–Elmer, Optima 5300DV, USA). The concentration ranges for standard solutions were typically between 50 and 5000 μg l^{-1}.

2.3. Analysis of hexavalent chromium [Cr(VI)] in candy packages

The extraction of water-insoluble Cr(VI) in candy packages was performed by alkaline digestion (EPA method 3060A) instead of microwave-assisted acid/dry ash digestion because of oxidation–reduction potential induced by reactions between Cr ions and polymer materials. However, as the digestion solution contains lots of sodium ions that could be interfered in measurement of chromium ions optically it is difficult to analyze the chromium by inductively coupled plasma (ICP) or AAS (atomic absorption spectrophotometer). From this point of view, the Cr(VI) reaction with diphenylcarbazide is the most common and reliable method for analysis of Cr(VI) solubilized in the alkaline digestate. The use of diphenylcarbazide has been well established in the colorimetric procedure (EPA method 7196A). It is highly selective for Cr(VI) and little interference was encountered when it was used on alkaline digestives.

Fig. 1 presents a flowchart of the solvent extraction, alkaline digestion, and color development of the samples. First, toluene was used as the solvent for effectively extracting water-insoluble pigments. Toluene is an effective organic solvent in extracting package components such as ink, resin and adhesives. In the present study extraction

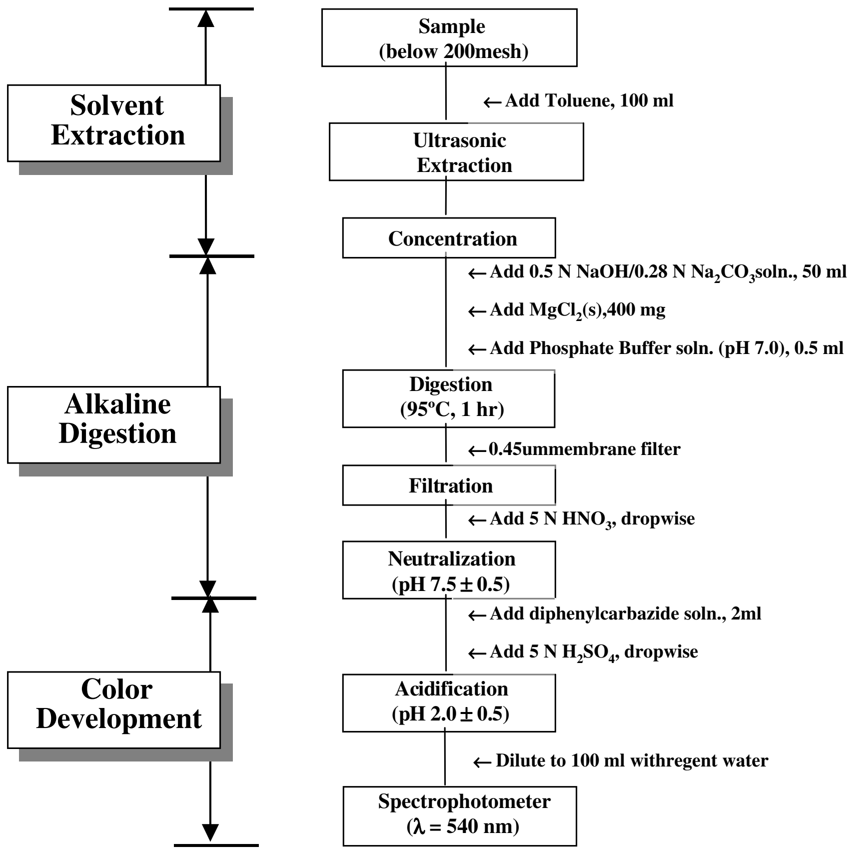

Fig. 1. Flowchart of sample treatment in hexavalent chromium analysis.

took place in a water bath at 40 °C, simultaneously with ultrasonication for an hour. Thereafter, ink pigments in the particulate form were dispersed in the solvent. After concentrating the extracts, 3–5 drops of isopropanol were added to activate the reaction between pigments and the digestion solution.

