Effect of Pre-treatments on the Content of Heavy Metals in Packaging Paper

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ABSTRACT

Pre-treatment methods to determine various heavy metal contents in packaging papers were investigated by ICP-ES (Inductively Coupled Plasma Emission Spectrometry) analysis. Pre-treatment methods utilized in this study include dry ashing and decomposition methods (HNO_3-$HClO_4$-HF, HNO_3, and H_2SO_4-HNO_3). They were compared with the conventional extraction (water) and migration (3% acetic acid) methods. The five representative heavy metals (Cd, As, Pb, Cr and Hg) were analyzed. For Cd, Hg, and As, the results were below detection limit of the instrument. In case of Cr and Pb, the migration test is considered to be a better method compared to the extraction test, but all pretreated methods showed much higher detection efficiency than the extraction or migration test. However, the detection ratio between the migration test and decomposition methods was different. Among all decomposition methods, the nitric acid - perchloric acid - hydrofluoric acid treatment brought a slightly higher detection value than others, but there was no significant difference among them except sulfuric acid - nitric acid method. Concerning Pb, the sulfuric acid - nitric acid method showed a low detection efficiency compared to other decomposition methods. The sulfuric acid - nitric acid method is, thus, not considered to be a suitable analysis method for Pb in packaging papers.

INTRODUCTION

Packaging papers are composed of various materials such as wood fibers and papermaking additives. Secondary fibers as well as virgin fibers have been widely used as a main source of wood fibers. However, the use of recycled paper for packaging can cause some problems such as toxicity (*1*). In addition to the functionality of the packaging paper, the paper's toxicity is very important because the paper is contacted with hands or foods during delivery or packaging. Heavy metals are considered to be one of the potential toxic materials in packaging papers. It has been reported that heavy metal toxicity can result in a damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. *(2-5)*.

As the regulation for the packaging paper's toxicity has been tightened in Korea, the technical demand for analyzing the low content heavy metals in packaging papers is growing. The regulation for heavy metals in packaging papers has been only applied to food packaging papers by Korea Food Manufacture Regulations. The category of the regulation includes the PCBs (polychlorinated biphenyls), heavy metals, formaldehyde and fluorescent materials (Table 1) in food packaging paper (*6*).

In the Council of Europe, heavy metals in packaging papers have been regulated strictly as purity limits (Table 2). The determination of heavy metals has been carried out by two different methods: the extraction test and the migration test. The extraction test is carried out by directly extracting heavy metals from a paper sample and the migration test is done by degrading organic materials in the sample using acids *(1, 7)*.

This study investigated the effect of different pre-treatment methods on the heavy metal contents. Pretreatments were used to increase the detection efficiency. Decomposition methods (dry ashing (*8*), HNO_3-$HClO_4$-HF (*9*), HNO_3, and H_2SO_4-HNO_3 (*2, 9, 10, 11*)), chosen as pretreatment methods, were compared with the conventional extraction and migration method (*1, 7*). Five representative heavy metals (Cd. AS, Pb, Cr and Hg) were analyzed using Inductively Coupled Plasma Emission Spectrometry (ICP).

Table 1. Chemical purification limits in food package paper (Korean food & drug administration 'Food Manufacture Regulations')

Dissolution Standard (mg/kg)	PCBs < 10
Extraction Standard (mg/L)	As < 0.1 Heavy metals < 0.1 (Based on Lead(Pb)) Formaldehyde < 4.0 (mg/L) Fluorescent material should not be Detected in packaging

Table 2. Heavy metals purity limits (mg/kg) as stated by the Council of Europe

Chemical element	Extraction test*	Migration test**
Cadmium	0.5	0.005
Chromium VI	0.05	0.05
Lead	3	0.01
Mercury	0.3	0.005

* In distilled water, 24h at T = 23℃

** In 3% acetic acid, 24h at T = 40℃

Material and Methods

Materials

Sample

All samples of packaging papers listed in Tables 1 ~ 3 were provided from Korean Corrugated Packaging Case Industry Association and stored at 23°C and RH 50% according to TAPPI test methods T 402.

18 types of paper samples are prepared: 4 types of food packaging papers in terms of different printing methods (Table 3), 10 types of colored corrugated containers (Table 4), and 4 types of recycled paper boards (Table 5). Printing conditions are listed in Table 6.

Reagents

All reagents were analytical grades. Sulfuric acid (95.0%, Wako), nitric acid (60~61%, Junsei), ammonia solution (28.0~30.0, Junsei), acetic acid (99.7%, J.T. Baker) hydrochloric acid (35.0~37.0, Wako), water (99.999%, Fischer scientific), hydrofluoric acid (48.0~51.0%, J.T. Baker) and perchloric acid (60.0~62.0%, Junsei) were used in the test.

