Development of Pre-concentration System for PCDDs and PCDFs in Seawater

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1. Introduction

Until recently, especially last decade, concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in various kinds of samples (e.g., waste water, pesticide, sludge, food, industrial material, organism, air and etc.) have been reported by many researchers. However, there have been a few reports (e.g., 1) and 2)) with respect to the seawater because of their low concentrations and sampling difficulties. In order to clear the geochemical cycle (e.g., bioconcentration, transport, fate and etc.) of PCDDs and PCDFs, it is indispensable to determine their concentrations in seawater (from the coastal to the pelagic) at the femto gram/l levels.

We developed pre-concentration system for determination of PCDDs and PCDFs in seawater. In this paper, we represent the system and some evaluations for the system.

2. Methods

Outline of pre-concentration system

Special pre-concentration system was developed because the concentration of PCDDs and PCDFs in pelagic seawater would be considered very low. Schematic diagram of this system is shown in Fig. 1. Seawater is sampled by electric pump, and led into cartridge filter unit. Cartridge filters are made by stainless steel core and cotton wound layer. Pore size of each cartridge filter C, D and E are selected from 50, 10, 5, 3 and 1 μm respectively. (B is employed to remove the pulse flow arisen from the pump.) Cartridge filters are effective in the point of their large filtration area. After passing through the cartridge filter, the water flow is led into disk filter unit (F) which have 0.5 μm pore size glass fiber filter. Final stage is adsorption on resin (I). Amberlite XAD-2 or XAD-4 resin (Rohm and Haas Company) was employed for absorbent and its volume was 5000 ml.

Flow late of this system is about 600 l/hour (10 l/min.), equivalent to 2.0 bed volumes/ min. (2.0 ml/min./cm3).

Almost portions of this instrument that contact with sample water are made of stainless steel (SUS304 or SUS316, JIS; Japan Industrial Standard) or Teflon.

Extraction from the filters and XAD resin

Cartridge filters and glass fiber filters were extracted in a "Soxhlet extractor" using methanol and toluene for 12 hours respectively. XAD resin was extracted by methanol and toluene for 12 hours using special "Continuous extraction unit". Methanol and toluene were combined after the extraction, and concentrated to about 5 ml using rotary evaporator and then solvent was changed to n-hexane.

Cleanup

Concentrated sulfuric acid and column chromatograph technique (silica gel and aluminum) were employed to separate the PCDDs and PCDFs from other impurities in sample. Descriptions in detail for cleanup technique are omitted here.

HRGC/HRMS determination

The final analysis of PCDDs and PCDFs in extracted sample was performed on high resolution gas chromatograph (5890 SERIES II, Hewlett Packard) equipped with a SP-2331 (Supelco) fused silica column / high resolution mass spectrometer (AutoSpec, VG Analytical) operating in the electron ionization procedure. In order to gain the high resolution and high sensitivity, MS measurements were carried out in one injection for each congener (five injections for one sample).

Contamination

In order to avoid contamination from the air, all analyses were performed in the "Chemical hazard clean room". The air supplied into this room is passed through several pre-filters and charcoal-filters. All glass wares were applied to 400W ultraviolet irradiation for more than 12 hours before in use.

4. Results

Blank test

Blank tests were carried out because, as mentioned above, this system requires several filters and 5000 ml XAD resin, 5000 ml methanol and toluene for extraction. All congeners and isomers were below in the detection level defined as five times the noise (equivalent to about <5 fg/l as 2,3,7,8-TetraCDD).

Recovery

In order to estimate the recovery of the system, coastal seawater was led into the system and spiked with the following Cambridge Isotope Laboratories' 13C12-labeled standards; 2,3,7,8-TetraCDD, 1,2,3,7,8-PentaCDD, 1,2,3,6,7,8-HexaCDD, 1,2,3,4,6,7,8-HeptaCDD, 1,2,3,4,6,7,8,9-OctaCDD, 2,3,7,8-TetraCDF, 1,2,3,7,8-PentaCDF, 1,2,3,4,7,8-HexaCDF, 1,2,3,4,6,7,8-HeptaCDF and 1,2,3,4,6,7,8,9-OctaCDF (10 ng of each isomer). After spiking standard, 1000 l seawater were flowed into the system. Then 10 l ion-exchanged water was led into the system to remove the salts in seawater. The

results of recovery test are shown in Table 1.

Apply to coastal seawater

Before using for open ocean water, this system was applied to 2000 l coastal seawater that is not so polluted. One example of results, concentrations of 2,3,7,8-substituted PCDDs and PCDFs trapped by XAD resin, is shown in Table 2. Almost isomers of penta-, hexa-, hepta- and octa-PCDD(s) and PCDF(s) were detected in sample.

4. Conclusion

The results obtained show that the concentrations of PCDDs and PCDFs in seawater are very low. This pre-concentration system is effective to concentrate the PCDDs and PCDFs from the large volume water sample, and would be utilize to other water samples, (e.g., lake, river, tap and waste water) and other organic compounds (e.g., PCBs, pesticides and hydrocarbons).

Table 1. Recovery of pre-concentration system for $^{13}C_{12}$-labeled Tetra-Octa CDDs and CDFs.

