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# Pinched Inlet Split Flow Thin Fractionation for Continuous Particle Fractionation: Application to Marine Sediments for Size-Dependent Analysis of PCDD/Fs and Metals

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**It is demonstrated that split-flow thin (SPLITT) fractionation, a continuous separation technique for sorting particles or macromolecules, can be utilized for the fractionation of environmental particles to study a size-dependent analysis of pollutants. In this study, focuses are made on the use of a pinched inlet gravitational SPLITT fractionation, a modified form of SPLITT channel formed by reducing the sample inlet thickness of the channel to improve separation efficiency, to separate marine sediments into five different sizes (<1.0, ~1.0 to 2.5, ~2.5 to 5.0, ~5.0 to 10, and ~10 to 53  $\mu\text{m}$ ). The resulting size fractions are examined with high resolution gas chromatography/high resolution mass spectrometry to determine the size-dependent distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans along with a statistical data treatment and are analyzed with inductively coupled plasma-atomic emission spectrometry and graphite furnace atomic absorption spectrometry to ascertain its major and trace metals. It is shown that the combined analytical methods detailed in this study can be powerfully utilized in such a way as to analyze pollutant distribution and its concentration with regard to particle sizes for an environmental assessment.**

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) have gained much attention due to their high toxicity and potential risk to human health. The main source of PCDD/Fs is believed to be emissions from incineration processes, such as municipal or chemical wastes.<sup>1–3</sup> Recent studies suggest that forest fires may be another source of PCDD/Fs.<sup>4,5</sup> Since these com-

pounds are highly hydrophobic, poorly water-soluble, and are resistant to chemical transformations, they strongly bind to dust particles and lead to a surface accumulation of sediments found in lakes or oceans. Due to the very low solubility of PCDD/Fs, they are immobile once they are adsorbed into sediment. Studies on the distribution of PCDD/Fs in an aquatic environment have revealed that considerable amounts of PCDD/Fs accumulate in river, lake, and sea sediments.<sup>6–9</sup> It has been suggested that these chemical substances accumulate in organisms via the food chain; thus, ingestion of fish could be a potential source of human exposure.<sup>10,11</sup> Since the accumulation of these toxic materials in sediments influences the bioaccumulation of toxicants in marine animals, an analysis of sediments is an important step in assessing a marine environment. To study such size-related patterns and concentrations of pollutants which are useful for the assessment of marine environmental quality, a considerable amount of sediments are required to be well-fractionated in advance.

Split-flow thin (SPLITT) fractionation (or SF) is a group of continuous and rapid separation techniques capable of fractionating macromolecules, cells, and particulate materials.<sup>12–19</sup> Separa-

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(1) Schatowitz, B. *Chemosphere* **1994**, 29, 2005–2013.

(2) Pearson, R. F.; Swackhamer, D. L.; Eisenreich, S. J.; Long, D. T. *Environ. Sci. Technol.* **1997**, 31, 2903–2909.

(3) Oh, J.-E.; Chang, Y.-S.; Ikonomou, M. *J. Air Wastes Manage. Assoc.* **2002**, 52, 69–75.

(4) Kim, E.-J.; Oh, J.-E.; Chang, Y.-S. *Sci. Total Environ.* **2003**, 311, 177–189.

(5) Prange, J. A.; Gaus, C.; Weber, R.; Pöpke, O.; Müller, J. F. *Environ. Sci. Technol.* **2003**, 37, 4325–4329.

(6) Witt, G.; Schramm, K. W.; Henkelmann, B. *Organohalogen Compd.* **1996**, 29, 132–135.

(7) Wu, W. Z.; Zhang, Q. H.; Schramm, K.-W.; Xu, Y.; Kettrup, A. *Ecotoxicol. Environ. Saf.* **2000**, 46, 252–257.

(8) Mamontova, E. A.; Mamontov, A. A.; Tarasova, E. N. *Organohalogen Compd.* **2001**, 52, 247–250.

(9) Sakurai, T.; Kim, J.-K.; Suzuki, N.; Nakanishi, J. *Chemosphere* **1996**, 10, 2007–2020.

(10) Sherman, W. R.; Keenan, R. E.; Gunster, D. G. *J. Toxicol. Environ. Health* **1992**, 37, 177–195.

(11) Abbott, J. D.; Hinton, S. W. *Environ. Toxicol. Chem.* **1996**, 15, 1163–1165.

(12) Giddings, J. C. *Sep. Sci. Technol.* **1985**, 20, 749–768.

(13) Jiang, Y.; Kummerow, A.; Hansen, M. *J. Microcolumn Sep.* **1997**, 9, 261–273.

(14) Contado, C.; Riello, F.; Blo, G.; Dondi, F. *J. Chromatogr., A* **1999**, 845, 303–316.

(15) Contado, C.; Dondi, F.; Beckett, R.; Giddings, J. C. *Anal. Chim. Acta* **1997**, 345, 99–110.

(16) Fuh, C. B. *Anal. Chem.* **2000**, 72, 266A–271A.

(17) Jiang, Y.; Miller, M. E.; Hansen, M. E.; Myers, M. N.; Williams, P. S. *J. Magn. Magn. Mater.* **1999**, 194, 53–61.

(18) Moon, M. H.; Kang, D.; Lee, D. W.; Chang, Y.-S. *Anal. Chem.* **2001**, 73, 693–697.

