Complete Isolation and Determination of Mono-ortho and Non-ortho Substituted PCBs and PCDDs/PCDFs by HPLC Porous Graphitic Carbon with HRGC/HRMS

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Increasing concern is centered on mono-ortho and non-ortho substituted PCBs because of their similar structural and toxicological properties as PCDDs/PCDFs. Development of analytical methods in high degree of isolation and determination of individual mono & non-ortho-PCBs is important for evaluating their toxic potentials as well as PCDDs/PCDFs by HRGC/HRMS in environmental samples. A porous graphitic carbon(PGC) HPLC column has been used for the isolation of these planar compounds[1, 2]. In this paper the results of the method developed and the example of application of this method are presented.

The standards used for this experiment are native and $^{13}C_{12}$-labelled non-ortho-PCBs (IUPAC No 77, 126, 169), native mono-ortho-PCBs (IUPAC No. 105, 114, 118, 123, 156, 157, 167, 189), Kanechlor mixture (KC-300:KC-400:KC-500:KC-600=1:1:1:1), PCB window defining mixture (IUPAC No. 0, 1, 3, 10, 15, 30, 37, 54, 77, 104, 126, 155, 169, 188, 189, 202, 194, 208, 206, 209) and $^{13}C_{12}$-labelled PCB cocktail mixture (IUPAC No 3, 77, 202, 209) for PCBs analysis and native and $^{13}C_{12}$-labelled 2, 3, 7, 8 substituted PCDDs/PCDFs. The sample applied for this experiment to evalute the method are flue gas from a municipal solid waste(MSW) incinerator. Clean up procedures, HPLC PGC conditions and HRGC/HRMS conditions are shown in **Figure 1**, **Table 1** and **Table 2**.

Figure 2 shows the elution profile of mono-ortho, non-ortho-PCBs and PCDDs/PCDFs on HPLC PGC column. It is easy to understand that this method using HPLC PGC column is excellent for isolation of planar compounds. From the recovery test of these planar compounds it was found to be allowable level such as more than 90%. It was effective for increasing the recovery of mono- & non-ortho-PCBs and PCDDs/PCDFs to excahnge of eluent and to elevate temperature to 50℃ during the reverse flow of the PGC column. In this PGC method, the first eluting isomers of mono-ortho-PCBs in hexane were IUPAC No. 189, 167 and next 114, which was different from the results of Hong et.al.[1].

The data obtained from the MSW samples(**Figure 3**) indicate good isolation and separation of individual mono- & non-ortho-PCBs from the other PCBs including the phenomena of interferences by the effect of flagment ions from higher levels of chlorination of PCBs and from specific interferences as well as nonspecific interferences which shows the deviations in the form of negative deflections of PFK lock-mass ion in the chromatograms. It was also indicated from these experiment that overload of sample extracts to the HPLC PGC column, insufficient solvent exchange from toluene to hexane and variation of room temperature may cause mistake in fractionation of PCBs by HPLC PGC column. Although there are no available $^{13}C_{12}$-labelled internal standards of mono-ortho-PCBs now, the combination of mono-ortho-PCBs fraction and non-ortho-PCBs fraction from PGC fractionation would be useful for the accurate determination of mono-ortho and non-ortho-PCBs by isotope dillution method in HRGC/HRMS.

1. Hong C-S, Bush B, Xiao J, Fifzgerald EF, Isolation and determination of mono-ortho and non-ortho substituted PCBs(coplanar PCBs) in human milk by HPLC porous graphitic carbon and GC/ECD. *Chemosphere* 24, 465-473 (1992).
2. Zebühr Y, Näf C, Bandh C, Broman D, Ishaq R, Patterson H, HPLC method with coupled columns for the separation of PCDD/Fs, non-ortho-PCBs, mono-ortho-PCBs, di-tetra-PCBs and PACs. *DIOXIN'92 EXTENDED ABSTRACTS* Volume 8 193-196 (1992).