The samples were digested using 0.28 mol l^{-1} Na_2CO_3/ 0.5 mol l^{-1} NaOH solution and heated at 95 °C for 1hr

Table 1
Analytical parameters of calibration curves of the heavy metals

Analytical instrument	Heavy metal	Concentration range (μg l^{-1})	Regression equation[a]		
			Slope ($b \pm$ SD)[b] $\times 10^2$	Intercept ($a \pm$ SD)[b] $\times 10^2$	$R^2(n)$[c]
ICP-OES	Pb	50–5000	0.150 ± 0.004	0.45 ± 0.59	0.9999(5)
		50–400	0.146 ± 0.002	1.14 ± 0.23	0.9998(4)
	Cd	50–5000	3.053 ± 0.017	8.96 ± 10.36	0.9999(5)
		50– 400	3.049 ± 0.020	−4.69 ± 1.88	0.9997(4)
	Cr	50–5000	1.054 ± 0.017	−3.98 ± 3.14	0.9999(5)
		50– 400	1.028 ± 0.004	0.43 ± 0.47	0.9999(4)
	Cu	50–5000	1.876 ± 0.047	40.51 ± 20.89	0.9999(5)
		50– 400	1.727 ± 0.038	80.87 ± 10.45	0.9991(4)
	Mn	50–5000	10.15 ± 0.14	56.01 ± 20.05	0.9999(5)
		50– 400	10.17 ± 0.04	−6.33 ± 2.55	0.9999(4)
	Co	50–5000	0.695 ± 0.011	−1.15 ± 4.45	0.9999(5)
		50– 400	0.683 ± 0.003	−0.31 ± 0.52	0.9996(4)
	Zn	50–5000	1.517 ± 0.014	27.97 ± 9.93	0.9999(5)
		50– 400	1.524 ± 0.013	20.60 ± 0.18	0.9999(4)
UV–Vis-spectrophotometer	Cr(VI)	200–1000	$(7.72 \pm 0.04) \times 10^{-4}$	$(1.36 \pm 0.23) \times 10^{-2}$	0.9997(5)
		200–500	$(7.90 \pm 0.04) \times 10^{-4}$	$(0.67 \pm 0.24) \times 10^{-2}$	0.9992(4)

[a] Linear unweighted regression analysis ($y = bx + a$, where x is concentration in μg l^{-1}).
[b] SD is the standard deviation of intercept and slope.
[c] R^2 is the square of correlation coefficient and n is the number of points in each calibration curve; each point is the mean of three experimental measurements.

to dissolve the Cr(VI) and stabilize it against reduction to trivalent chromium. After cooling to ambient temperature the solution was filtrated through a 0.45 μm membrane filter. The dissolved Cr(VI) of the digestion solution was analyzed colorimetrically by reaction with diphenylcarbazide in acid solution. Addition of an excess of diphenylcarbazide yielded a red-violet product, and its absorbance was measured photometrically at 540 nm by UV–Vis spectrophotometer (Scinco, S-3100, South Korea). To compensate for possible slight losses of Cr during digestion or other operations of the analysis, Cr(VI) standard solutions were treated by using the same procedure as that used for the sample, and reagent water was used as the sample blank.

The calibration ranges for Cr(VI) were typically between 200 and 1000 $\mu g\, l^{-1}$. To verify the absence of interference during solvent extraction, alkaline digestion and color development, recovery tests were accomplished by analyzing the samples that has been spiked with Cr(VI).

2.4. Migration test

Migration test was carried out to investigate the migration possibility of heavy metals from candy packages to candies. As a sample for the migration test, pieces of polyethylene film (yellow candy packages, total surface area: 50 cm^2) were immersed in 200 ml of food simulant solutions under acidic (pH 4.0), neutral (pH 7.0), and basic (pH 10.0) conditions, and all the samples used in the migration test contained 6394 $mg\, kg^{-1}$ of Pb and 1428 $mg\, kg^{-1}$ of Cr. This was a 30-day test with interim measurements being taken at days 1, 2, 3, 4, 5, 7, 10, 15, 20, 25 and 30 at room temperature. For each measurement, 20 ml was taken and concentrated to 1–2 ml, and then diluted to 10 ml with 0.5 $mol\, l^{-1}$ HNO_3. All the migration measurements were made in duplicate.

