DL-PCBs AND PCDD/Fs ANALYSIS BY HRGC/QITMS/MS

Cobo M[1], López A[1], Aristizábal B[1], Montes de Correa C[1], Avalos M[2], Abad E[2], Rivera J[2]
[1]Universidad de Antioquia, Environmental Catalysis Group, Medellín-Colombia; [2]Dept. of Ecotechnologies, CID-CSIC, Jordi Girona 18-26, Barcelona-08034, Spain

Abstract
The simultaneous analysis of polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) in fly ash samples from a urban colombian incinerator was performed by HRGC/QIMS/MS. Specifically 29 target compounds were characterized, seventeen 2,3,7,8-PCDDs/Fs, four no-ortho PCBs and eight mono-ortho PCBs which configure the so called dioxin-like-PCBs (DL-PCBs). High WHO-TEQ values and a very low contribution of DL-PCBs congeners were obtained.

Introduction
Dioxins and DL-PCBs are a group of structurally related chemicals which persist in the environment, bio accumulate in the food chain and are toxic. Since they have similar mechanisms of toxicity are grouped together when considering potential risks, even though they originate from different sources [1]. Dioxins and DL-PCBs are a global problem. They may undergo long-range environmental transport, moving from warmer to colder climates through air and other media, so, actions to control them are necessary at an international level. Recently, PCDD/Fs emissions from municipal solid waste incinerators in Colombia have been characterized [2]. However, no data on DL-PCBs compounds have been reported.

DL-PCBs are chlorinated compounds with no chlorine atoms in the ortho-positions (coplanar-PCBs, IUPAC Nos. 77, 81, 126 and 169) or with only a chlorine atom in one of the four ortho-positions (mono-ortho-PCBs, IUPAC Nos. 105, 114, 118, 123, 156, 157, 167 and 189) [3]. These compounds are present at lower concentrations than PCDD/Fs and matrix treatment must assure acceptable recovery yields. Several cleanup processes have been reported [3-5]. Automatic devices have often been used for extract purification and instrumental analysis has been based on the use of high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC–HRMS). In this work, a manual cleanup procedure and HRGC/QITMS/MS were evaluated for characterizing dioxins and DL-PCBs. Measurement of recovery percents of ^{13}C-labelled compounds in each column with different solvents was determined to assess test method performance.

Materials and methods

Establishment of cleanup procedure
In order to establish an adequate cleanup procedure for PCDD/Fs and DL-PCBs analysis, known amounts of ^{13}C-labelled PCBs (WP-LCS standard from Wellington Labs., Canada) were added to the top of the respective column and eluted with different solvents. Table 1 lists the type of column and elusion solvent used for obtaining each fraction. Obtained fractions (F1-F7) were concentrated, transferred to vials and spiked with EPA1613-ISS and WP-ISS standards for final injection to HRGC-QITMS/MS.

Table 1. Extracts from silica, florisil and alumina column elusions

Column	Silica	Florisil		Alumina			
Extract	**F1**	**F2**	**F3**	**F4**	**F5**	**F6**	**F7**
Solvent	Hxn	Hxn	Toluene:ether 90:10	Hxn	Hxn:Dcm 98:2	Hxn:Dcm 50:50	Dcm
Volume (ml)	170	250	170	25	25	50	50

Dcm: Dichloromethane, Hxn: Hexane

Sample treatment

Fly ash samples were collected from a bag filter in a local incineration plant (Medellín-Colombia). A four- gram solid sample was labeled with EPA1613-LCS and WP-LCS standards. Then, it was acid digested with 30 ml of 1M HCl during 2 h, for releasing PCDD/Fs, water washed and dried for 12 h. Afterwards, sample was soxhlet extracted with toluene during 48 h, roto evaporated and cleaned-up by liquid-solid adsorption chromatography at atmospheric pressure using glass columns filled with acidic/basic silica gel, florisil and basic alumina as adsorbents. The sample cleanup procedure is outlined in figure 1.