Pre-treatment of samples

Extraction test

A five gram sample specimen was cut to small pieces (2 ×2cm) and then immersed in 100ml of water at 23 °C for 24 hr in a shaking incubator. At the end of this treatment, the liquid was filtered and analyzed by ICP to determine the heavy metal concentration.

Table 3. List of food package papers

No.	Sample	Specification		Printing method
		Liner	Types of papers	
1	F1	Top	Food packaging paper(70g/m^2)	Unprinted
		medium	Grease-proof paper(50g/m^2)	
		bottom	Food packaging paper(70g/m^2)	
2	F1-P	Top	Food packaging paper(70g/m^2)	Flexo
		medium	Grease-proof paper(50g/m^2)	
		bottom	Food packaging paper(70g/m^2)	
3	F2	Top	Grease-proof paper(50g/m^2)	Unprinted
		medium	Food packaging paper(70g/m^2)	
		bottom	Food packaging paper(35g/m^2)	
4	F2-P	Top	Grease-proof paper(50g/m^2)	Flexo
		medium	Food packaging paper(70g/m^2)	
		bottom	Food packaging paper(35g/m^2)	

Table 4. List of corrugated containers

No.	Samples	Specification		The country of origin
		Flute types	Colors	
5	J-B	F	Black	Japan
6	J-W	F	White	Japan
7	J-R	F	Red	Japan
8	J-V	G	Blue	Japan
9	J-Y	G	Yellow	Japan
10	K-R	G	Red	Korea
11	K-V	G	Blue	Korea
12	K-Y	G	Yellow	Korea
13	K-U	G	Unprinted / Recycle fiber	Korea
14	K-P	G	Printed / Recycle fiber	Korea

Table 5. List of paper boards

No.	Samples	Specification	Printing method
15	S1	Recycled paper, 200 g/m^2	Unprinted
16	S1-P	Recycled paper, 200 g/m^2	Flexo
17	S2	Recycled paper, 220 g/m^2	Unprinted
18	S2-P	Recycled paper, 220 g/m^2	Flexo

Table 6. Printing conditions

Models	3 FR 1214 (Mitsubishi, Japan)
Type of Printing	Off-set
Printing Size	Maximum 1030mm×720mm Minimum 540mm×390mm
Printing Speed	1000 sheets/hour
Printing Pressure	0.50mm

Migration test

The sample was prepared in the same method with the extraction test. After that, the sample was immersed in 100ml of 3% (v/v) acetic acid at 40°C for 24h in a shaking incubator.

Decomposition Methods

Dry ashing method

Five grams of a sample was put into a crucible and carbonized in a muffle furnace at 500°C for 3hr. The residue was dissolved in 5ml of nitric acid (60-61%), and then dried. The sample was dissolved to a final volume of 25ml in nitric acid (1N) and filtered.

Nitric acid method

Five grams of a sample was transferred to a Kjeldahl flask. 50ml of nitric acid was added and then heated. The procedure was duplicated. Finally, the sample was dissolved to a final volume of 50ml in nitric acid (1N) and filtered.

Sulfuric acid - Nitric acid method

The sample was prepared in the same method with the nitric acid method, except that 10ml of sulfuric acid and 30ml of water was added instead of 10ml of nitric acid, and then heated. This procedure was duplicated. After treating with the acid solution, the sample was cooled and neutralized with an ammonia solution (28.0~30.0%). Finally, the sample was dissolved to a final volume of 50ml in 2ml of sulfuric acid and filtered.

Nitric acid - perchloric acid - hydrofluoric acid method

4.5-5.5g of a sample was weighed into Kjeldahl flask. 50ml of nitric acid and 20ml of perchloric acid (60.0~62.0%) were added. It was heated and the procedure was duplicated. Then, 20ml of perchloric acid and 40ml of hydrofluoric acid (48.0~51.0%) were added after the decomposition. The sample was cooled and neutralized with an ammonia solution (28.0~30.0%). 10ml of hydrofluoric acid was added, and then heated. Finally, the sample was dissolved to a final volume of 50ml in nitric acid (1N) and filtered.

Measurement

ICP-AES (Leeman PS 950, Leeman Lab. Inc. USA) was used to determine the representative heavy metals: Cd, Pb, Hg, Cr and As. The operating conditions are listed in Table 7.

Table 7. Operating conditions for Inductively Coupled Plasma Emission Spectrometry.