3. Results and discussion

3.1. Analytical quality assessment

3.1.1. Linearity of calibration curves

Under the experimental conditions described in the above materials and methods section, linear calibration

Table 2
Recovery studies for the determination of the heavy metals

Analytical instrument	Heavy metals	Spiked concentration ($\mu g\, l^{-1}$)	Mean recovery ± SD (%)[a]
ICP-OES	Pb	200	98.5 ± 2.1
	Cd	200	102.4 ± 1.9
	Cr	200	100.2 ± 1.4
	Cu	200	98.5 ± 2.4
	Mn	200	102.3 ± 2.2
	Co	200	99.5 ± 1.7
	Zn	200	103.2 ± 2.4
UV–Vis- spectrophotometer	Cr(VI)	400	100.9 ± 1.5

[a] SD is the standard deviation of the mean recovery.

Table 3
Levels of heavy metals in candy packages

Manufacturing country (sample no.)	Concentration of heavy metals ($mg\, kg^{-1}$)						
	Cu	Cd	Pb	Mn	Cr	Co	Zn
South Korea (31)	ND–115.3 (8.18)[a]	ND[b]	ND–9.9 (1.05)	ND–1.1 (0.1)	ND–44.2 (2.38)	ND–3.0 (0.15)	ND–114.8 (6.61)
China (39)	ND–354.6 (20.38)	ND–7.74 (0.5)	ND–6394.1 (356.9)	ND–5.5 (0.39)	ND–1429.3 (81.52)	ND–1.2 (0.18)	ND–2579.5 (187.7)
Mexico (3)	10.9–66.1 (30.34)	ND	2.0–45.0 (17.65)	ND	ND	ND	2.4–9.4 (5.29)
Malaysia (3)	0.8–8.55 (3.43)	ND–0.20 (0.06)	0.5–158.4 (53.3)	ND	0.3–29.3 (10.03)	ND–0.3 (0.15)	ND–230.0 (78)
Indonesia (3)	3.7–529.8 (181.2)	ND	0.3–6.5 (2.53)	ND	0.2–1.5 (0.76)	0.2–0.3 (0.24)	0.7–81.6 (30.6)
USA (2)	16.4, 87.2	ND	ND	ND	ND	ND	3.2, 74.3
Colombia (2)	3.3, 33.1	ND	ND	ND, 0.3	ND	ND	ND, 1
Others (9)	0.9–46.3 (11.38)	ND	ND–13.7 (1.88)	ND–8.3 (0.93	ND–82.6 (9.58)	ND–6.5 (0.86)	0.2 –102.6 (23.39)

[a] (): average concentrations of heavy metals.
[b] ND: not detected.

curves were constructed in the concentration range of 50–5000 μg l^{-1} and 200–1000 μg l^{-1} for the seven heavy metals and Cr(VI), respectively. Regression analysis gave that all the calibration curves were linear in the investigated concentration range. The linearity of the method was also tested by standard solutions treated using the same method for the samples in the concentration range of 50–400 μg l^{-1} and 200–400 μg l^{-1} for the seven heavy metals and Cr(VI), respectively. Their slopes were similar with the above ones, which was an additional proof that there was no interference from sample pretreatments. Calibration curves were constructed by plotting the instrumental response against the concentration of heavy metals in the standard solution. The correlation coefficients were usually higher then 0.999. The analytical parameters of representative calibration curves are summarized in Table 1.

3.1.2. Precision and accuracy

To verify the precision of the method, a homogenized candy package (about 1.2 g) was divided in six aliquots of 0.2 g each, which were submitted the overall analytical method and measured five times for the same sample. The percent relative standard deviations were found less than 3% in all the above cases.