tion in SF is carried out in a thin rectangular channel with splitters located at both the channel inlet and outlet. A typical SF channel uses two different inlet flow streams: a suspended sample solution is continuously fed into a SF channel through the sample inlet while carrier streamflow is being introduced through the other inlet. When sample particles are introduced to the channel, they meet a carrier flow stream, which is normally delivered at a relatively high speed compared to that of a feed stream, and they are pushed toward one wall of the SF channel. Once they are initially transported upward, they start migration along the channel with a simultaneous settlement by an appropriate force applied to the direction perpendicular to the channel axis. When using a gravity force, the particle settlement in gravitational SF (or GSF) is dependent on the sedimentation coefficient, which itself relies on the mass or diameter of the particles. Those of a large mass or diameter will settle faster than will smaller ones and, at the end of the GSF channel, will be distributed vertically according to mass.<sup>12,16</sup> Since there are two outlets located at the end of the GSF channel, those particles settling slowly will emerge at the upper outlet, whereas faster ones will exit the lower one. Thus, fractions collected at both outlets contain particles larger than or smaller than a certain diameter, the so-called cutoff diameter, which can be adjusted by control of the two outlet stream rates. The cutoff diameter,  $d_c$ , in SF systems utilizing gravity or centrifugal acceleration as a driving force is related to channel dimensions and flow rates as expressed by<sup>12,20</sup>

$$d_c = \left( \frac{18\eta(\dot{V}(a) - 0.5\dot{V}(a'))}{bLG\Delta\rho} \right)^{1/2} \quad (1)$$

where  $\eta$  is the viscosity of carrier solution,  $\dot{V}(a')$  the feed flow rate,  $\dot{V}(a)$  the carrier flow rate,  $b$  the channel breadth,  $L$  the channel length (the distance between the splitters),  $G$  the gravity or centrifugal acceleration, and  $\Delta\rho$  the density difference between the carrier liquid and particles.

In this study, it is demonstrated that GSF can be effectively utilized for the continuous separation of sea sediments and that the resulting fractions of a narrow diameter range can be analyzed for the study of the size-dependent levels of PCDD/Fs and heavy metals. To enhance SPLITT fractionation efficiency, our work adopts the pinched inlet SPLITT channel design (shown in Figure 1) that was developed in a previous work<sup>21</sup> by reducing the thickness of the sample inlet conduit of GSF channel. By applying the pinched inlet design to the GSF channel, particles leaving the inlet splitter can be quickly transported and efficiently pushed against the upper wall of the GSF channel by the carrier stream so that the number of particles leaving from an ideal trajectory expected during sample injection is decreased to some degree. A performance test comparing a conventional GSF channel and a pinched inlet channel is made using sediments. For the on-line concentration of the eluting particle suspension, a PCUU (particle concentrator with upstream ultrafiltration)<sup>18</sup> is integrated with the channel outlet of the pinched inlet GSF channel, as shown in

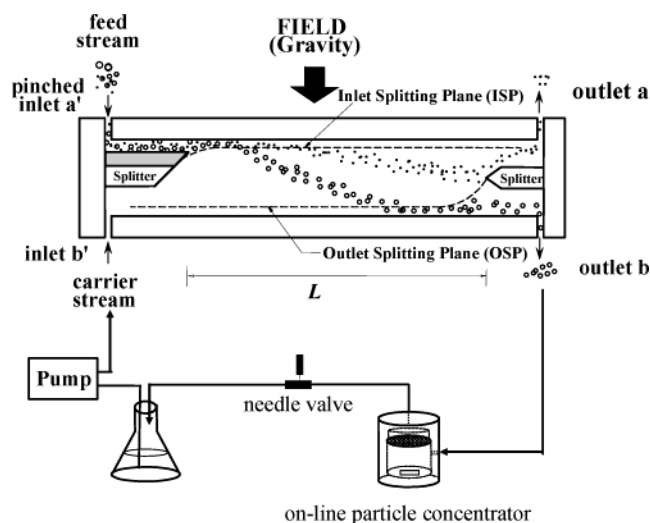


Figure 1. Schematics of pinched inlet gravitational SPLITT (PI-GSF) channel along with PCUU for the on-line particle concentration and circulation of carrier liquid.

Table 1. Experimental Conditions for Each SF Run of Sea Sediments

$d_c$ $\mu\text{m}$	channel dimension <sup>a</sup> $b \times L$ , cm	$\dot{V}(a')$ mL/min	$\dot{V}(b')$ mL/min	$\dot{V}(a)$ mL/min	$\dot{V}(b)$ mL/min
10.0	3 × 15	2.0	17.2	17.2	2.0
		1.0	16.7	16.7	1.0
5.0	4 × 20	2.0	8.2	8.2	2.0
		1.0	7.7	7.7	1.0
2.5	6 × 20	1.5	3.4	3.4	1.5
		0.5	2.9	2.9	0.5
1.0	6 × 20	0.3	0.6	0.6	0.3

<sup>a</sup> All the channels have the same total thickness, 300  $\mu\text{m}$ . The pinched inlet thickness is fixed at 50  $\mu\text{m}$ . For each cutoff diameter run condition, a relatively high feed rate was used to make a rough cut and then was repeated at a reduced feed rate for a precise cut.

Figure 1. The sea sediments collected in the Masan Bay area in Korea were fractionated into five different size groups (<1.0, ~1.0 to 2.5, ~2.5 to 5.0, ~5.0 to 10, and ~10 to 53  $\mu\text{m}$ ), with a gram scale for each fraction. The resulting fractions were further analyzed with high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) to determine the size-dependent concentration of PCDD/Fs and with inductively coupled plasma-atomic emission spectrometry (ICP-AES) and graphite furnace atomic absorption spectrometry (GFAAS) to measure the size-dependent metal concentration.

## EXPERIMENTAL SECTION

**SPLITT Fractionation.** Three different pinched inlet GSF (or PI-GSF) systems were utilized in this study. They were built in-house, and the assembly of the PI-GSF channel is the same as reported in a previous work.<sup>21</sup> The thickness of the sample inlet conduit in a PI-GSF was reduced to one-half of the thickness of the carrier inlet conduit by using two 50- $\mu\text{m}$ -thick Mylar spacers layered above a stainless steel splitter ( $w_s = 100 \mu\text{m}$ ). The sample inlet ( $a'$ ) pathway was made pinched by leaving a spacer right above the splitter without cutting it while the outlet  $a$  region of both spacers was cut into a triangular shape. For the spacer layered below the splitter, a 100- $\mu\text{m}$ -thick Mylar spacer was used

(19) Contado, C.; Gabriella, B.; Conato, C.; Dondi, F.; Beckett, R. *J. Environ. Monit.* **2003**, 5, 845–851.

(20) Moon, M. H.; Kang, D.; Lim, H.; Oh, J.-E.; Chang, Y.-S. *Environ. Sci. Technol.* **2002**, 36, 4416–4423.

(21) Moon, M. H.; Kang, D.; Kwon, S.-Y.; Lee, S. *J. Sep. Sci.* **2003**, 26, 1675–1682.

