

PCDDs, PCDFs, Co-PCBs and PCB Congener Analysis in Environmental Samples Using the Automated Sample Cleanup System

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Introduction

The organochlorine compounds such as PCDDs, PCDFs, Coplanar PCB, PCB congeners, PAHs and chlorinated pesticides etc. are well known to the endocrine disruptor(EDs) or persistent organic pollutants(POPs), because of the their toxicities and affects of the environment. Over the past years at the National Institute of Environmental Research(NIER), the demand for the high quality laboratory measurements for toxic environmental pollutants has increased continually. Because of the increased demand, the various analytical methods were studied to produce the high quality data and improve the analytical method by simplifying in the organochlorine compounds[1,2,3]. This study were evaluated to the analytical method of PCDDs, PCDFs, co-PCB and PCB congeners using automated cleanup system(FMS, Dioxin Prep Station) in the two fly ash samples by applying the korean official method.

Experimental Methods

The Korean analytical method were developed to simplify and evaluate the automated cleanup system(Fluid Management Systems' Inc.(FMS) Dioxin-Prep System). The Dioxin Prep System can be run the 5 extracts for 2 hour. During the automated cleanup procedure, two solvent

Table 1. HRGC/MS Analytical Conditions

	PCDDs/PCDFs, co-PCB	PCBs
GC/MS	VG Co., Model Autospec Ultima	VG Co., Model Autospec Ultima
Inject Temp.	250 °C	250 °C
Colum	DB-5MS (60m × 0.32mm ID × 3.0 μm)	DB-5MS (60m × 0.32mm ID × 3.0 μm)
Oven Temp.	150 °C (1min) → 210 °C (10 °C/min, 8min) → 235 °C (3 °C/min, 8min) → 310 °C (6 °C/min, 20min)	50 °C (4min) → 260 °C (10 °C/min, 5min)
Carrier Gas		He, 2.5ml/min
Injection Mode	He, 2.5ml/min	
Ion Mode	Splitless	Splitless
Ionization Energy	EI	EI
Ion Source Temp	36eV	36eV
Resolution	260 °C	260 °C
Monitoring	10,000 SIM, 5 Function	10,000 SIM, 4 Function

fractions can be collected. The first fraction contains the PCB congeners, and the second fraction contains the PCDDs, PCDFs and coplanar PCBs. The two fly ash and one sludge samples selected and analyzed by the developing method. The analytical procedure showed in Figure 1, and analytical condition represented in Table 1. As shown in the Figure 1, the disposal silica and basic alumina manufactured by FMS. These columns are made of Teflon and individually sealed in Mylar packing.