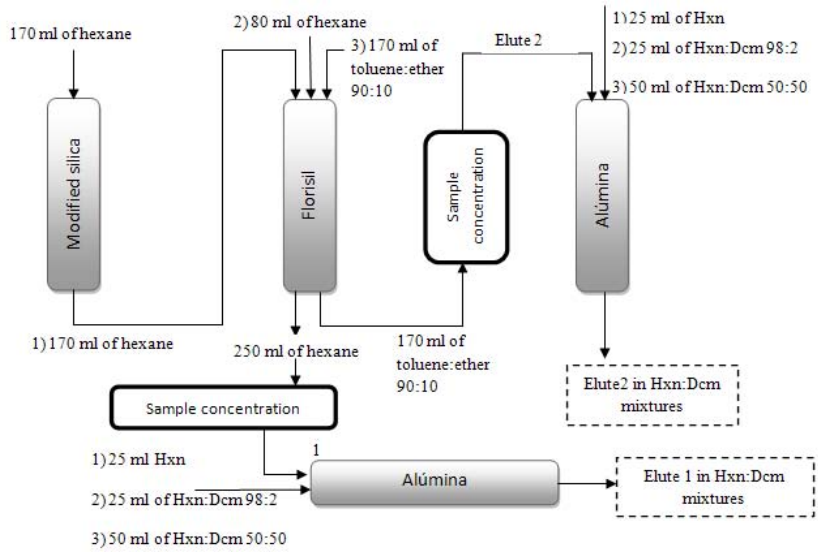

Figure 1. Cleanup procedure for simultaneous analysis of PCDD/Fs and DL-PCBs

HRGC-QITMS/MS measurements

Samples were analyzed by high resolution gas chromatography coupled to ion-trap low resolution mass spectrometry- (HRGC-QITMS/MS) in a Varian CP-3800 GC equipped with an 8400 auto sampler and coupled to a Saturn 2000 ion-trap spectrometer. Specific conditions for dioxin and furan analysis have been previously reported [2] using a DB-5MS column (60 m x 0.25 mm I.D., 0.25 µm film thickness). The optimum MS/MS parameters were found for each DL-PCB congener group.

Quantification

Quantification of dioxins, furans and DL-PCBs were performed using the isotope dilution method. Relative Response Factors (RRFs) were determined using calibration standards for PCDD/Fs and DL-PCBs analysis (EP1613-CS and WP-CS solutions from Wellington Labs., Canada). Recovery percent of ^{13}C-labelled compounds was calculated from area comparison between LCS and ISS compounds. Toxic equivalents (WHO-TEQ) were determined using WHO-TEF factors.

Results and discussion

Establishment of cleanup procedure

Recovery percent of DL-PCBs congeners for each elution fraction are shown in table 2. Fraction 1 yields acceptable recovery percents, indicating that most DL-PCBs congeners were eluted in the first step of the cleanup process. When florisil column was eluted with hexane (F2) most PCBs were recovered, however PCB 169 was retained and PCB 126 was only partially eluted. EPA1668A method [6] indicates that only mono-ortho chlorinated PCBs can be eluted from florisil with hexane. Nevertheless, in our experiments we observed elution of some no ortho-chorinated PCBs congeners in fraction 2. Fraction 3 obtained by using 170 ml of toluene:ether 90:10 eluted PCDD/Fs congeners from florisil, but from recovery results, PCB 169 and part of PCB 126 must also be analyzed in this fraction. First hexane elusion from alumina column did not contain any PCB congener

(F4) but both 98:2 and 50:50 hexane: dichloromethane mixtures draw most compounds at different proportions (F5 and F6, respectively). Last fraction (F7) did not contain any PCB congener.

Table 2. Recovery percent of dioxin-like PCBs congeners (%)

	Column	Silica	Florisil		Alumina		
	Extract	**F1**	**F2**	**F3**	**F4**	**F5**	**F6**	**F7**
%Recovery	**PCB 81**	71,73	90,45	0	0	0	78,69	0
	PCB 77	73,14	95,02	0	0	0	84,23	0
	PCB 123	73,14	68,00	0	0	38,97	0	0
	PCB 118	69,85	69,08	0	0	41,50	0	0
	PCB 114	69,09	62,58	0	0	36,15	0	0
	PCB 105	65,06	65,41	0	0	20,40	33,51	0
	PCB 126	61,73	51,22	26,17	0	0	73,75	0
	PCB 167	127,67	98,30	0	0	88,03	0	0
	PCB 156	117,44	100,82	0	0	86,22	0	0
	PCB 157	124,18	100,71	0	0	78,06	0	0
	PCB 169	107,04	0	94,52	0	59,08	26,89	0
	PCB 189	62,90	101,08	0	0	80,78	0,00	0

Note: PCBs 81, 77, 126, 169 are no-ortho chlorinated PCBs congeners.