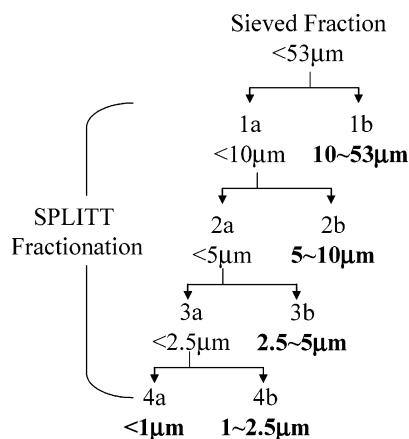


Figure 2. Schemes of particle fractionation by GSF according to the cutoff diameters.

with both ends cut. All three channels had the same thickness dimension:  $w_d = 50 \mu\text{m}$ ,  $w_f = 100 \mu\text{m}$ , and  $w_{\text{total}} = 300 \mu\text{m}$ . The three channels had different channel areas (breadth  $\times$  length, as  $3 \times 15$ ,  $4 \times 20$ , and  $6 \times 20$  in cm), and each channel was utilized to achieve a separation at a different cutoff diameter. The cutoff diameters selected for this study and their corresponding channel dimensions are listed in Table 1, along with the flow rate conditions.

The sediment samples tested in this study were obtained from the Korea Ocean Research & Development Institute (KORDI) and were collected at three different locations in the Masan Bay area in Korea during August 1996 and 1997. Crude sediments were dried at  $105^\circ\text{C}$ , and the density was measured as  $2.1 \text{ g/cm}^3$ . About 30-g of dried sediment sample was suspended in carrier liquid and sonicated for 2 h. The solution used to disperse the sediments and for the GSF carrier liquid was made from ultrapure water ( $>18 \text{ M}\Omega$ ) containing 0.02%  $\text{NaN}_3$  as a bactericide and 0.1% FL-70 from Fisher Scientific (Fairlawn, NJ), which is a mixture of

ionic and nonionic surfactants containing 3.0% oleic acid, 3.0%  $\text{Na}_2\text{CO}_3$ , 1.8% Tergitol, 1.4% tetrasodium ethylenediamine tetraacetate, and 1.0% poly(ethylene glycol) 400 in water. The sediment slurry was initially treated with a 270-mesh sieve ( $\sim 53 \mu\text{m}$  in pore diameter) to remove fractions larger than  $53 \mu\text{m}$ . The solution used for sieving was filtered through a membrane filter having a pore size of  $0.2 \mu\text{m}$  and was utilized for GSF run. Sediment fractions smaller than  $53 \mu\text{m}$  were subjected to sequential fractionation using PI-GSF. Sediments were dispersed at a concentration of 1.0% (w/w) in the carrier liquid and sonicated for 2 h. The delivery of particle suspension to pinched inlet  $a'$  was made with a Minipulse3 peristaltic pump from Gilson (Villers-le-Vel, France). The carrier liquid was pumped through inlet  $b'$  by using an FMI lab pump from Fluid Metering, Inc. (Oysterbay, NY). Feed concentration was varied from  $\sim 0.4$  to 1.0% (w/v). For the collection of particles eluted at both outlets and for simultaneous concentration, a PCUU (particle concentrator with upstream ultrafiltration) unit was connected on-line at the end of the SPLITT outlet (see Figure 1), and the filtrate solution was circulated. For an accurate control of the flow rates during the SPLITT run, a fine metering valve from Crawford Fitting Co. (Solon, OH) was placed at the end of a PCUU that was directly connected to channel outlet  $b$ . Collected particles were examined using a S-4200 scanning electron microscope from Hitachi Ltd. (Tokyo, Japan). Particle size measurement and counting were made using  $\sim 270$  to 300 particles for each fraction.

**PCDD/Fs Analysis.** For the analysis of PCDD/Fs, U.S. EPA method 1613 was utilized to prepare the sample. About 1–3 g of each dried marine sediment collected from PI-GSF was spiked with 1 ng of a mixture of  $^{13}\text{C}_{12}$ -labeled PCDD/F internal standards from Wellington Laboratory (Ontario, Canada) and was extracted for 16 h using toluene under glass Soxhlet thimbles. The extracts were washed with sulfuric acid until colorless and then with distilled water saturated with hexane for neutralization. A sample cleanup was made using a multilayer silica column (neutral silica

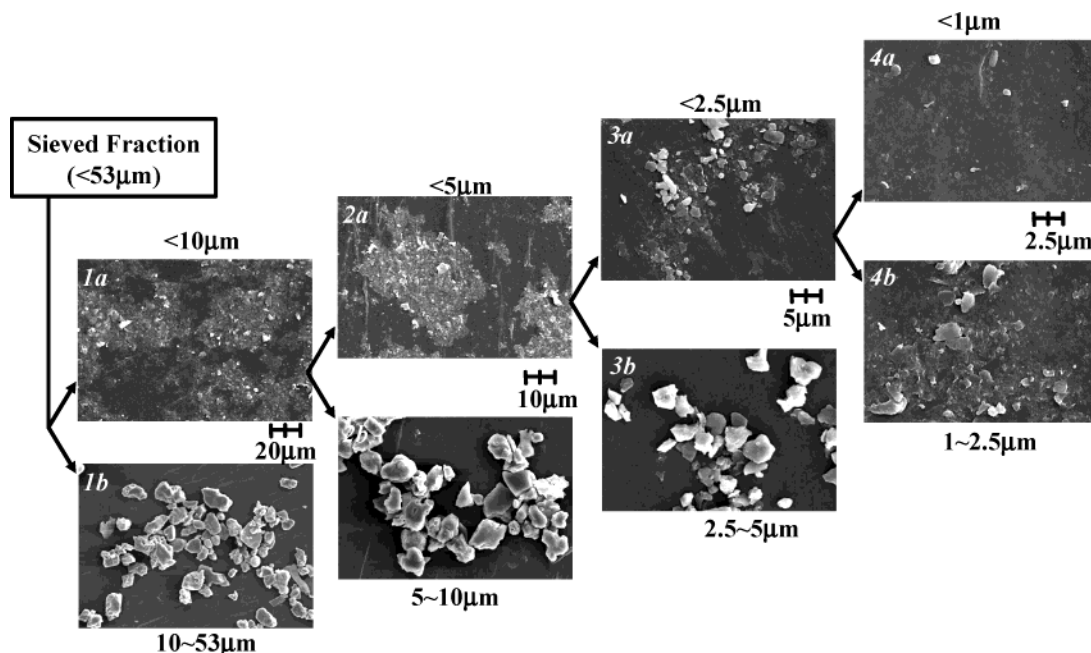


Figure 3. Electron micrographs of fractions collected from a SPLITT run. Expected particle sizes or size ranges calculated from theory based on the experimental conditions are marked for each fraction.

