TANDEM COLUMN CLEAN-UP METHOD USING MICROPORE-FREE SURFACE-ACTIVATED CARBON FOR THE ANALYSIS OF PCDD/FS, NON-*ORTHO*-PCBS AND MONO-*ORTHO*-PCBS

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Introduction

The World Health Organization assigned toxic equivalent factors (TEF) to seventeen 2,3,7,8-substituted polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDD/Fs) and twelve isomers of 209 PCBs, including four non-*ortho*-substituted isomers and eight mono-*ortho*-substituted isomers as dioxin-like PCBs[1].

Various types of activated carbon column supporters and extraction apparatus have been tested in an effort to improve sample preparation efficiency[2-5]. None of them, however, have optimized the pore size on the surface. Micropore-free surface-activated carbon had an excellent selectivity for PCDD/Fs and non-*ortho*-PCBs[6]. Nonetheless, the adsorption power of the carbon for mono-*ortho*-PCBs was very weak so that a single micropore-free surface-activated carbon column could not retain mono-*ortho*-PCBs. On the other hand, conventional activated carbon column, such as C-1000, adsorbed PCDD/Fs very strongly and required large amount of organic solvent for the elution.

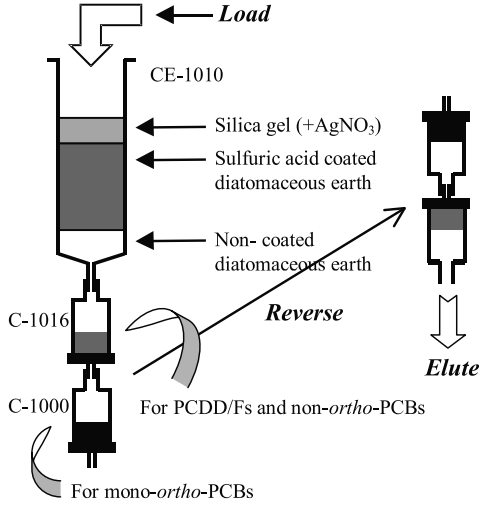

Figure1. Tandem carbon column

ANALYSIS I

The aim of the present study was to establish a rapid, robust, and high-throughput sample preparation method for the analysis of PCDD/Fs, non-*ortho*-PCBs, and mono-*ortho*-PCBs. We established a tandem column clean-up method using micropore-free surface-activated carbon column (C-1016) followed by conventional activated carbon column (C-1000). The former column had excellent selectivity for PCDD/Fs and non-*ortho*-PCBs, and prevented PCDD/Fs from running into the C-1000. The latter column retained mono-*ortho*-PCBs that flowed out from the C-1016. Sulfuric acid-coated diatomaceous earth was applied above the tandem column to improve the reproducibility of the column chromatography.

Methods and Materials

NK-LCS-AD PCDD/Fs mixture and MBP-MXS PCB mixture (Wellington Laboratories, Ontario, Canada) were used as ^{13}C-labeled.standard. Carboxen 1016 (C-1016; Supelco, Bellefonte, PA) was used as the micropore-free surface-activated carbon column and Carboxen 1000 (C-1000) was used as the conventional activated carbon. BET surface area and pore size distribution of the carbon was determined with a Omnisorp 360 (Beckman-Coulter, Fullerton, CA). CE-1010 (Varian, Harbor City, CA) was used for the diatomaceous earth column. Sediment samples were extracted with toluene using an ASE 300 (Dionex, Salt Lake City, UT) accelerated solvent extractor, and concentrated using a rotary evaporator prior to the following sample preparation.

Sulfuric acid was applied to the top of the CE-1010 and was naturally dispersed in the column. Silica gel (+$AgNO_3$) was then put on top of the acid-coated CE-1010. C-1016 was placed just under the CE-1010, followed by C-1000 (Figure 1). ^{13}C-labeled standards (1 ng each; 2 ng for OCDD/F) were added to the sediment extract (2mL; equivalent to 30g of the sediment), then the extract was put through the tandem column. The tandem column was washed with 30mL of n-hexane, followed by 30mL of 3:1 n-hexane dichloromethane mixture. C-1016 and C-1000 were then detached, reversed, and PCDD/Fs and PCBs were eluted with heated (45-50 °C) toluene (Figure 2). The toluene was supplied using a standard HPLC pump (Waters, Milford, Ma) and six parallel SUS tubes in an isothermal oven (Yamato, Tokyo, Japan). The temperature of the toluene for the elution was 45 to 50 °C. Concentrations

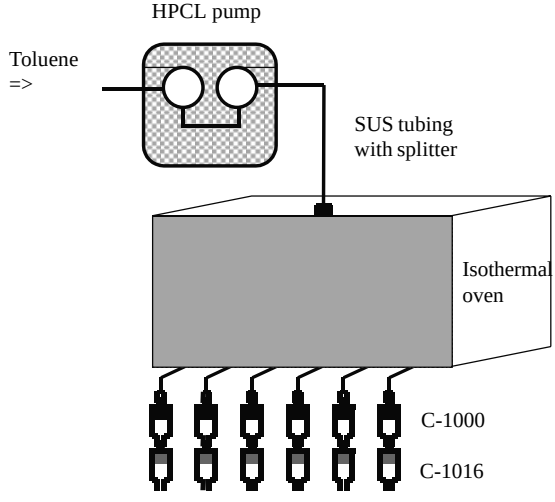

Figure 2. Simultaneous reverse elution with heated toluene

of PCDD/Fs and PCBs in the treated extract was determined with a Polaris ion trap mass spectrometer (ThermoQuest, Austin, TX).