In order to evaluate the accuracy of the method, the recovery tests were studied for seven heavy metals and hexavalent chromium [Cr(VI)]. A homogenized candy package containing known concentrations of the seven heavy metals and Cr(VI) was prepared and divided into two sets of three aliquots of 0.2 g each. For one set of samples, the spike solution of seven heavy metals was added directly to the sample aliquots, and the spike solution of Cr(VI) was added to the other set of samples. Each set of samples was analyzed by the described overall method. The recoveries from the spiked solutions were 98.5–103.2% and 100.9% for seven heavy metals and Cr(VI), respectively (Table 2).

3.1.3. Limit of detection (LOD) and limit of quantification (LOQ)

The LOD is defined as the lowest concentration of an analyte in a sample that can be detected. The LOQ is defined as the lowest concentration of an analyte in a sample that can be determined with acceptable precision and accuracy under the analytical conditions of the method. The LOD/LOQ could be calculated by the unweighted least-squares method. In this studies, LOD/LOQ were calculated based on the slope (S) of the calibration curve and the standard deviation (SD) of y-intercepts of regression lines according to the formula: $\mathrm{LOD} = 3.3\ (\mathrm{SD}/S)$, $\mathrm{LOQ} = 10\ (\mathrm{SD}/S)$. Based on the above equations, the calculated LOD values for Pb, Cd, Cr, Cu, Mn, Co, Zn, and Cr(VI) were 13.0, 11.2, 9.8, 36.8, 6.5, 21.1, 21.6, and 9.8 μg l^{-1}, respectively. The calculated LOQ values were 39.3, 33.9, 29.8, 111.4, 19.8, 64.0, 65.5, and 29.8 μg l^{-1}, respectively.

3.2. Levels of heavy metals in candies and candy packages

Table 3 presents the level of heavy metals in packages of candies that are likely to be consumed by small children. We obtained 92 samples from retail stores near elementary schools in South Korea. Results are presented for seven heavy metals in candy packages, of which 31 were from South Korea and 61, imported from foreign countries. Eight or nine samples were simultaneously analyzed as a sample batch. A sample blank was analyzed with each sample batch.

Most of the samples were made of splendidly colored polyethylene and polypropylene films. In particular, candy packages from China were very colorful, and the heavy metal levels in these samples were considerably high as compared to others. Pb levels of over 100 mg kg^{-1} were detected in 10 of 92 samples, of which nine samples were from China and one, Malaysia.

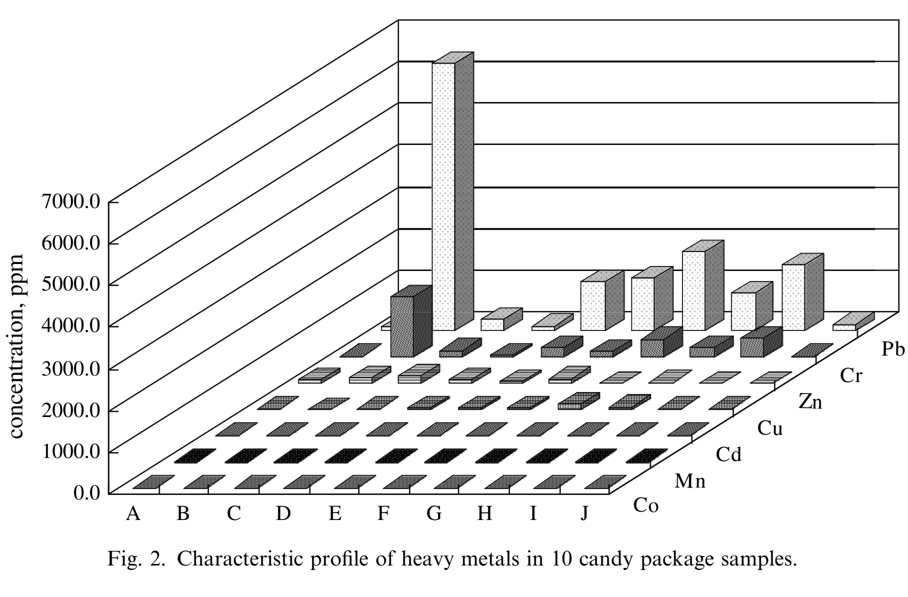

Fig. 2. Characteristic profile of heavy metals in 10 candy package samples.