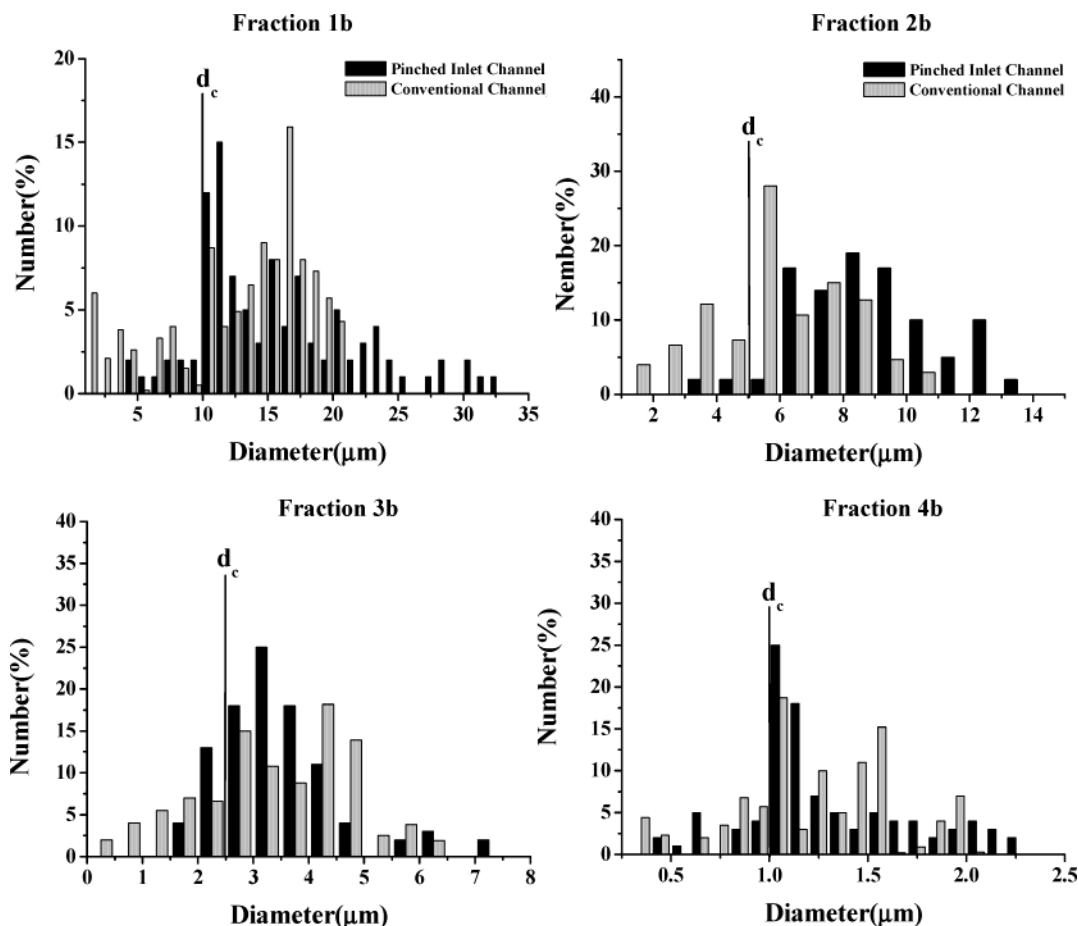


Figure 4. Comparison of distribution of particle percentages for four fractions between conventional GSF and pinched inlet GSF. In each distribution, the theoretical cutoff diameter,  $d_c$ , position is marked inside. Measurements were made with  $\sim 270$  to 300 particles of each fraction.

gel (2 g), basic silica gel conditioned with 1 N NaOH (4 g), neutral (2 g), acidic with  $\text{H}_2\text{SO}_4$  (8 g), neutral (2 g) silica gel, and anhydrous  $\text{Na}_2\text{SO}_4$ , followed by an alumina column (activated alumina (10 g) and anhydrous  $\text{Na}_2\text{SO}_4$ ). Finally, all the samples were concentrated with  $\text{N}_2$  gas, and 1 ng of  $^{13}\text{C}_{12}$ -labeled PCDD/F recovery standard mixture was added. The same procedure was applied to the carrier solution used for GSF operation in order to test any dissolved dioxins.

A measurement of PCDD/Fs was made with a model 6890 HRGC from Hewlett-Packard (Palo Alto, CA) interfaced with a model 700T HRMS from JEOL (Tokyo, Japan). For HRGC runs, a DB-5MS column (length/i.d./film thickness: 60 m/0.25 mm/0.25  $\mu\text{m}$ ) was used with the following temperature program: an initial hold at 140  $^\circ\text{C}$  for 4 min, a linear ramp of 15  $^\circ\text{C}/\text{min}$  to an isothermal hold at 220  $^\circ\text{C}$  for 3 min, another ramp of 1.5  $^\circ\text{C}/\text{min}$  to an isothermal hold at 240  $^\circ\text{C}$  for 2 min, and a final ramp of 4  $^\circ\text{C}/\text{min}$  to an isothermal hold at 310  $^\circ\text{C}$  for 6 min. For an HRMS analysis, a single ion monitoring (SIM) mode was utilized under positive EI conditions set at 38 eV with a resolution over 10 000. Two ions among  $[\text{M}^+]$ ,  $[\text{M} + 2]$ , and  $[\text{M} + 4]$  were monitored. Tetra- to octa-chlorinated homologues were quantified as the toxic 2,3,7,8-substituted PCDD/Fs as well as the total PCDD/Fs. The PCDD/Fs peaks were selected only when the following criteria were met: (1) isotope ratios within  $\pm 15\%$  of theoretical values and (2) a signal-to-noise ratio  $\geq 2.5$ . The recoveries of the  $^{13}\text{C}_{12}$ -labeled PCDD/F internal standards were in the range of 50–120%,

which meets EPA method 1613 protocols. The limits of detection for sediment analysis, defined as 2.5 times the noise level, were calculated as 0.01 pg/g for tetra- and penta-CDD/Fs, 0.02 pg/g for hexa- and hepta-CDD/Fs, and 0.05 pg/g for OCDD/Fs.

