

## Determination of Cadmium Transfer Rate from the Tobacco to Cigarette Smoke

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**ABSTRACT** : Tobacco plants absorb cadmium from soil and accumulate it in high concentrations in their leaves. Additionally, a significant portion of the cadmium contained in cigarettes passes into the smoke. Cadmium is known to be a toxic and carcinogenic compound that has harmful effects on the human body due to smoking. In this study, the concentrations of cadmium in the Ky3R4F reference cigarette and two commercial cigarettes were analyzed by inductively coupled plasma mass spectrometry. Each cigarette sample was partitioned into a tobacco rod and filter and then analyzed in order to determine the concentration of cadmium. The concentrations of cadmium in the mainstream smoke, ash, residue, and cigarette butt were also analyzed after the cigarettes were smoked under ISO smoking conditions. Transfer rates of the cadmium from the tobacco rod to the mainstream smoke, ash, and cigarette butt were 0.8 ~ 5%, 17 ~ 22%, and 5 ~ 7%, respectively. As a result, we estimated that the sidestream smoke contained about 70% of the cadmium from the tobacco rod.

**Key words** : Cadmium, transfer rate, mainstream smoke

Metal ions are generally found in our environmental compartments such as soil, water, and atmosphere. They may accumulate in plant tissues to levels that may be toxic to crops. This may be problematic for human or animal consumption(Wagner, 1993).

Tobacco can accumulate relatively high concentrations of cadmium in its leaves. The variation in the cadmium concentration depends on various factors, such as agricultural practices, soil characteristics, and climate conditions. Also, this metal has a relatively high transfer efficiency to smoke. Therefore, smoking may

represent an additional source of exposure to cadmium(Bache et al., 1987; Lugon Moulin et al., 2004; 2006).

About 30 metals have been detected in tobacco smoke, some of them associated with potential health risks. Of these metals, cadmium is the most toxic compound. The metal in mainstream smoke presents a high concentration level. Also, this metal classified as Group I carcinogens, according to the international agency for research on cancer. Cadmium, which is present in tobacco and tobacco smoke, has long been associated with various diseases, such as lung diseases, cancer,

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and peripheral artery disease(Borgerding et al., 2005; Lugon Moulin et al., 2006; Pappas et al., 2006; Stavrides, 2006). Therefore it is important that studies be carried out to assess the levels of cadmium in smoke because of its human health effects.

Until now, many laboratories have performed various studies regarding cadmium concentrations in tobacco and smoke. Transfer rate studies are commonly performed. The transfer of metal from tobacco into mainstream smoke has been of interest for a number of years. Many researchers have addressed the question by employing a variety of different cigarette types, collection devices, and analysis techniques. Depending on the metal of interest, the method used, and the cigarette type, the reported results cover a wide range of values(Kalcher et al., 1993; Menden et al., 1972; Mussalo Rauhamaa et al., 1986; Pappas et al., 2006).

We shed new light on research regarding the transfer of cadmium content from tobacco to

cigarette smoke. During smoking, cadmium content originally present in the tobacco filler partitions among the mainstream smoke, sidestream smoke, ash, and cigarette butt. Therefore, in order to better understand how cadmium is transferred to the smoker and nonsmoker, we analyzed the concentration of cadmium in the cigarette fractions, such as the tobacco rod, filter, cigarette paper, ash, residue, cigarette butt, and mainstream smoke.

## EXPERIMENTAL

### Apparatus

For the collection of ash, residue, and cigarette butt, smoking was performed on a 20 port Filtrona Model SM450 smoking machine. To collect mainstream smoke from the cigarettes, smoking was performed on a Borgwaldt 20 port rotary smoking machine(RM-20H) equipped with an electrostatic precipitation trap(H. Borgwaldt, Hamburg, Germany). An electrostatic precipitation

Table 1. Operating conditions for ICP-MS

Operation parameters	
RF power	1300 - 1500 W
Nebulizer	Concentric type
Spray chamber	Quartz, 2°C
Sampler and skimmer con	Nickel, 1 and 0.4 mm id
Sample uptake rate	0.4 mL/min
Plasma gas flow rate	Ar 15 L/min
Auxiliary gas flow rate	Ar 1 L/min
Carrier gas flow rate	Ar 1.2 L/min
Data acquisition parameters	
Acquisition mode	Peak hopping
Integration time	0.1 - 0.3 /point
Peak Pattern	3 points/peak
Replicates	3

(EP) tube 160 mm in length with an inner 24/40 ground joint was constructed of quartz glass to minimize the potential sources of contamination and was used to collect the TPM(total particulate matter). The EP voltage was set to 19 kV.