Table 4
Levels of heavy metals in candies likely to be consumed by small children

Manufacturing country (sample no.)	Concentration of heavy metals ($mg\ kg^{-1}$)						
	Cu	Cd	Pb	Mn	Cr	Co	Zn
South Korea (31)	0.1–3.2 (0.53)[a]	ND[b]	ND–0.1 (0.02)	ND–6.0 (0.55)	ND–0.1 (0.02)	ND–0.05 (0.005)	0.01–8.3 (1.18)
China (39)	ND–10.0 (0.78)	ND–0.05 (0.001)	ND–1.3 (0.12)	ND–11.2 (2.61)	ND–25.1 (1.14)	ND–0.04 (0.003)	0.1–20.8 (2.8)
Mexico (3)	0.03–0.2 (0.1)	ND	ND	ND	ND–0.03 (0.008)	ND–0.4 (0.13)	ND–0.23 (0.14)
Malaysia (3)	0.1–3.5 (0.37)	ND	0.02–0.16 (0.08)	ND–6.6 (2.21)	0.1–0.6 (0.26)	ND–0.02 (0.008)	0.1–7.9 (2.74)
Indonesia (3)	ND–2.2 (0.83)	ND–0.01 (0.003)	0.02–0.06 (0.04)	0.8–5.1 (2.26)	ND –0.3 (0.12)	ND–0.04 (0.02)	0.1–13.2 (5.36)
USA (2)	0.31, 0.38	ND	ND, 0.01	ND, 0.11	ND	ND	0.09, 0.94
Colombia (2)	0.86, 0.17	ND	0.07, ND	0.29, 0.02	0.005, ND	ND	0.37, ND
Others (9)	0.08–2.7 (1.28)	ND	ND–0.3 (0.06)	ND–7.3 (2.03)	ND–0.4 (0.14)	ND–0.07 (0.02)	0.1–11.3 (3.37)

[a] (): average concentrations of heavy metals.
[b] ND: not detected.

The directive factor of lead contamination had originated in the lead-based color ink of the outer cover. In particular, Pb was detected at high concentrations in cases of green- or yellow-coloured packages; pigments such as lead chromate, lead sulphate, and lead oxide could confer these colours.

The concentration of chromium was also higher in cases when the lead concentration was high, as illustrated in Fig. 2. These results demonstrate that harmful pigments such as lead chromate, which have been prohibited by law from being used in packaging materials, are being intentionally used in some countries.

Table 4 illustrates the levels of heavy metals in candies that are likely to be consumed by small children. We obtained 92 samples from retail stores near elementary schools in South Korea. Like candy package, sample blank was analyzed with each sample batch. In general, zinc, manganese, and copper were detected at high concentrations at averages of 2.14, 1.58, and $0.70\ mg\ kg^{-1}$, respectively, as compared to the concentrations of other metals in the 92 samples. The types of candies sampled were lollipops, chocolate, chewing gum, jelly, etc. On the whole, the migration of heavy metals from the candy package to the candy was not observed in this result.

However, a part of the samples appeared to be contaminated due to their packages, as described in Table 5. These results illustrate that some heavy metals could migrate from the package when the candy surfaces are sticky, allowing the surface of the candy to adhere to the inner cover of the package. Further, this would allow lead-based inks in the outer package layer to migrate into the candy because the packages, as mentioned in Table 5, were so poorly designed that their inner coatings did not maintain their structural integrity.

3.3. Analysis of hexavalent chromium [Cr(VI)] in candy packages

Table 6 presents the concentrations of Cr(VI) and Pb in candy packages that were detected at levels over $100\ mg\ kg^{-1}$ of the total Cr. The colors of these candy packages were mainly yellow or green. In this table, numbers 1 and 2 were box-type candy packages, which were made of polyethylene hard plastic, and the Cr(VI) were detected less than 15% of the total Cr. This result does not indicate that the packages were not made using Cr(VI), but it means that extraction of the Cr compounds by toluene was difficult in hard plastic materials. On the other hand, sample numbers from 3 to 7 were wrapper-type candy packages, which were coated with polypropylene and had printed outer covers, and Cr(VI) was detected in these packages at 87–105.0% of the total Cr, and the ink components could be perfectly extracted from the printed outer covers using the toluene solvent. These results imply that the Cr(VI) in the package originates from ink pigments such as $PbCrO_4$ and CrO_3.