**Metal Analysis.** A model JY-138 sequential ICP-AES with a nitrogen purge from Jovin-Yvon (Longjumeau Cedex, France) equipped with a 40.68-MHz RF generator with a demountable standard torch and a 1-m focal length monochromator was used to determine Fe, Ca, and Al in the sediment fractions. The instrument was operated at the forward power of 1.0 kW with a coolant gas flow rate of 12 L/min. The flow rates of auxiliary gas and aerosol gas were 0.1 and 0.9 L/min, respectively. A sample solution was introduced into a model PFA-100 microflow nebulizer from Elemental Scientific, Inc. (Ventura, CA) at an uptake rate of 100  $\mu\text{L}/\text{min}$  using a model Minipuls 3 peristaltic pump from Gilson (Villers-le-Vel, France). A Scott-type spray chamber was used.

A model SOLAAR FS-95 graphite furnace atomic absorption spectrometer (GFAAS) from ThermoElemental (Franklin, MA) was used to determine trace elements in the sediment, such as Ni, Cd, As, and Pb. The temperature programming condition for each element was optimized using the given manufacturers' guidelines.

For the sample pretreatment, a high-pressure acid digestion method was used. About 0.02–0.04 g of each sediment fraction obtained from the GSF were dried in an oven at 60  $^\circ\text{C}$  for 3–4 days and then transferred into a model HU-50 high-pressure acid



Table 2. Percentages for the Marine Sediment Fractions Collected from GSF

(a) Percentage Values for Site 1 between Conventional and Pinched Inlet Channels						
SF fraction ID	expected diam range ( $\mu\text{m}$ )	cutoff diam, $d_c$ ( $\mu\text{m}$ )	percent at conventional SF channel		percent at pinched SF channel	
			$< d_c$	$> d_c$	$< d_c$	$> d_c$
1b	~10.0 to 53	10.0	24.0	76.0	9.8	90.2
2b	~5.0 to 10.0	5.0	26.0	74.0	5.5	94.5
3b	~2.5 to 5.0	2.5	25.1	74.9	15.6	84.4
4b	~1.0 to 2.5	1.0	25.0	75.0	14.5	85.5
4a	<1.0	1.0	88.0	12.0	88.2	11.8

(b) Percentage Values for Sites 2 and 3 by Pinched Inlet GSF						
SF fraction ID	expected diam range ( $\mu\text{m}$ )	cutoff diam, $d_c$ ( $\mu\text{m}$ )	site 2 %		site 3 %	
			$< d_c$	$> d_c$	$< d_c$	$> d_c$
1b	~10.0 to 53	10.0	13.8	86.2	18.9	81.1
2b	~5.0 to 10.0	5.0	16.9	83.1	16.5	83.5
3b	~2.5 to 5.0	2.5	19.9	80.1	18.9	81.1
4b	~1.0 to 2.5	1.0	18.9	81.1	17.7	82.3
4a	<1.0	1.0	98.8	1.2	96.7	3.3

Table 3. Weight Percentage of the Sediment Particles (from Three Different Locations) Measured in Each SF Fraction<sup>a</sup>

SF fraction no.	expected diam range ( $\mu\text{m}$ )	weight in grams (percent)		
		site 1	site 2	site 3
	<53	28.2 (100)	21.8 (100)	21.2 (100)
1b	~10.0 to 53	2.5 (8.9)	3.5 (16.0)	3.2 (15.1)
2b	~5.0 to 10.0	7.6 (27.0)	4.6 (21.0)	4.1 (19.3)
3b	~2.5 to 5.0	6.7 (23.7)	3.1 (14.2)	3.7 (17.5)
4b	~1.0 to 2.5	7.0 (24.8)	4.8 (22.0)	4.5 (21.2)
4a	<1.0	4.4 (15.6)	5.8 (26.8)	5.7 (26.9)

<sup>a</sup> A pinched SPLITT channel design was used throughout the runs. (Site 1 is the same sample utilized in Table 2).

digestion bomb from Sankai, Co. (Nagoya, Japan) with 12 mL of acid mixture ( $\text{H}_2\text{O}_2/\text{HNO}_3/\text{H}_2\text{SO}_4/\text{HF} = 1:3:1:1$ ) for 6 h at 160 °C. The digestion bomb consisted of a PTFE vessel with stainless steel housing and a lid. The vessel containing the dissolved solution was slightly heated to evaporate the HF and  $\text{SiF}_4$  that was converted from silicon oxides by HF, and these were then transferred to a volumetric flask of 50 mL and marked. All the chemicals were semiconductor grade and were purchased from Dong Woo Pure Chemical Co., Ltd. (Iksan, Korea). MESS-2 (originating from the Beaufort Sea), a CRM (certified reference material) for sediments obtained from NRC (National Research Council, Canada), was utilized to verify the analytical method. All calibrations were carried out by using the standard addition method.

## RESULTS & DISCUSSION

**PI-GSF for Marine Sediments.** The continuous fractionation of marine sediments by GSF began with a sieved fraction ( $<53 \mu\text{m}$ ). The first GSF run was carried out at a cutoff diameter of 10  $\mu\text{m}$ . Fraction 1b was indicated as the fraction collected at channel outlet b in the first fractionation scheme (a cutoff diameter of 10  $\mu\text{m}$ ). Fraction 1b, which was expected to be larger than 10  $\mu\text{m}$  (presumably ~10 to 53  $\mu\text{m}$ ), was stored separately, and the fraction smaller than 10  $\mu\text{m}$  (fraction 1a) was transferred for

