

# Quantitative Analysis of Heavy Metals in Packaging Papers

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## ABSTRACT

This study was carried out to investigate various heavy metal contents in packaging papers by pre-treatments for ICP-ES (Inductively Coupled Plasma Emission Spectrometry) analysis. Pre-treatment methods of heavy metals in this study include extraction, migration and decomposition methods (dry ashing, HNO<sub>3</sub>-HClO<sub>4</sub>-HF, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub>). Test results were compared with 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 instrumental technique. It was considered that the migration test was a better method compared to extraction test, but all the decomposition methods showed much higher detection values than the extraction or migration test. In case of recycled corrugated containers, 3% acetic acid solution extracted about 25% of chromium and 30% of lead compared to the content by decomposition methods. 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.

**Keywords :** *packaging paper, heavy metals, extraction, decomposition*

## 1. Introduction

Packaging papers are composed of various materials such as wood fibers and papermaking additives. Virgin as well as secondary fibers have been widely used as a main source of packaging papers. 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 during delivery or

packaging, contact with hands or foods is required. Heavy metals are considered to be one of the potential toxic materials in packaging papers. Extraction standards (mg/L). It has been reported that heavy metal toxicity can result in 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 of the packaging paper's toxicity has been tightened in Korea, the technical demand for

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**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

analyzing the low content of 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 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, namely the extraction test and the decomposition test. The extraction test has been done by the direct extraction of heavy metals in the paper and the decomposition test done by the degradation of organic materials in the papers using acids (1, 7).

This study investigates heavy metal content in several different packaging papers and compare the detected amount between extraction (water, 3% acetic acid) and decomposition (dry ashing (8), HNO<sub>3</sub>-HClO<sub>4</sub>-

HF (9), HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub> (2, 9, 10, 11)) methods as the pre-treatment method (1, 7). Five representative heavy metals (Cd, AS, Pb, Cr and Hg) were analyzed using Inductively Coupled Plasma Emission Spectrometry (ICP).

## 2. Materials and Methods

### 2.1 Materials

#### 2.1.1 Samples

All samples of packaging papers listed from Tables 3 ~ 5 were provided by Korean Corrugated Packaging Case Industry Association and stored at 23°C and RH 50% according to TAPPI Test Methods T 402.

Totally, 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.

#### 2.1.2 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%, Fisher Scientific), hydrofluoric acid (48.0~51.0%, J.T. Baker) and perchloric acid (60.0~62.0%, Junsei) were used in the test.

**Table 2. Heavy metals purity limits (mg/kg) as stated by the Council of Europe (1, 7)**

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°C

\*\* In 3% acetic acid, 24h at T = 40°C

**Table 3. List of food package papers**

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

**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 <sup>2</sup>	Unprinted
16	S1-P	Recycled paper, 200 g/m <sup>2</sup>	Flexo
17	S2	Recycled paper, 220 g/m <sup>2</sup>	Unprinted
18	S2-P	Recycled paper, 220 g/m <sup>2</sup>	Flexo

**Table 6. Printing conditions**

Specification	
Model	3 FR 1214 (Mitsubishi, Japan)
Type of printing	Off-set
Printing size	Maximum 1030×720 mm Minimum 540×390 mm
Printing speed	1000 sheets/hour
Printing pressure	0.50 mm

## 2.2 Pre-treatment of samples

### 2.2.1 Extraction test

Five grams of a sample was cut by a small piece

(2×2 cm) and was kept in 100 ml of water at 23 °C for 24 hr in shaking incubator. At the end of this treatment, the contact liquid solution was filtered and analyzed by

ICP for quantifying the heavy metal concentration.

### 2.2.2 Migration test

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

### 2.2.3 Decomposition Methods

#### 2.2.3.1. Dry ashing method

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

#### 2.2.3.2 Nitric acid method

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

#### 2.2.3.3 Sulfuric acid - Nitric acid method

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

#### 2.2.3.4 Nitric acid - perchloric acid - hydrofluoric acid method

The sample (4.5~5.5 g) was weighed in Kjeldahl flask. The sample was added to 50 ml of nitric acid and 20 ml of perchloric acid (60.0~62.0%). It was heated and the procedure was duplicated. Then, the sample was added to 20 ml of perchloric acid and 40 ml of hydrofluoric acid (48.0~51.0%) after decomposition. The sample after treating with acid solution was cooled. The sample was added to 10 ml of hydrofluoric

acid, and then heated. Finally, the sample was dissolved to the final volume of 50 ml in nitric acid (1 N) and filtered.