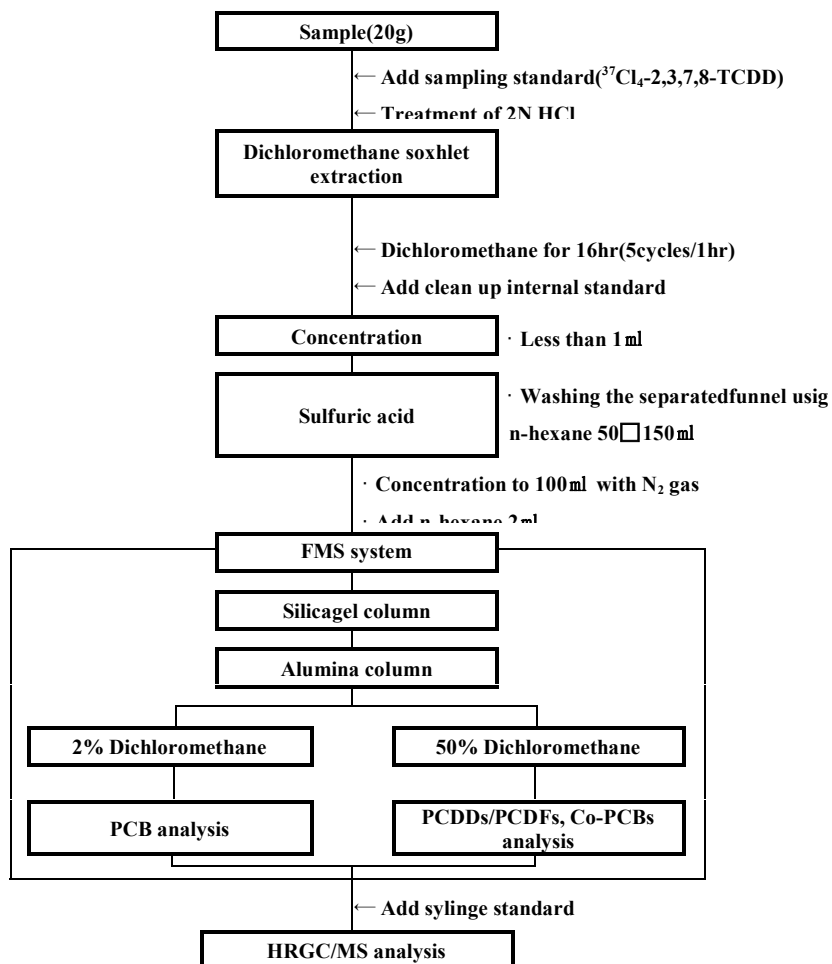


Figure 1. Flowchart of the PCDDs, PCDFs, co-PCB and PCB congener using Automated Cleanup System

Results and Discussion

Recovery of the PCBs in the aluminar column: The PCB recoveries estimated from di- to octa-chlorinated PCB congeners eluted with 100ml of the 2% dichloromethane with n-hexane in

the aluminar column. The recoveries of each congeners is 74%~108%.

Recoveries of PCDDs/PCDFs using three types of elution solvent: Three types of elution solvent were used to get the high recovery of PCDDs/PCDFs each congener using tetra- to octa-PCDDs as shown the Table 2. The C solvent is showed the highest recovery ranges when compared with solvent A+B and B, therefore the C solvent is used to the elution solvent in the alumina column to analyze the PCDDs, PCDFs and PCBs.

*1: This result represented to the 100 ml of 50% dichloromethane with n-hexane

* A solvent: 50 ml of 2% dichloromethane with n-hexane

* B solvent: 50 ml of 50% dichloromethane with n-hexane

*C solvent: 100 ml of 2% dichloromethane with n-hexane + 150 ml of 50% dichloromethane with n-hexan

Table 2. The Recoveries of PCDDs/PCDFs in the Three types of Solvent

Recoveries Elution Solvent	2,3,7,8-TCDF (2.4 µg)	1,2,3,7,8-PCDD (2.0 µg)	1,2,3,4,7,8-HCDD (2.0 µg)	OCDD (2.0 µg)
A solvent+B solvent	100.8	99.1	98.1	84.8
B solvent	99.5	99.0	97.5	86.4 ^{*1}
C solvent	100.1	99.7	100.0	96.9

The Result of PCDDs/PCDFs and PCBs recoveries using Automated Cleanup System: The Dioxin-Prep system operated to get the recoveries of each congeners from tetra- to octa-PCDDs/PCDFs. The recovery range was investigated between 80.7 to 94.9 using 150ml of the 50% dichloromethane with hexane. The average recoveries of 17 kinds of 2,3,7,8-substituted isomers is 89.5% in the silica column eluted with n-hexane and 86.5% in alumina column eluted with 50% dichloromethane with n-hexane as shown in the Table 3. Therefore the recoveries of each congener are satisfied to the Korean official method(50~120%), EPA 8290 method(40~135%) and JIS method(50~120%) using Dioxin-Prep system.

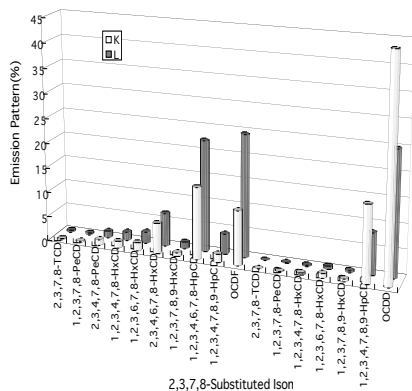
PCDDs/PCDFs Analysis in

Environmental Samples: The one blank(B), two samples of fly ash from MSWI(K and L) and one sample of sludg(S) were analyzed using the Dioxin-Prep system as shown the Figure 1. The