further SPLITT fractionation at a smaller cutoff diameter. The entire fractionation scheme is shown in Figure 2, and the resulting size fractions were ~53 to 10, ~10 to 5.0, ~5.0 to 2.5, ~2.5 to 1.0, and  $<1.0 \mu\text{m}$ . In each cutoff diameter separation, a repeat process was employed for the improvement of separation efficiency: an initial, rough cut was made at a relatively high sediment suspension feed rate in order to increase throughput and followed by a precise cut done at a reduced feed rate. It has been already noticed in earlier experiments that separation accuracy in GSF can be enhanced when a reduced feed rate is used at a dilute sample concentration (~0.1% w/v).<sup>18,21</sup> However, such conditions were not appropriate for the separation of sediment particles into a semipreparative scale ( $>2 \text{ g}$  for each size fraction) due to the increase in processing time. Therefore, two sequential runs were applied for each GSF run, along with a variation of feed concentration. Table 1 lists the flow rate conditions used for each cutoff process. In the case of the sediments fractionated at a cutoff diameter of 10 mm, an initial cut was made at the feed rate,  $\dot{V}(a')$ , of 2.0 mL/min. with a feed concentration of ~1.0% (w/v), then the collected fraction larger than 10  $\mu\text{m}$  that was concentrated on-line in a PCUU (see Figure 1) was subjected to repeated fractionation at the same cutoff diameter, but a sample suspension was fed at a lower flow rate (1.0 mL/min.), with a decreased feed concentration of ~0.4 to 0.5% (w/v). Consecutive fractionations at different cutoff diameters were made in the same manner, except for that of the GSF run at  $d_c = 1.0 \mu\text{m}$ , which was repeated at the same feed rate.

To evaluate the separation efficiency of PI-GSF channels, experiments were carried out using both conventional and pinched inlet SPLITT channels. A comparison was made by measuring the percentage of particles present at each outlet. Figure 3 shows electron micrographs of the collected fractions using pinched inlet channels. For each cutoff diameter stage, different channel dimensions (length and breadth) were employed for the appropriate selection of flow rates, but the thickness of the pinched inlet was fixed at 50  $\mu\text{m}$ . The sediment particles used for this run were screened out using a mechanical sieve having a pore size of 53  $\mu\text{m}$ , but most particles were found to be less than or ~10  $\mu\text{m}$ ,

Table 4. Concentration<sup>a</sup> of PCDD/Fs of Sediment Fractions (Site 1) According to Five Different Size Groups Fractionated by GSF

	fraction				
	1b (10–53 $\mu\text{m}$ )	2b (5.0–10 $\mu\text{m}$ )	3b (2.5–5.0 $\mu\text{m}$ )	4b (1.0–2.5 $\mu\text{m}$ )	4a (<1.0 $\mu\text{m}$ )
extraction (g)	0.8063	0.9968	1.0063	0.8413	1.006
TCDD	ND <sup>b</sup>	ND <sup>b</sup>	ND <sup>b</sup>	ND <sup>b</sup>	ND <sup>b</sup>
PCDD	53.49	47.33	52.43	51.64	29.66
HxCDD	ND <sup>b</sup>	ND <sup>b</sup>	ND <sup>b</sup>	ND <sup>b</sup>	ND <sup>b</sup>
HpCDD	2.50	7.89	24.65	36.52	44.66
OCDD	7.94	40.61	139.18	206.13	280.03
TCDF	7.06	12.53	19.41	16.96	20.52
PeCDF	8.14	13.08	14.54	20.05	29.00
HxCDF	12.21	13.37	30.35	28.33	46.38
HpCDF	1.11	6.92	18.23	27.22	50.39
OCDF	1.76	1.86	8.15	11.40	34.73
PCDDs	63.93	95.83	216.26	294.29	354.35
PCDFs	30.28	47.76	90.68	103.96	181.02
PCDD/Fs	94.21	143.59	306.94	398.25	535.37

<sup>a</sup> Unit: pg/g. <sup>b</sup> Not detected.

and blocking of channel inlet by particles was not observed to be serious in this experiment. However, possible blockage of the pinched inlet conduit by particles can be a minor drawback to applying PI-GSF toward particles having sizes larger than two-thirds of the channel inlet thickness, since particle transportation in such a case could be sluggish. The micrograph of fraction 1b in Figure 3 shows that most of the particles appeared to be larger than 10  $\mu\text{m}$ , except for a few small particles. Subsequent fractions showed that the separation was achieved successfully, except for a few oversized particles. Since most of the particles observed at fractions of 1b, 2b, and 3b were not entirely flat or elongated, deviations due to shape were not serious according to the apparent micrographs. For the case of odd shaped particles, particle aspect ratio must be considered in the calculation of cutoff diameter. Particle sizes were measured manually from micrographs, and ~270 to 300 particles were counted for each fraction. The resulting size distribution is plotted in Figure 4. When the number percentage was compared with that obtained by a conventional SPLITT channel, the difference in performance between the two channels was clearly shown; this is detailed in Table 2a. Fraction 1b obtained at a conventional channel appeared to contain 76.0% particles (in number) larger than the cutoff diameter (10  $\mu\text{m}$ ); however, this percentage was increased to 90.2% when a pinched inlet channel was utilized. It is clearly shown in Figure 4a that undersized particles (smaller than the cutoff diameter) were depleted in fraction 1b obtained at the pinched inlet channel. A similar tendency was observed at later fractions, although the percentage decreased to some degree. As for fraction 3b, which was expected to be larger than 2.5  $\mu\text{m}$ , it appeared to contain few particles smaller than 2.5  $\mu\text{m}$ , as seen in Figure 4c; however, fraction 3b obtained at the pinched inlet channel showed fewer undersized particles. From this study, it was demonstrated again that the pinched inlet SPLITT channel provided an improved separation compared to the conventional channel design. When the cutoff diameter decreased, the carrier flow rate required for the initial compression of particles toward the upper wall subsequently decreased, as listed in Table 1. The increase in the relative ratio of feed rate to carrier flow rate resulted in a substantial lowering of the inlet splitting plane (ISP shown in Figure 1). As

the gap between the upper wall and the ISP increased, the variation in the starting point of particle settling during initial compression widened, and deviations from the ideal became larger. In addition, the effect of compression was not strong at a decreased carrier flow rate, and this led to an incomplete transportation of particles toward the upper wall. The fractionation process was carried out further for two other sediment samples collected at nearby locations by using pinched inlet channels; the resulting data are listed in Table 2.b. The percentage values of each fraction for sites 2 and 3 appeared to be above 80% and were similar to each other. The recovery level obtained for the sediments was analogous to that reported for other types of particles at the current feed concentration. Since the feed concentration of the sediments used for each repeat run in PI-GSF was ~0.4 to 0.5%, the percentage values that could be achieved were relatively lower than that (~90%) obtained with a feed concentration of 0.1% at a preliminary evaluation.<sup>21</sup>

