

# PRETREATMENT OF DIOXIN ANALYSIS IN ENVIRONMENTAL SAMPLES

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## Introduction

With great concern for the contamination by highly toxic dioxins (PCDDs/PCDFs) from waste incineration, the sociological demands to understand the environmental distribution and movement of these compounds arouse rapidly. An analytical method for PCDD/DF originated from municipal waste incineration was directed by the document (Japan EPA guideline, September 1, 1996), and the official analytical methods for the environment samples may soon be forthcoming. Conventional preparation for dioxin analysis is a complicated and time-consuming, and dissipation of solvent in order to maintain the accuracy.

In this study, extraction efficiency of dioxins from soil and sediment samples were compared to the Soxhlet extraction, ultrasonic extraction and accelerated solvent extraction (ASE), and the suitability of low boiling point solvent, acetone and hexane in Soxhlet extraction was investigated. In order to improve a laborious cleanup procedure by using active carbon impregnated Silicagel, commercial pre-packed cartridge (ENVI-CARB, ENVI-CARB-C, Carboxene1000, and Carboxene1000R) were tested with their elution of dioxins.

## Materials and Methods

### *Soil and sediment*

The Soxhlet extraction with toluene, ultrasonic extraction with acetone/n-hexane and ASE with acetone were evaluated.

### *Air sample*

Air samples (ca. 1000m<sup>3</sup>) were collected by high volume air sampler with quartz fiber filter (QMF) for particle and poly urethane foam plug (PUF) for gas phase dioxins. Soxhlet extractions were used for QMF with acetone followed by toluene and PUF with n-hexane followed by acetone.

### *Cleanup*

Each extract was purified by hexane partitioning, washing with sulfuric acid, washing with water, column chromatograph with Silicagel, and column chromatograph with active carbon impregnated Silicagel successively.

### *Tested mini cartridge for cleanup*

ENVI-CARB, ENVI-CARB-C, and Carboxene1000, Carboxene1000R (Supelco).

### *ASE(DIONEX ASE-200)*

Extraction using acetone was performed at 150°C, 2000psi, 60% flashing solvent and equilibration for 5~10 minutes in triplicate.

### *HRGC/HRMS-SIM*

HP-5890/JEOL JMS-700, GC column: SP-2331 (60m×0.25mmID. film: 0.20um) 120°C(1min)-50°C/min-200°C-2°C/min-270°C(14.7min), carrier gas: helium (1.5ml/min),

injection: 250°C, ionization chamber: 250°C, ionization energy: 70eV. Details of GC/MS analysis were described in our previous works.

#### **Sample Extraction**

Soil and sediment samples were extracted by below three ways, ultrasonic extraction, Soxhlet extraction and accelerated solvent extraction (ASE). Extracts were reduced to 30mL and re-extraction with n-hexane, after treated in the same way as air sample.

PUF and QMF were several extracted in acetone for 24 hours using Soxhlet extractors, then extracts were reduced to 30mL and re-extraction with n-hexane. Extracts were purified by sulfuric acid, then washed by water. Organic layer was dried on sodium sulfate. Slightly amount of activated copper added to for reducing sulfur, after concentrated to 1mL(Air-G) or 0.3mL(Air-P and seawater).

**Table 1 Methods of extraction.**

Sample		Ultrasonic	Soxhlet	ASE
Soil and sediment (sample amount 20g~50g)	solvent	acetone 30mlx2 n-hexane 30mlx2	toluene 500ml	acetone 50ml
	time	10 min each	24 hours	45 min
Air PUF	solvent		n-hexane 500ml acetone 500ml	
Air QMF	solvent		acetone 500ml toluene 500ml	acetone 50ml

#### **Results and Discussion**

The extraction efficiency of PCDD/DF with ASE to soil and sediment were valid according to the property of samples and dioxin isomers and these were the same as Soxhlet extraction. The ASE significantly save time and solvent compared to Soxhlet which need overnight extraction and removing solvent (toluene) under deduced pressure. The sonication-assisted extraction was lower recovery to PCDD/DF less than 50% of Soxhlet extraction. The ASE was very useful to extract dioxins from numerous samples at the same time rapidly and a small quantity of acetone used as extracting solvent was easily convert to n-hexane for farther cleanup procedure.