Table 5
Concentrations of heavy metals in candies and candy packages

No.	Concentration ± SD[a] (mg kg^{-1})				Surface type of candy
	Pb		Cr		
	Package	Candy	Package	Candy	
A	110.3 ± 2.0	ND[b]	26.5 ± 0.5	ND	Hard
B	6394.2 ± 43.8	0.06 ± 0.001	1429.3 ± 30.8	0.23 ± 0.005	Powdery
C	273.3 ± 3.8	ND	158.0 ± 0.7	ND	Powdery
D	125.4 ± 1.9	ND	43.0 ± 0.4	ND	Powdery
E	1192.1 ± 9.2	ND	225.0 ± 4.1	5.45 ± 0.10	Sticky
F	1254.0 ± 13.4	1.31 ± 0.03	136.9 ± 1.1	0.48 ± 0.01	Sticky
G	1893.7 ± 25.9	0.21 ± 0.005	422.7 ± 3.6	5.66 ± 0.12	Sticky
H	920.5 ± 12.0	0.13 ± 0.004	219.7 ± 1.7	0.26 ± 0.01	Sticky
I	1581.2 ± 39.0	0.32 ± 0.007	445.8 ± 3.9	25.13 ± 1.20	Sticky
J	158.5 ± 4.3	0.16 ± 0.004	29.3 ± 0.5	0.26 ± 0.005	Hard

[a] SD is the standard deviation of intercept and slope.
[b] ND: not detected.

Table 6
Concentration of chromium (total, hexavalent) and lead in candy package

No.	Type of package (inner cover)	Main color of package	Cr (mg kg^{-1})		Pb (mg kg^{-1}) ($n = 3$)
			Total Cr[a] ± SD[c] ($n = 3$)	Cr(VI)[b] ± SD[c] ($n = 5$)	
1	Hard plastic (not coated)	Yellow	1429.3 ± 30.8	188.5 ± 2.4	6394.2 ± 43.8
2	Hard plastic (not coated)	Green	158.0 ± 0.7	ND[d]	273.3 ± 3.8
3	Wrapper (PP coated)	Green	422.7 ± 3.6	400.3 ± 2.1	1893.7 ± 25.9
4	Wrapper (PP coated)	Yellow	445.8 ± 3.9	440.5 ± 2.0	1581.2 ± 39.0
5	Wrapper (PP coated)	Yellow and green	225.0 ± 4.1	196.8 ± 3.3	1192.1 ± 9.2
6	Wrapper (PP coated)	Yellow and red	219.7 ± 1.7	230.2 ± 2.7	920.5 ± 12.0
7	Wrapper (PP coated)	Green	136.9 ± 1.1	126.7 ± 1.4	1254.0 ± 13.4

[a] Total Cr is determined by ICP-OES.
[b] Cr(VI) is determined by UV–Vis spectrophotometer (λ = 540 nm).
[c] SD is the standard deviation of intercept and slope.
[d] ND: not detected.

3.4. Effect of pH on migration of heavy metals from candy packages

In general, the pH of the foodstuffs including that of traditional food ranges from 4.0 to 10.0 in South Korea. Because the migration of heavy metals could be generated from food packages and packaging, the packages of food have to be carefully considered in relation to the pH of the packed food. In this study, acidic, neutral, and basic reagent water, which were provided with large surface area to candy packages, were used as simulants instead of candies themselves in order to investigate the outstanding