Table 3. The Recoveries of 2,3,7,8-Substituted Isomer

Cleanup,Process 2,3,7,8-Isomer	Silica Column	Alumina Column
¹³ C-2,3,7,8-TCDF	73	71
¹³ C-1,2,3,7,8-PeCDF	92	85
¹³ C-2,3,4,7,8-PeCDF	73	71
¹³ C-1,2,3,4,7,8-HxCDF	94	89
¹³ C-1,2,3,6,7,8-HxCDF	96	94
¹³ C-2,3,4,6,7,8-HxCDF	80	77
¹³ C-1,2,3,7,8,9-HxCDF	91	109
¹³ C-1,2,3,4,6,7,8-HpCDF	95	93
¹³ C-1,2,3,4,7,8,9-HpCDF	86	76
¹³ C-OCDF	84	79
¹³ C-2,3,7,8-TCDD	94	92
¹³ C-1,2,3,7,8-PeCDD	96	91
¹³ C-1,2,3,4,7,8-HxCDD	89	81
¹³ C-1,2,3,6,7,8-HxCDD	85	85
¹³ C-1,2,3,7,8,9-HxCDD	98	90
¹³ C-1,2,3,4,6,7,8-HpCDD	95	94
¹³ C-OCDD	100	94
Average Recoveries	89.5	86.5

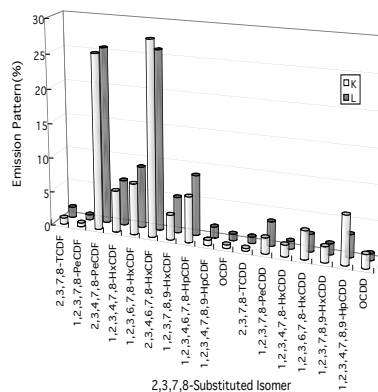
average recoveries of each ¹³C-2,3,7,8-substituted isomer are obtained 86%(B), 88%(K), 90%(L) and 86%(S). As shown the results, the recoveries are satisfied to the Korean official method(50-120%). The PCDDs/PCDFs emission levels are 3.59 ng/g and 0.078 ng-TEQ/g for K sample, and 26.502 ng/g and 0.679 ng-TEQ/g for L sample. Figure 2 shows the emission patterns of 2,3,7,8-substituted isomer. As shown in figure 2 (a), the greater than 80% of PCDDs/PCDFs were consisted of hepta-, octachlorinated PCDDs/PCDFs and the 2,3,4,7,8-PeCDF and 2,3,4,6,7,8-HxCDF were mainly emitted in the TEQ pattern(Figure 2 (b)). In the sample S, the



PCDDs/PCDFs was detected to 0.508 ng/g and less than 0.005 ng-TEQ/g.

(a) 2,3,7,8-Substituted Isomer TEQ

(b) Figure 2. PCDDs/PCDFs Emission Patterns of Fly Ash in the MSWI



PCBs Analysis in Environmental Samples: The PCB also analyzed as show the Figure 3. The greater than 95% PCB congeners were emitted to the nona- and decachlorinated biphenyls, and some kinds of coplanar PCB(IUPAC No. 118,123,156,157,167,189) also detected in the fly ash samples as shown in Table 4. The PCDDs, PCDFs, Co-PCB and PCB congeners

were analyzed very easily by applying the simplified method using the Dioxin-Prep System. Therefore we currently investigating the possibility of expanding our cleanup method to include polyaromatic hydrocarbons(PAHs), polychlorinated naphthalene(PCNs) and chlorinated pesticides in the environmental samples, and the simplifyfing methods of PCDDs/PCDFs analysis will be studied to applied the Korean official method.

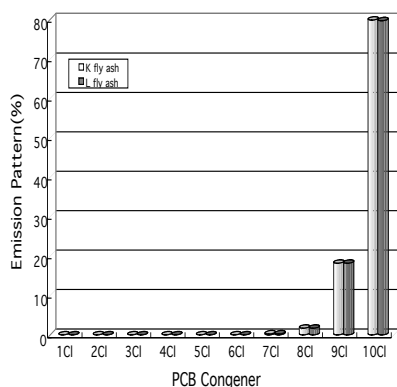


Figure 3. PCB Congener Profile

Table 4. Coplanar PCB in Fly Ash Samples

	K Sample (pg/g)	L Sample (pg/g)
2,3',4,4'5-PeCB(118)	1.69	4.98
2',3',4,4',5-PeCB(123)	0.57	1.11
2,3,3',4,4',5-HxCB(156)	0.64	5.36
2,3,3',4,4',5'-HxCB(157)	-	1.63
2,3',4,4',5,5'-HxCB(167)	2.98	3.95
2,3,3',4,4',5,5'-HpCB(189)	15.0	30.0

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