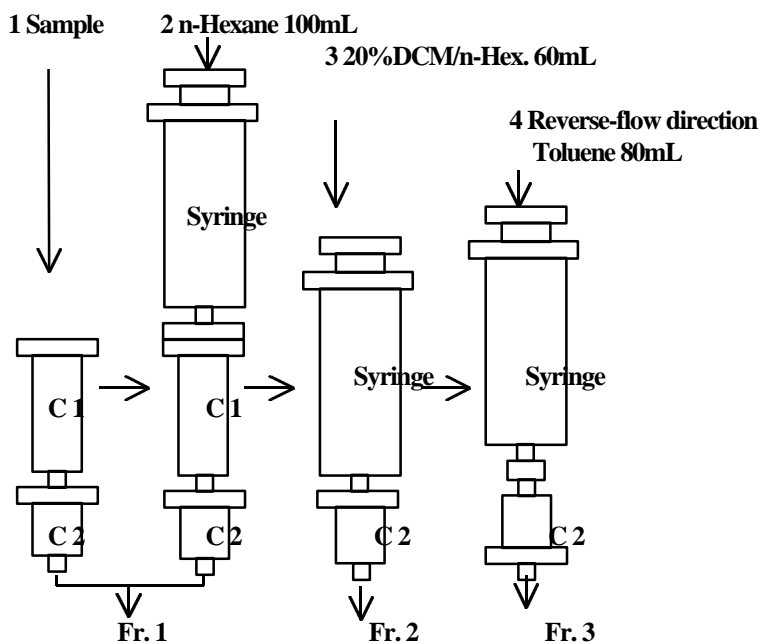
The QMF that collected particle PCDD/DF in air were extracted by Soxhlet with acetone and then followed by toluene. The PCDD/DF were found mostly in the first extract of acetone and scarcely in the second extracts of toluene. Acetone was very useful extracting solvent for PCDD/DF in QMF, which was able to replace the solvent to n-hexane for farther cleanup procedure easily. The PUF were also extracted by Soxhlet with n-hexane and then acetone, and PCDD/DF were found mostly in n-hexane and nothing in second extract of acetone.

Several carbon type pre-packed cartridges were examined their elution for PCDD/DF, PCBs and PCNs. The eluent volume for PCDD/DF on graphited nonporous carbons, ENVI-CARB (100m<sup>2</sup>/g) and ENVI-CARB-C (10m<sup>2</sup>/g) were varied widely and sometimes PCDD/DF were eluted in dichloromethane/n-hexane (20/80) fraction. It was considered that channeling phenomena were occurred in the cartridge and solvent pass through only on the surface not into the pore of the particle by lack of macro pore. On the contrary, carboxene1000 and