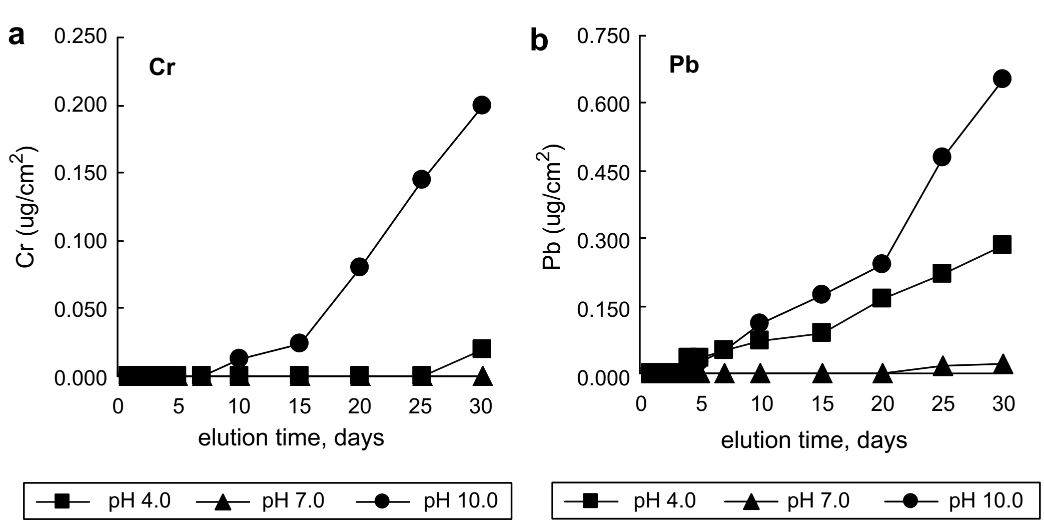

Fig. 3. Effect of pH on migration of (a) Cr and (b) Pb in food simulants.

effect of pH on migration of heavy metals from candy packages within 30 days.

Fig. 3 illustrates the effect of pH on migration of Cr(VI) and Pb ions from candy packages to food simulants, which are acidic (pH 4.0), neutral (pH 7.0), and basic (pH 10.0) solutions. The migration of Cr(VI) increased with elution time up to 0.20 μg $(cm^2)^{-1}$ for 30 days in basic (pH 10.0) solution; however, no migration was observed in acidic (pH 4.0) and neutral (pH 7.0) solutions. On the other hand, Pb migrated considerably as compared with Cr(VI) up to 0.65 μg $(cm^2)^{-1}$ and 0.28 μg $(cm^2)^{-1}$ in basic (pH 10.0) and acidic (pH 4.0) solutions, respectively. However, hardly any migration was observed in neutral (pH 7.0) solution. These results demonstrate that Cr(VI) ion could migrate from the printed outer covers to foods with basic pH.

4. Conclusion

There are many kinds of candy products likely to be consumed frequently by small children. Most of them are sold at retail stores near elementary schools in South Korea. Generally, wrappers with colorfully printed outer covers are used to packages of candy products in order to induce small children to purchase them. Most of the pigments of the printing inks were based on metallic compounds such as Zn, Cu, Pb and Cr. However, harmful metals such as Pb and Cr have been prohibited by law in most of the countries from being used in food packaging.

In this study, harmful metals such as Pb and Cr(VI) were detected at high concentrations in a part of candy packages. Pb was detected from 110.3 mg kg^{-1} to 6394.1 mg kg^{-1} in 10 of 92 candy packages. Cr was detected at high concentrations in cases where Pb was also detected at high concentrations, and the Cr concentration ranged from 136.9 mg kg^{-1} to 1429.3 mg kg^{-1} in 7 of the 92 candy packages. The outer cover of these candy packages was green or yellow in color. It is assumed that these metals result from lead chromate used as inorganic pigments in ink or paint. Generally, lead chromate is known as a water-insoluble compound; however, as stated above, it can migrate into acidic or basic foods. These results indicate that heavy metals could migrate from the printed outer packages to food. In addition, scientific studies have demonstrated that these metals pose significant environmental and health hazards as toxic constituents of incinerator ash and stack emissions or landfill leachate. Therefore, the intentional use of pigments such as lead chromate in food packages or packaging materials must be strictly regulated.