$^{13}C_{12}$ - labeled Tetra-Octa CDD	Recovery (%)	$^{13}C_{12}$ - labeled Tetra-Octa CDF	Recovery (%)
2,3,7,8-Tetra CDD	95	2,3,7,8-Tetra CDF	102
1,2,3,7,8-Penta CDD	96	1,2,3,7,8-Penta CDF	98
1,2,3,6,7,8-Hexa CDD	95	1,2,3,4,7,8-Hexa CDF	100
1,2,3,4,6,7,8- Hepta CDD	94	1,2,3,4,6,7,8-Hepta CDF	95
1,2,3,4,6,7,8,9-Octa CDD	89	1,2,3,4,6,7,8,9-Octa CDF	89

Table 2. Concentrations of 2,3,7,8-substituted Tetra-Octa CDDs and CDFs trapped by XAD-2 resin.

Isomer(s)		Concentration(fg/l)	Isomer(s)		Concentration (fg/l)
Tetra	2,3,7,8-	20	Tetra	2,3,7,8-	50
Penta	1,2,3,7,8-	14	Penta	1,2,3,7,8-	20
				2,3,4,7,8-	35
Hexa	1,2,3,4,7,8-	40	Hexa	1,2,3,4,7,8-	28
	1,2,3,6,7,8-	70		1,2,3,6,7,8-	20
	1,2,3,7,8,9-	88		1,2,3,7,8,9-	< 5
				2,3,4,6,7,8-	55
Hepta	1,2,3,4,6,7,8-	250	Hepta	1,2,3,4,6,7,8-	380
				1,2,3,4,7,8,9-	390
Octa	1,2,3,4,6,7,8,9-	340	Octa	1,2,3,4,6,7,8,9-	560

5. References

1) Broman D., C.Naf, C.Roiff, and Y.Zebuhr (1991): Occurrence and dynamics of polychlorinated dibenzo-*p*-dioxins and dibenzofurans and polycyclic aromatic hydrocarbons in the mixed surface layer of remote coastal and offshore waters of Baltic. *Environ.Sci.Technol.* **25**, 1850-1864

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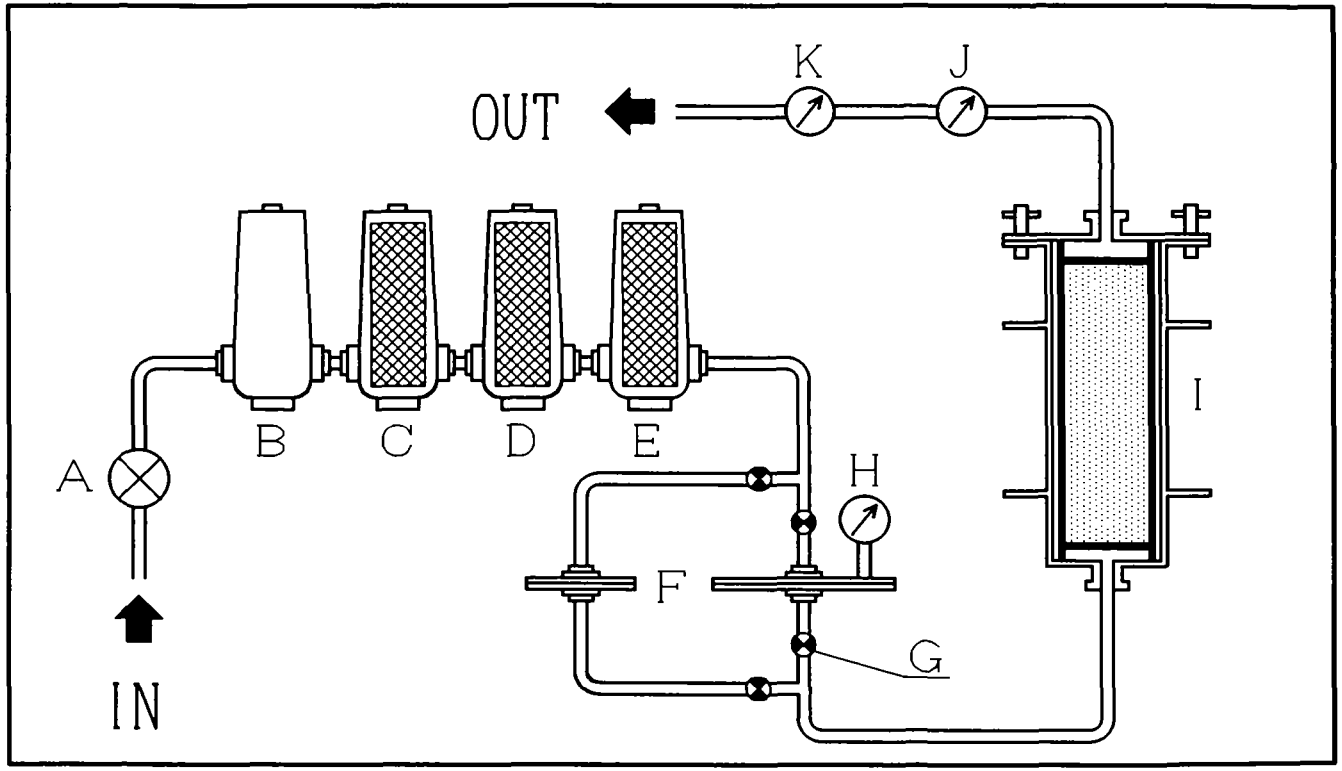

Fig.1. Schematic of the pre-concentration system.

A : Electric pump; B,C,D and E : Cartridge filter housing; F : Glass fiber filter holder;
G : Valve; H : Pressure gauge; I : XAD resin column; J : Flow rate meter; K : Flow meter