**Homologue Patterns and Distribution of PCDD/Fs of SPLITT Fractions.** Table 3 lists the weight and percentage of each dried fraction of sediment samples according to size. Approximately 85% of the sieved sediment particles (<53  $\mu\text{m}$ ) was shown to be smaller than 10  $\mu\text{m}$  for all samples. The collected fractions were analyzed to determine the concentration of PCDD/Fs and metals. Table 4 lists the concentration of PCDD/F homologues in the sediment fractions from site 1. It shows that the concentration of PCDD/Fs appeared to increase as particle size decreased in most homologues. An analysis of the carrier solution used for the PI-GSF runs revealed that PCDD/F detection was below the detection limit given the extremely low solubility of these materials in water. The general tendency of concentration increase is attributed to the increase in surface area as particle size decreases.<sup>22</sup> In particular, octachlorodibenzo-*p*-dioxin (OCDD) seemed to be dominant among the listed homologues, and it increased dramatically as particle size decreased. This can be explained by the known fact that OCDD is readily deposited into sediments due to its low solubility in water and high octanol–water partitioning coefficient.<sup>24</sup> It was also noted that the total

(22) Gao, J. P.; Maguhn, J.; Spitzauer, P.; Kettrup, A. *Water Res.* **1997**, *31*, 2811–2819.

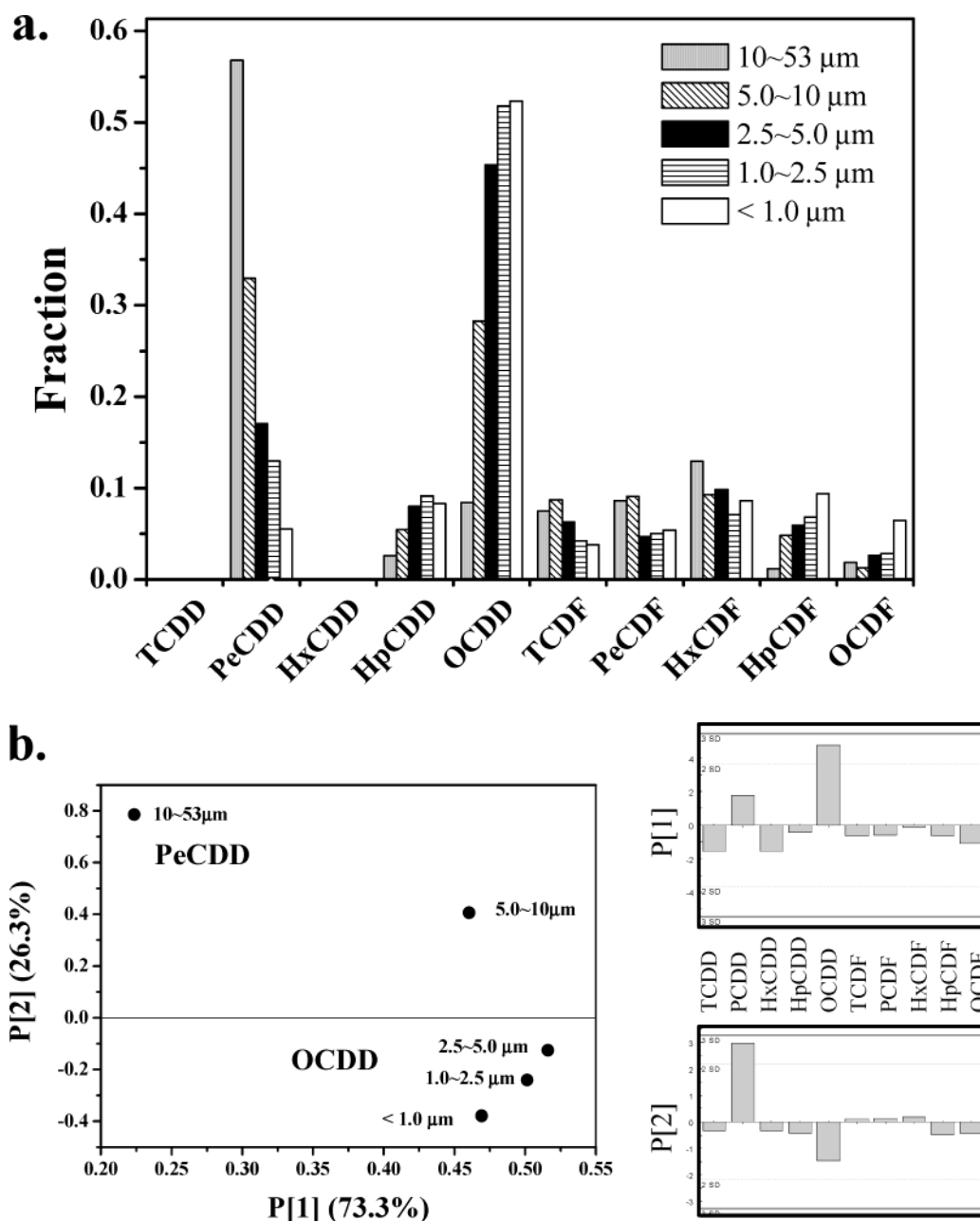


Figure 5. (a) Normalized homologue profiles of the total PCDD/Fs for marine sediments (site 1) and their relative amounts are compared to each size fraction. (b) The loading plot of principal component analysis for the different size fractions collected from Masan Bay, Korea, and the two score plots on the right side of the PCA plot represent what is the dominating homologue at each axis.