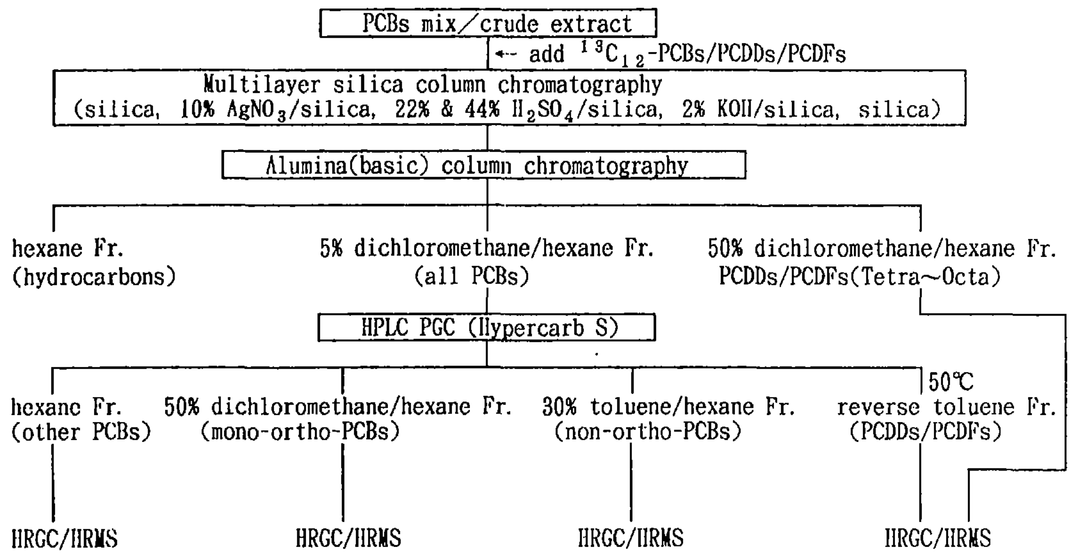

Figure 1. Clean up procedure for mono-ortho, non-ortho-PCBs and PCDDs/PCDFs.

Table 1. HPLC PGC Conditions

HPLC:	SHIMADZU LC-6A
Column:	SHANDON Hypercarb S(porous graphitic carbon) 100mm(length) X 4.6mm(i.d.)
Injector:	RHEODYNE 7125 loop volume:1ml, Injection volume:200μl
Flow:	2ml/min
Detector:	UV-254 nm
Eluent:	fraction I <other-PCBs> hexane 8ml
	fraction II <mono-ortho-PCBs> 50% dichloromethane/hexane 40ml
	fraction III <non-ortho-PCBs> 30% toluene/hexane 40ml
	fraction IV <PCDDs/PCDFs> toluene 30ml *reverse flow & heat at 50℃ and solvent washed with toluene followed by hexane until no absorption by a UV detector

Table 2. HRGC/HRMS conditions

Instrument:	SHIMADZU GC14A／KRATOS CONCEPT 32 1S			
GC column:	DB-5(J&W) 60m(length) X 0.32mm(i.d.), 0.25μm(film)			
column temp.:	150℃1min, 10℃/min to 180℃, 3℃/min to 290℃			
ion source:	dedicated EI ion source, positive			
source temp.:	270℃			
interface temp.:	295℃	masses	native	$^{13}C_{12}$-labelled
ionization voltage:	35～40 eV	TeCBs	289.9224, 291.9195	301.9626, 303.9597
trap current:	500 μA	PeCBs	325.8805, 327.8776	337.9207, 339.9178
accel. voltage:	8000 V	HxCBs	359.8415, 361.8386	371.8817, 373.8788
resolution:	10,000(10% valley)	HpCBs	393.8025, 395.7996	

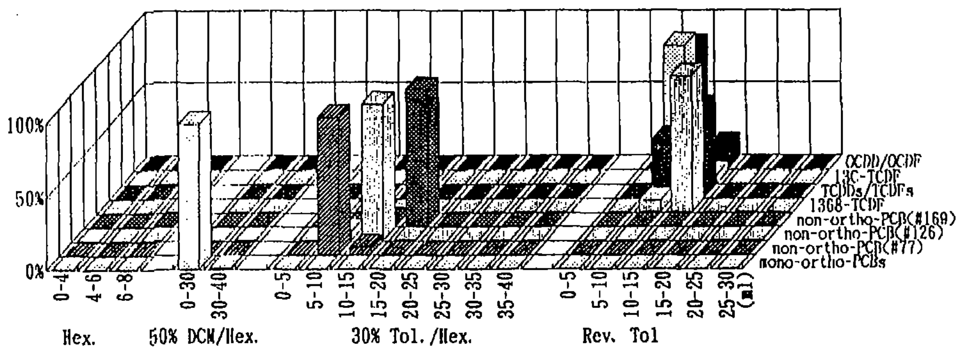

Figure 2. Elution profiles of mono-ortho, non-ortho-PCBs and PCDDs/PCDFs on HPLC PGC column.