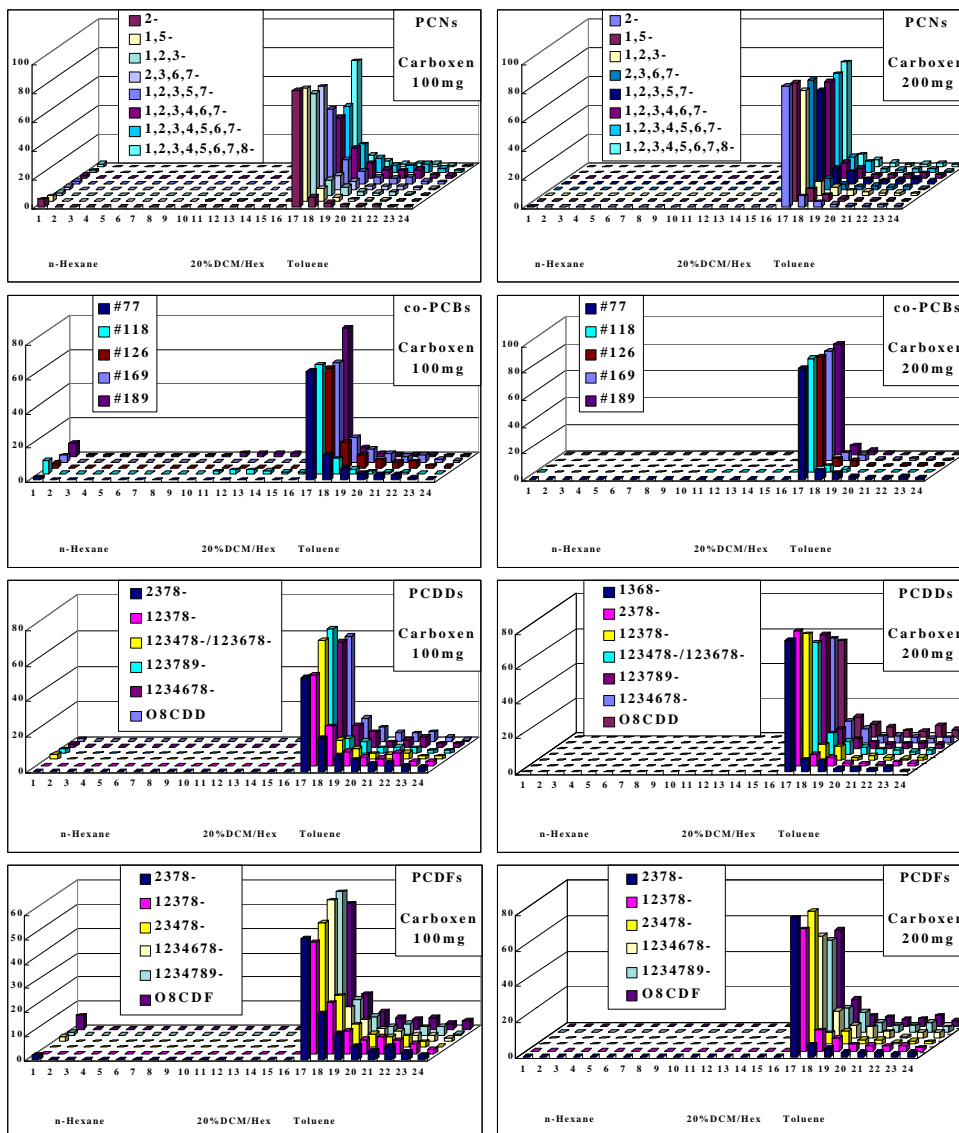
Carboxene1000R were molecular sieving carbon and the globulet have a vast specific surface, 1200m<sup>2</sup>/g and packed tightly in a cartridge. These synthetic adsorbents have strong adsorbing power because of their macro pore (500A) and this strong adsorption to the analytes caused an eluting time lag at normal elution. But Carboxene1000R is the both forward and reverse elusion type cartridge. So, after the forward flush with n-hexane and dichloromethane/n-hexane (20/80), the back-flush elution of PCDD/DF with toluene was good separation from other interference and ideal better than silica gel carbon chromatography. Figure 1 showed the dioxins' elution pattern with a series connection of Sep-Pak silica and Carboxene1000R. The ideal elution pattern was found when reverse elution with toluene to Carboxicen1000R. But in this condition, non-ortho, mono-ortho PCBs and some di-ortho PCBs and PCNs also eluted in dioxins fraction. The use of Carboxene1000R and back-flush elution with pre-heated toluene is recommended to cleanup PCDD/DF.

### References

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**Scheme 1. Scheme of clean-up system for environmental samples.**  
(C1: Sep-Pak Plus Silica. C2: Carboxen 1000R.)



**Figure 1. Elution pattern of Dioxin and relative compounds with Carboxen 1000R (100 & 200mg) and Sep-Pak Plus Silica.**

A vertical axis: percentage of recovery. A horizontal axis: elution number, 1~10: forward flush with n-hexane (100mL), 11~16: forward flush with 20% dichloromethane/n-hexane (60mL), 17~24: back flush with toluene (80mL).