For sample preparation, we used a MARS Xpress microwave digestion system(CEM, Canada), which is a fast method and able to decrease analyte losses and sample contamination. The ICP-MS instrument used in this study was an Agilent 7500c(Agilent Technologies, Tokyo, Japan). Optimized instrumental operating conditions are summarized in Table 1.

### Samples and Reagents

The two cigarette samples used in this experiment are sold in Korea, and all are commercial domestic 84 mm cigarettes. The ky3R4F reference cigarette was obtained from the University of Kentucky Tobacco. Table 2 shows a list of the cigarettes analyzed in this experiment.

Nitric acid used to digest samples was ultra pure reagent grade manufactured from eco research, Inc., Korea. In this study, ultrapure water of more than  $18 \text{ M}\Omega\text{cm}^{-1}$  obtained through Millipore Mill-Q system was used. ICP-MS calibration was

Table 2. List of the cigarettes used in this study

Cigarettes	Remarks
A	3 mg tar
B	6 mg tar
United States of America, Ky3R4F (Reference cigarette)	9 mg tar

established using a multi-element standard solution with 29 elements(AccuStandard, Inc., 10 mg/L).

### Analytical procedure

All cigarettes were conditioned for at least 48 h in an environmental chamber(JEIO TECH, Inc., Korea) maintained at a temperature of 22°C and 60% relative humidity as specified in ISO 3402:1991. The smoking condition was examined under ISO conditions, including a 35 mL puff volume with 2 sec puff duration at an interval of 60 sec. All cigarettes were smoked to the length of the filter tipping paper plus 3 mm for filtered varieties. Before smoking, cigarette samples were separated in the tobacco rod and filter parts using a cutting machine, and then decomposed by a microwave digestion device. After smoking, the ash, residue, and cigarette butt were directly

Table 3. Operating programs for microwave digestion system

First digestion program					
Step	Type	Temp.(°C)	Power(%)	Ramp(min)	Dwell(min)
1	Time to temp	140	60	10	10
2	Time to temp	180	60	10	10
3	Cooling				30
Second digestion program					
Step	Type	Temp.(°C)	Power(%)	Ramp(min)	Dwell(min)
1	Time to temp	140	60	10	10
2	Time to temp	180	60	10	10
3	Time to temp	200	60	10	20
4	Cooling				30

collected in experimental weighing paper to avoid sample loss. Mainstream smoke was collected by an electrostatic precipitation trap. All samples, except the mainstream smoke, were digested in 10 mL of concentrated nitric acid using a microwave system.

Upon completion of digestion, samples were transferred to 100 mL or 50 mL volumetric flasks, brought to a final volume with ultrapure water, and the cadmium concentration was assessed by ICP-MS. After every 20 samples, an aliquot of HNO<sub>3</sub> was injected as a blank. All analyses were performed using raw <sup>111</sup>Cd concentrations.

## RESULTS AND DISCUSSION

### Recoveries

The recovery of the analysis method was evaluated by using results obtained from the Ky3R4F reference cigarette analysis. Samples were spiked with a standard solution at 2 ng/mL. Table 4 shows the recovery of the samples, such as the tobacco rod, ash, residue, and cigarette butt. Recovery of the tobacco rod and ash were close to 100%. On the other hand, recovery of the residue and cigarette butt exhibited differences of more than 10%. These results indicate that there was possible contamination from the external environment when we collected the residue and cigarette butt.

Table 4. Recovery of the spiked cadmium using the Ky3R4F reference cigarette (concentrations in ng/mL) (n≥4)

	Amount added (Conc.)	Amount found (Conc.)	Recovery(%)
Tobacco rod	2	1.88	94
Ash	2	1.84	92
Residue	2	2.21	111
Cigarette butt	2	2.24	112

### Transfer of cadmium from tobacco to cigarette smoke

First, we investigated the cadmium content in the parts of the Ky3R4F reference cigarette, such as the cut tobacco, cigarette paper, and cigarette filter. The results are shown in Table 5. As the table has shown, the concentration of cadmium in the Ky3R4F sample was found to be high in the cut tobacco, but rather low in the filter and in the paper. We knew that the concentration of cadmium was highest in cut tobacco. The existing trend of these cadmium concentrations were similar to those of French filter cigarettes(Kalcher et al., 1993). The entire cigarette contained a concentration of about 0.83 µg/cig.

Through this data, we learned that the cadmium content in the Ky3R4F sample was transferred

Table 5. Concentration of cadmium in the Ky3R4F sample parts, such as the tobacco, cigarette paper, and cigarette filter (concentrations in µg/cig) (n≥4)

	Cd Conc. ± SD	%
Cut tobacco	0.82 ± 0.05	98.5
Cigarette filter	0.0089 ± 0.0004	1.1
Cigarette Paper	0.0033 ± 0.0001	0.4
Total	0.83	100

from the cut tobacco to smoke. For understanding how cadmium is transferred from cigarette to smoke, we partitioned cigarettes into parts for sample analysis as seen in Fig.1. The tobacco rod is a part that is burnt under smoking condition. And then it contains cut tobacco and cigarette paper. The cadmium content in the tobacco rod was transferred to the ash, residue, cigarette butt, mainstream smoke, and sidestream smoke.