Acknowledgement

This research was supported financially by Gyeonggi-do (Local Government), Republic of Korea.

References

Bradley, E. L., Castle, L., Dines, T. J., Fitzgerald, A. G., Gonzalez Tunon, P., Jickells, S. M., et al. (2005). Test method for measuring non-visible set-off from inks and lacquers on the food contact surface of printed packaging materials. *Food Additives and Contaminants, 22*(5), 490–502.

Castle, L., Jickells, S. M., Gibert, J., & Harrison, N. (1990). Migration testing of plastics and microwave-active materials for high-temperature food-use applications. *Food Additives and Contaminants, 7*, 779–797.

Duffy, E., Hearty, A. P., Gilsenan, M. B., & Gibney, M. J. (2006). Estimation of exposure to food packaging materials – 1: Development of a food packaging database. *Food Addictives and Contaminants, 23*(6), 623–633.

Franz, R., Huber, M., & Piringer, O. G. (1994). Testing and evaluation of recycled plastics for food packaging use – possible migration through a functional barrier. *Food Additives and Contaminants, 11*, 479–496.

Holmes, Amie L., Wise, Sandra S., Xie, Hong, Gordon, Nancy, Thompson, W. Douglas, & Wise, John Pierce Sr., (2005). Lead ions do not cause human lung cell to escape chromate-induced cytotoxicity. *Toxicology and Applied Pharmacology, 203*, 167–176.

IARC. (1990). Monographs on the evaluation of carcinogenic risks to humans; chromium, nickel and welding. International Agency for Research on Cancer, Lyons, France 49.

Johns, S. M., Hickells, S. M., Read, W. A., Framshaw, H. W., & Castle, L. (1996). Studies on functional barriers to migration. 2. Use of model substances to investigate transfer from paper and board packaging to Food. *Eeutsche Lebensmittel-Rundschau, 92*, 273–278.

Laoubi, S., & Vergnaud, J. M. (1996). Theoretical treatment of pollutant transfer in a finite volume of food from a polymer packaging made of a recycled film and a functional barrier. *Food Additives and Contaminants, 13*, 293–306.

Léonard, A., & Lauwerys, R. R. (1980). Carcinogenicity and mutagenicity of chromium. *Mutation Research, 76*, 227–239.

Levy, L. S., & Vanitt, S. (1986). Carcinogenicity and mutagenicity of chromium compounds: The association between bronchial metaplasia and neoplasia. *Carcinoginesis, 7*, 831–835.

Newman, D. A. (1981). A case of adeno-carcinoma of the left inferior turbinated body, and perforation of the nasal septum, in the person of a worker in chrome pigments. *Glasgow Medical Journal, 33*, 469–470.

Parry, S. J., & Aston, D. S. J. (2004). Migration of inorganic contaminants into dry food from packaging made from recycled paper and board. *Food Additives and Contaminants, 21*(5), 506–511.

Patierno, S. R., Banh, D., & Landolph, J. R. (1988). Transformation of C3H/10T1/2 mouse embryo cells by insoluble lead chromate but not soluble calcium chromate: relationship to mutagenesis and internalization of lead chromate particles. *Cancer Research, 47*, 2342–2346.

Summerfield, W., & Cooper, I. (2001). Investigation of migration from paper and board into food-development of methods for rapid testing. *Food Additive and Contaminants, 18*, 77–88.

Thompson, D., Parry, S. J., & Benzing, R. (1997). The validation of a method for determining migration of trace elements from food packaging materials into food. *Journal of Radioanalysis and Nuclear Chemistry, 217*, 147–150.

Wise, J. P., Orenstein, J. M., & Patierno, S. R. (1993). Inhibition of lead chromate clastogenesis by ascorbate: relationship to particle dissolution and uptake. *Carcinogenesis, 14*, 429–434.

Wise, J. P., Stearns, D. M., Wetterhahn, K. E., & Patierno, S. R. (1994). Cell-enhanced dissolution of carcinogenic lead chromate particles: the role of individual dissolution products in clastogenesis. *Carcinogenesis, 15*, 2249–2254.