Results and Discussion

The first 30 mL heated (45-50 °C) toluene fraction contained 95 % or more of PCDD/Fs and non-*ortho*-PCBs (Table 1). The results corresponded to the previous study[6]. C-1016 had excellent selectivity to PCDD/Fs and non-*ortho*-PCBs. Thus, these isomers were retained at the upper column (Figure 1), and then, were eluted from the bottom of lower column (Figure 2). The advantages of the "tandem column – reverse elution with heated toluene" system are 1) sharp elution peaks of PCDD/Fs and non-*ortho*-PCBs, 2) excellent recovery rate of PCDD/Fs and non-*ortho*-PCBs. In case PCDD/Fs were flowed out into the lower column, conventional activated carbon in the C-1000 adsorbed them very strongly and the desorption was very difficult. The role of the C-1016 was to prevent PCDD/Fs from running into the C-1000. On the other hand, the adsorption power of C-1016 against mono-*ortho*-PCBs was very weak. So, C-1000 needed to be placed just under the C-1016 to recover mono-*ortho*-PCBs.

Table 1. Fractionation of PCDD/Fs, Non-*ortho*-PCBs, and Mono-*ortho*-PCBs (%)

	1	2	3	4	5
T4-P5CDD/Fs	0	0	95	4	< 1
H6CDD/Fs	0	0	96	3	< 1
H7-O8CDD/Fs	0	0	95	4	< 1
Non-*ortho*-PCBs	0	0	95	3	2
Mono-*ortho*-PCBs	4	1	78	7	10

Fraction 1: 30 mL of n-hexane
Fraction 2: 30 mL of 3:1 n-hexane dichloromethane mixture
Fraction 3: First 30 mL of heated (45-50°C) toluene
Fraction 4: Second 30 mL of heated (45-50°C) toluene
Fraction 5: Remaining in the tandem column

4 % of mono-*ortho*-PCBs flowed out into the n-hexane fraction. In the 3:1 n-hexane dichloromethane fraction, however, only 1 % of mono-*ortho*-PCBs were found. In present study, the crude sediment extract was loaded onto the tandem column as toluene solution. The results suggested that small amount of mono-*ortho*-PCBs flowed out along with the toluene of sample extract.

The differences of the adsorption profile of C-1016 and C-1000 are explained by their pore size distribution (Figure 3). With conventional activated carbon (C-1000), most adsorption occurs between the two graphite-like walls of the micropores (<2 nm). In addition, Suzuki (1990) suggested that oxygen complexes had an important role on the carbon surface[7]. Pore size distribution of C-1016 and C-1000 suggested that PCDD/Fs and non-*ortho*-PCBs were adsorbed in mesopores (2-50 nm). On the contrary, mono-*ortho*-PCBs were adsorbed in micropores. Inside mesopores, an average space between two graphite-like walls is larger than that of micropores. Thus, an interaction occurs only between a single graphite-like wall and a compound. The fractionation results indicate that the interference between mono-*ortho*-PCBs and the surface oxide or a single graphite-like wall is very weak. In

contrast, PCDD/Fs and non-*ortho*-PCBs interact sufficiently with the surface oxide or a single graphite-like wall.

Tandem column technique has the best of both activated carbon columns, conventional activated carbon (C-1000) and micropore-free surface-activated carbon (C-1016).

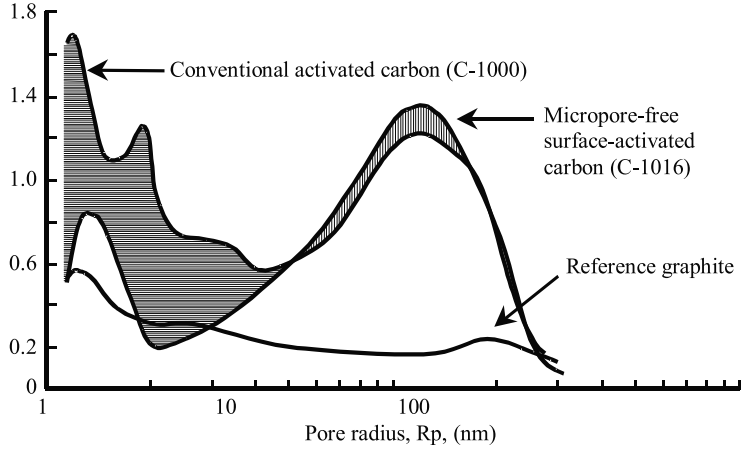

Figure 3. Pore size distribution

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