PCDD levels accumulated in sediments were  $\sim 2$  times larger than that of the total PCDFs in most size fractions. The homologue concentration of the sediment sample (site 1) is plotted according to the particle sizes in Figure 5a. When the normalized concentrations (normalization was based on each particle size) were compared, it was clearly shown that the relative abundance of pentachlorodibenzo-*p*-dioxin (PeCDD) decreased as particle size decreased. Fractions of lowly chlorinated PCDD/Fs increased as particle sizes decreased; however, the fractions of highly chlorinated PCDD/Fs showed the reverse. For the visualization of statistical similarities or differences in PCDD/F homologue patterns among particle sizes, a principal component analysis (PCA) was utilized. The PCA plot in Figure 5b indicates that two significant principal components (P[1] and P[2]) accounted for

the variation in data. The P[1] score of OCDD was high for sediments smaller than 5.0  $\mu\text{m}$ , whereas the P[2] score of PeCDD was high for particles larger than 5.0  $\mu\text{m}$ . On the basis of this PCA result, it can be stated that particles could be clustered into two groups: particles smaller than 5.0  $\mu\text{m}$  are dominated by OCDD, whereas those larger than 5.0  $\mu\text{m}$  are dominated by PeCDD. Since this paper's purpose is to demonstrate the potential applicability of PI-GSF to environmental particulates, detailed explanations are not given here regarding the environmental aspects of relative homologue abundances. Since the sediment samples used in this study were collected from Masan Bay, which is surrounded by a number of industrial (petrochemical, metal processing, electrical, and plastic manufacturing) complexes and urban areas, the existence of PCDD/Fs in sediments was expected



Table 5. Concentrations of Metal Elements for Sediment Fractions (Site 1) Analyzed by ICP-AES and GFAAS

fraction element	1b (~10 to 53 $\mu\text{m}$ )	2b (~5.0 to 10 $\mu\text{m}$ )	3b (~2.5 to 5.0 $\mu\text{m}$ )	4b (~1.0 to 2.5 $\mu\text{m}$ )	4a (<1.0 $\mu\text{m}$ )
(a) Concn (wt % ( $\pm$ SD)) of Major Elements Analyzed by ICP-AES					
Fe	3.85 $\pm$ 0.01	3.25 $\pm$ 0.01	4.26 $\pm$ 0.16	4.29 $\pm$ 0.02	3.26 $\pm$ 0.03
Ca	3.61 $\pm$ 0.10	3.61 $\pm$ 0.09	6.80 $\pm$ 0.12	3.53 $\pm$ 0.07	3.90 $\pm$ 0.03
Al	8.92 $\pm$ 0.02	6.67 $\pm$ 0.02	5.58 $\pm$ 0.06	4.02 $\pm$ 0.02	6.80 $\pm$ 0.01
(b) Concn ( $\mu\text{g/g}$ ( $\pm$ SD)) of Trace Elements Analyzed by GFAAS					
As	13.9 $\pm$ 1.3	13.1 $\pm$ 2.8	10.7 $\pm$ 0.2	14.2 $\pm$ 4.3	14.5 $\pm$ 5.9
Ni	32.8 $\pm$ 2.2	25.1 $\pm$ 1.3	42.2 $\pm$ 0.8	37.3 $\pm$ 7.2	36.6 $\pm$ 0.22
Pb	11.5 $\pm$ 3.2	12.9 $\pm$ 0.83	8.10 $\pm$ 2.6	7.9 $\pm$ 1.3	6.2 $\pm$ 0.4
Cd	24.4 $\pm$ 3.3	24.5 $\pm$ 6.2	24.6 $\pm$ 2.2	45.8 $\pm$ 3.0	37.5 $\pm$ 2.1

to occur here due to terrestrial and atmospheric inputs.<sup>23–25</sup> In addition, they were believed to contain complicated information regarding the source of these pollutants, particle composition, and so on. Detailed studies are needed to clarify the environmental relationship between these pollutants and their sources, as well as their impact on marine animals.

**Elemental Analysis for SPLITT Fractions.** An elemental analysis of sediment fractions was carried out using atomic spectroscopic methods. To confirm the sample treatment method applied to the Masan Bay sediments, a recovery test was done on Al and Fe using the MESS-2, a Certified Reference Material (CRM) from the National Research Council (NRC) at Canada, and this gave results above 93%, which is acceptable. Metals such as Fe, Ca, and Al, which were found to be the major elements in the sediments, were analyzed using ICP-AES. Table 5a lists the ICP-AES results for the metals contained in each size fraction from PI-GSF. Silicon, the most abundant element contained in sediment, was removed by evaporation after the HF addition. The data given in Table 5 shows the net amount of each metal, excluding Si. It appeared that there was no strong dependency of metal concentrations on particle sizes, but Al concentration increased as particle size larger than 5.0  $\mu\text{m}$  occurred. Trace elements, such as As, Ni, Pb, and Cd, were determined using GFAAS, and the results are listed as micrograms per gram in Table 5b. Concentrations of Ni and Cd were found to be ~2 to 3 times larger than those of As and Pb. While As and Ni did not show a strong dependency on particle size, the concentration of Pb increased as particle size

increased; however, Cd showed a reverse trend, and especially the concentration of sediments smaller than 2.5  $\mu\text{m}$  were much higher than those of larger ones. Since the sediment sample examined in this measurement was collected from the Bay area close to an engineering complex area, including chemical plants and so on, the heavy metals were thought to originate from the industrial complex area's waste.

In this study, it was demonstrated that PI-GSF can be powerfully utilized for the semipreparative fractionation of marine sediments into narrow-diameter fractions for a multidimensional analysis of toxic organic pollutants and metals. Although the PI-GSF channel dimensions employed in this study were of an analytical scale having some throughput limitations, the amount of particles to be processed can be enlarged once the dimensions of GSF channels and PCUU employed for on-line particle concentration are expanded. This work shows a potential method that is applicable to the environmental assessment of aquatic sediments with regard to size-dependent origin and type of contaminants and the impact these sediments can have on aquatic animals and on human health.

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(23) Moon, H.-B.; Choi, H.-G.; Kim, S.-S.; Jeong, S.-R.; Lee, P.-Y. *J. Fish. Sci. Technol.* **2001**, 4 (2), 51–57.

(24) Oh, J. R.; Ikononou, M. G.; Fernandez, M. P.; Hong, S.-H. *Arch. Environ. Contam. Toxicol.* **2003**, 44, 224–236.

(25) Im, S. H.; Kannan, K.; Matsuda, M.; Giesy, J. P.; Wakimoto, T. *Environ. Toxicol. Chem.* **2002**, 21 (2), 245–252.