Power	0.82 KW
Coolant Air Framerate	15 ℓ/min
Auxiliary Air Flow Rate	0.5 ℓ/min
Nubulizer Flow Rate	0.5 ℓ/min
Wavelength(nm)	As : 193.695 Cd : 214.438 Pb : 220.353 Cr : 267.716 Hg : 194.163

Result and Discussion

Cd, Hg, and Ar were not detected from all samples. Their concentrations were below the detection limit of the instrument.

Extraction test and migration test

The result of the extraction and migration test is reported in Table 8. The migration test showed higher detection sensitivity than the extraction test, especially for Pb. The extraction test showed that it could not detect Pb, but the migration test showed that 9 out of 18 samples showed significant detectable levels. The possible reason for this is the different solubility between water and acetic acid for Pb.

All the samples from colored corrugated containers (series of J and K) and recycled corrugated containers (series of S) had Cr and Pb. Some of the colored corrugated containers showed higher levels of Cr and Pb than the recycled corrugated containers.

In terms of printing effect, the printing itself could not be considered as the source of the heavy metals because Cr and Pb were not detected from unprinted paper (F1 and F2) and printed paper (F1-P and F2-P). However, these results are not valid for all printing papers because there are many other variables such as types of ink, printing area, adsorbed ink amount in papers and storage conditions (*12*). Therefore, continuing research on these variables will be needed.

Decomposition methods

Tables 9 and 10 show the content of Cr and Pb tested with the pre-treatment (decomposition) methods. All pretreatment methods show much more sensitive detection results than the extraction or migration tests.

Table 8. The chromium and lead content in packaging papers by the extraction and migration methods.(㎍/g)

Sample	Extraction		Migration	
	Cr	Pb	Cr	Pb
F1	n,d.	n,d.	n,d.	n,d.
F1-P	n,d.	n,d.	n,d.	n,d.
F2	n,d.	n,d.	n,d.	n,d.
F2-P	n,d.	n,d.	n,d.	n,d.
J-B	n,d.	n,d.	0.52	1.88
J-R	0.22	n,d.	0.57	2.40
J-W	n,d.	n,d.	n,d.	n,d.
J-V	n,d.	n,d.	0.43	1.55
J-Y	n,d.	n,d.	0.37	2.11
K-R	n,d.	n,d.	<0.14	n,d.
K-V	n,d.	n,d.	<0.11	n,d.
K-Y	n,d.	n,d.	<0.14	n,d.
K-U	<0.10	n,d.	1.29	5.47
K-P	<0.13	n,d.	1.19	6.88
S1	<0.10	n,d.	0.46	2.55
S1-P	0.19	n,d.	0.60	2.69
S2	<0.10	n,d.	0.32	2.63
S2-P	<0.10	n,d.	0.4	2.64

Table 9. Comparisons of chromium contents in package papers determined by four decomposition methods. (㎍/g)

Sample	Dry Ash*	HNO_3**	H_2SO_4***	HF****
F1	n.d.	<0.10	<0.10	n.d.
F1-P	n.d.	<0.10	<0.10	<0.10
F2	n.d.	<0.10	<0.10	<0.10
F2-P	n.d.	<0.10	<0.10	<0.10
J-B	3.32	3.35	3.38	3.59
J-R	3.31	3.40	3.30	3.66
J-W	n.d.	n.d.	n.d.	n.d.
J-V	2.84	2.65	2.48	2.86
J-Y	2.67	2.60	2.77	2.64
K-R	0.27	0.36	0.35	0.37
K-V	0.37	0.35	0.44	0.51
K-Y	0.58	0.47	0.46	0.62
K-U	5.30	5.64	5.72	5.89
K-P	5.36	5.55	5.73	5.87
S1	4.36	4.44	4.50	4.79
S1-P	4.26	4.15	4.49	4.48
S2	3.32	3.06	3.35	3.11
S2-P	3.16	3.08	3.56	3.21

*Dry Ash : Dry ashing method

**HNO_3 : Nitric acid method

*** H_2SO_4 : Sulfuric acid-Nitric acid method

****HF : Nitric acid-perchloric acid-hydrofluoric acid method

Nitric acid - perchloric acid - hydrofluoric acid method showed slightly higher efficiency than other decomposition methods. Dry ashing method showed a little bit lower detection values than other decomposition methods. However, there was no significant difference between the decomposition methods. Furthermore, variations in the sampling weight and experimental procedures could account for the small difference.