## 2.3 Measurement

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

## 3. Results and Discussion

Cd, Hg, and As were not detected from all samples. They were below the detection limit of the instrumental technique. Among these, some of As and Hg should be lost by decomposition because As and Hg were low boiling point compound than the other heavy metals. Therefore, it needs to further studying if they were lost by decomposition or had below the detection limit content in packaging paper.

### 3.1 Extraction and migration test

The results of extraction and migration test is shown 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 9 out of 18 samples showed significant detectable levels. The reason is thought to be different solubility between water and

**Table 7. Inductively Coupled Plasma Emission Spectrometry operating conditions.**

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
	As : 193.695
	Cd : 214.438
Wavelength (nm)	Pb : 220.353
	Cr : 267.716
	Hg : 194.163

**Table 8. The chromium and lead content in packaging papers by the extraction and migration methods ( $\mu\text{g/g}$ )**

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

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 paper boards.

In terms of printing effect, the printing itself could not be considered as the source of heavy metals because Cr and Pb were not detected for 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 or storage conditions (12). Therefore, continuing research on these variables will be needed.

### 3.2 Decomposition methods

Tables 9 and 10 show the content of Cr and Pb by the

**Table 9. The comparisons of chromium content in packaging paper as the decomposition methods ( $\mu\text{g/g}$ )**

Sample	Dry ash*	HNO <sub>3</sub> **	H <sub>2</sub> SO <sub>4</sub> ***	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<sub>3</sub> : Nitric acid method

\*\*\* H<sub>2</sub>SO<sub>4</sub> : Sulfuric acid-Nitric acid method

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

decomposition methods. All decomposition methods show much more sensitive detection results than extraction or migration test.

From the overall results, 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.

Nitric acid has a high solubility for Pb and Cd, it can't make a complexes for others. Hydrofluoric acid was weak acid but it was a higher complexation than other acids. It usually used to be decomposed with other acids. Sulfuric acid has a higher boiling point than other acids. If it is used with nitric acid for decomposition,

**Table 10. The comparisons of lead content in packaging paper as the decomposition methods ( $\mu\text{g/g}$ )**

Sample	Dry ash	HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	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

the mixture should have a high solubility.

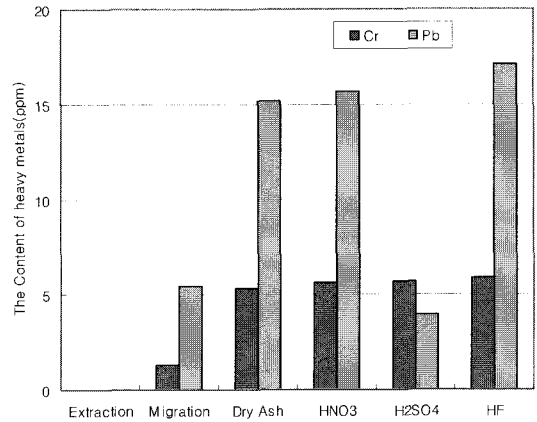
Though the acids have a different property as acidity, oxidation, complexation and boiling point, it is thought to be similar decomposition properties for packaging paper.

The sulfuric acid - nitric acid method showed lower detection value for Pb than other decomposition methods. The sulfuric acid is known that it has a low solubility for Pb because insoluble lead sulfate is formed when sulfuric acid was added to Pb. Therefore, sulfuric acid - nitric acid method is thought not to be suitable for analysis of 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



**Fig. 1. Comparison of chromium and lead in recycled corrugated containers between extraction (extraction and migration) methods and decomposition methods.**

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

Fig. 1 shows the comparison between the extraction (extraction and migration) and the decomposition method for recycled corrugated containers. As shown in Fig. 1 the extraction method by water could not detect Cr and Pb, and 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 Tables 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 discrepancy of results.

## 4. Conclusions

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

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

The migration test was thought to be a better method compared to extraction test. However, the detection ratio between the migration test and decomposition methods was different. Therefore, the test is not valid for all packaging papers because there are many other variables for heavy metal detection such as filler, 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 value compared to other decomposition methods. Therefore, the sulfuric acid - nitric acid method was not thought to be suitable for analysis of Pb in packaging papers.

For the effect of printing on the heavy metal content in papers, we found out that there was no significant difference between unprinted paper and printed paper. However, this might be highly dependant on the types of ink, and so on.

It could be concluded that the determination of heavy metals by pretreating method using nitric acid-perchloric acid-hydrofluoric acid was more efficient way compared to other methods.

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