Figure 3-1.
mono & non-ortho-PCBs standard

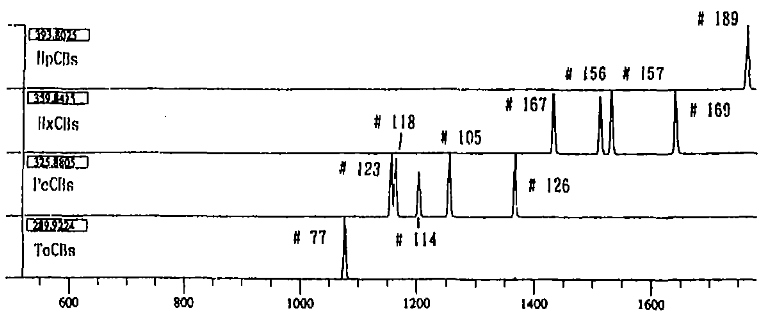

Figure 3-1～5. HR-SIM chromatograms for PCBs(tetra～hepta)

Figure 3-2.
Alumina
5% dichloromethane/
hexane Fr.

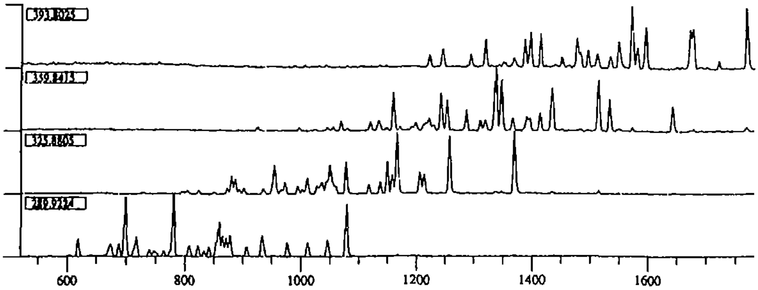

Figure 3-3.
HPLC PGC
hexane Fr.

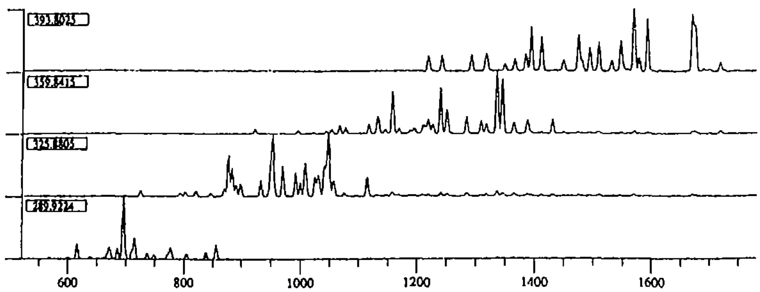

Figure 3-4.
HPLC PGC
50% dichloromethane/
hexane fraction

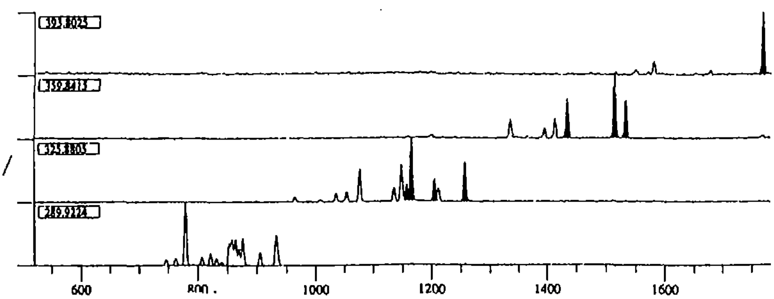

Figure 3-5.
HPLC PGC
30% toluene/hexane
fraction