The sulfuric acid - nitric acid method showed lower detection efficiency for Pb than other decomposition methods. Sulfuric acid has a low solubility for Pb since insoluble lead sulfate is formed when sulfuric acid is added to Pb. Therefore, sulfuric acid - nitric acid method is not considered to be a suitable analysis method for Pb in packaging papers.

For food packaging papers and white corrugated containers, Pb and Cr were not detected by the decomposition methods.

For the effect of printing, there was no big difference between unprinted papers and printed papers. The printing effect will be investigated more in detail in the future.

In addition to our determination method, research about the microwave and autoclave method for pretreatment will be needed to compare with our research (*9,13,14*).

Table 10. Comparisons of lead contents in package papers determined by four decomposition methods. (㎍/g)

Sample	Dry Ash	HNO_3	H_2SO_4	HF
F1	n.d.	n.d.	n.d.	n.d.
F1-P	n.d.	n.d.	n.d.	n.d.
F2	n.d.	n.d.	n.d.	n.d.
F2-P	n.d.	n.d.	n.d.	n.d.
J-B	3.56	2.53	2.36	3.46
J-R	4.35	4.02	1.77	4.52
J-W	n.d.	n.d.	n.d.	n.d.
J-V	2.38	2.77	2.18	2.31
J-Y	2.92	2.98	1.10	3.18
K-R	n.d.	n.d.	n.d.	n.d.
K-V	n.d.	n.d.	n.d.	n.d.
K-Y	n.d.	n.d.	n.d.	n.d.
K-U	15.15	15.65	3.99	17.06
K-P	15.36	15.61	3.97	17.35
S1	4.18	4.28	1.28	4.26
S1-P	4.22	4.35	1.27	4.31
S2	2.78	2.82	0.89	3.12
S2-P	2.73	2.97	0.91	3.11

Fig. 1 compares the extraction (extraction and migration) and the decomposition method for recycled corrugated containers. The extraction method by water could not detect Cr (<0.1) and Pb. 3% acetic acid solution extracted about 25% of chromium and 30% of lead, compared to the decomposition methods (excepting sulfuric acid - nitric acid method). From the results from Table 8 to 10, the detection ratio between the migration test and decomposition methods was different, which might be caused by the different characteristics of each sample. Some papermaking additives such as fillers, functional agents might cause this difference.

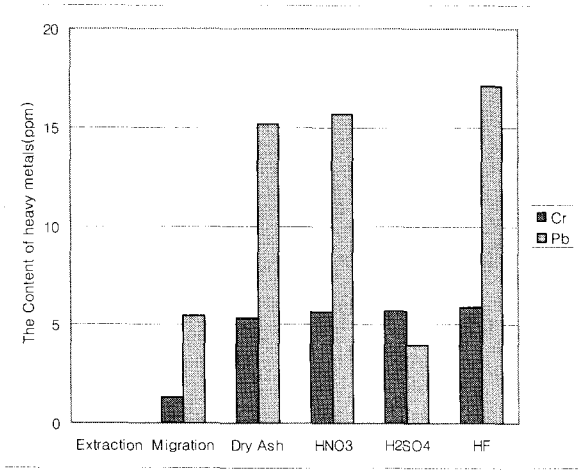

Fig. 1 Comparison of chromium and lead in recycled corrugated containers determined by the extraction (extraction and migration) methods and those by the decomposition methods.

Conclusion

All decomposition methods for heavy metal quantification showed much higher detection efficiency than the extraction or migration tests.

The extraction test is not considered to be suitable for the analysis of Pb and low heavy metal contents in packaging papers.

The migration test is considered to be a better method compared to extraction test. However, the detection ratio between the migration test and decomposition methods was different. Therefore, migration test is not valid for all packaging papers because there are many other variables for heavy metal detection such as filler and functional agents in packaging paper.

In terms of decomposition methods, nitric acid - perchloric acid - hydrofluoric acid brought a slightly higher detection value than other decomposition methods, but there was no significant difference between them except sulfuric acid - nitric acid method. The sulfuric acid - nitric acid method for detecting Pb resulted in too lower detection efficiency compared to other decomposition methods. Therefore, the sulfuric acid - nitric acid method is not considered to be a suitable analysis method for Pb in packaging papers.

For the effect of printing on the heavy metal content in papers, there was no significant difference between unprinted paper and printed paper. However, this might be highly dependant on printing variables such as types of ink, printing area and the amount of absorbed ink.

It can be concluded that the determination of heavy metals by the pretreatment methods using nitric acid method, dry ash method, or nitric acid-perchloric acid-hydrofluoric acid is the more efficient way compared to the conventional methods.

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