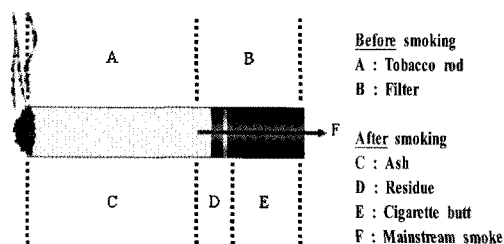


Fig 1. Cigarette's design for use in analysis.

The cigarettes under investigation were the Ky3R4F cigarette and two commercial cigarettes. To determine transfer rates in the samples, we changed the raw data adding experimental values to  $\mu\text{g}/\text{cig}$ . These values are given in Table 6. We determined the cadmium contents in the residue and cigarette butt by subtracting the values of

the unsmoked residue and cigarette butt from the experimental values given. Following the estimation data added by this calculation process, cadmium content was nothing left in the residue. The cadmium content in the sidestream smoke was not directly determined, but calculated from the mass balance which was added by the cadmium content in the tobacco rod, ash, cigarette butt, and mainstream smoke.

Table 7 displays the transfer rates of the samples. The transfer rates in the mainstream smoke were 0.8 ~ 5%, and it has been known that the cadmium transfers the least from the tobacco rod to the mainstream smoke. Nevertheless it may be a source of cadmium as health hazard to the smoker. The transfer rates from the tobacco rod to the ash and cigarette butt were 22 ~ 17% and 5 ~ 7%, respectively. As a result, we estimated that about 70% of the cadmium in the tobacco rod may be present in the sidestream smoke.

Although the transfer rates of cadmium into the various smoking fraction types exhibited a slight difference depending on the types of the cigarette paper and filter, the samples had similar transfer rates.

Table 6. Mass balance of cadmium in the tobacco rod, ash, cigarette butt, mainstream smoke, and sidestream smoke, mean  $\pm$  standard deviation (concentrations in  $\mu\text{g}/\text{cig}$ ) ( $n \geq 4$ )

	Commercial cig. (3 mg tar)	Commercial cig. (6 mg tar)	Ky3R4F
Tobacco rod	0.34 $\pm$ 0.04	0.97 $\pm$ 0.1	0.67 $\pm$ 0.03
Ash	0.075 $\pm$ 0.005	0.20 $\pm$ 0.02	0.11 $\pm$ 0.01
Cigarette butt	0.018 $\pm$ 0.001	0.065 $\pm$ 0.009	0.033 $\pm$ 0.002
Mainstream smoke	0.0028 $\pm$ 0.0001	0.010 $\pm$ 0.001	0.036 $\pm$ 0.001
Sidestream smoke*	0.24	0.69	0.49

\* Sidestream smoke was calculated from the mass balance which was added by the cadmium content in the tobacco rod, ash, cigarette butt, and mainstream smoke.

Table 7. Transfer rates(%) of cadmium into the smoking fractions

	Commercial cig. (3 mg tar)	Commercial cig. (6 mg tar)	Ky3R4F
Ash	22.1	20.7	16.6
Cigarette butt	5.4	6.7	5.0
Mainstream smoke	0.8	1.2	5.3
Sidestream smoke	71.7	71.4	73.1

## CONCLUSIONS

In this study, we investigated the cadmium transfer rates of two cigarettes currently on the market as well as the Ky3R4F reference cigarette.

We demonstrated good recoveries based on the analysis method with regards to the samples, including the tobacco rod, ash, residue, and cigarette butt.

As shown in Table 5, most of the cadmium content in the cigarettes presented in cut tobacco. Therefore, we expected that the cadmium content in the tobacco rod was transferred from the cut tobacco to the smoke. The cadmium concentration that transferred from the tobacco rod to smoke was found at the highest level in the sidestream smoke and at the lowest level in the mainstream smoke. In other words, regardless of cigarette type, more than 70 % of the cadmium in a tobacco rod was dispersed as part of the sidestream smoke, while less than 5 % of the cadmium was found in the mainstream smoke.

These facts indicate that a higher content of cadmium in the cut tobacco largely transfers to the smoke. So, to produce good cigarettes, it is necessary to control the raw materials.

Through these results, we can try to minimize exposure to toxic substances by understanding the heavy metal transfer from cigarettes to smoke. These results may be used in cigarette development to reduce exposure to harmful substances.

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