Dioxin, furan and DL-PCB in fly ash samples

The cleanup procedure outlined in figure 1 allowed us to analyze dioxins, furans and DL-PCBs in fly ash samples. The first elute with mono-ortho PCBs 105, 114, 118, 123, 156, 157, 167 and 189, and no-ortho 77 and part of 126 was obtained from silica and florisil columns. The second elute with no-ortho PCBs 169, part of 126 and PCDD/Fs congeners was recovered from 90:10 toluene-ether elution from florisil column. Either elute was purified through an alumina column using hexane-dichloromethane mixtures. Afterwards, the first elute was spiked with WP-ISS standard and the second one with a mixture of EPA1613-ISS and WP-ISS standards. Then, both fractions were independently injected to GC/MS for DL-PCBs analysis. PCDD/Fs concentrations were obtained by injecting samples of the second fraction. Table 2 shows the results of dioxins and DL-PCBs concentrations, as well as recoveries percent. The method used allowed us to simultaneously determine DL-PCBs congeners in fly ash samples with acceptable compound recovery. High values of WHO-TEQ from PCDD/Fs compounds (upper 180 ng/g) and low values of DL-PCBs congeners (1,2 ng/g) were found. The pattern for DL-PCBs is similar to that previously reported for fly ash and gas stack emissions samples from incineration plants [5].

Table 3 Dioxins, furans and dl-PCBs contents in a fly ash sample

COMPOUND	Conc. Pg/g	WHO-TEF	WHO-TEQ pg/g	Recovery (%)
DIOXINS				
"2378-TCDD"	4594.083	1.000	4594.083	55.208
"12378-PCDD"	38413.608	1.000	19206.804	49.492
"123478-HxCDD"	19007.996	0.100	1900.800	116.412
"123678-HxCDD"	19892.572	0.100	1989.257	116.548
"123789-HxCDD"	20532.510	0.100	2053.251	NA
"1234678-HpCDD"	255722.246	0.010	2557.222	30.978
"OCDD"	80234.342	0.0001	80.234	71.621
Total PCDD	**438397.356**		**32381.651**	

FURANS				
"2378-TCDF"	32118.486	0.100	3211.849	58.474
"12378-PCDF"	105066.783	0.050	5253.339	105.670
"23478-PCDF"	155782.213	0.500	77891.106	56.535
"123478-HxCDF"	150518.641	0.100	15051.864	88.631
"123678-HxCDF"	196330.341	0.100	19633.034	67.235
"234678-HxCDF"	161756.048	0.100	16175.605	85.982
"123789-HxCDF"	35787.900	0.100	3578.790	100.642
"1234678-HpCDF"	1198608.323	0.010	11986.083	33.506
"1234789-HpCDF"	109793.091	0.010	1097.931	104.395
"OCDF"	990457.419	0.0001	990.457	70.349
Total PCDF	**3136219.244**		**154870.059**	
TOTAL WHO-TEQ PCDD/Fs (pg/g)			**187251.710**	
DL-PCBs				
"PCB 81"	1563.352	0.00010	0.156	69.740
"PCB 77"	5990.189	0.00010	0.599	53.597
"PCB 123"	198.550	0.00010	0.020	80.893
"PCB 118"	1728.697	0.00010	0.173	75.230
"PCB 114"	349.175	0.00050	0.175	70.446
"PCB 105"	1911.373	0.00010	0.191	69.207
"PCB 126"	11882.521	0.10000	1188.252	33.658
"PCB 167"	1526.157	0.00001	0.015	65.486
"PCB 156"	4088.597	0.00050	2.044	77.160
"PCB 157"	2478,486	0.00050	1.239	77.778
"PCB 169"	6738.051	0.01000	67.381	78.098
"PCB 189"	5826.383	0.00010	0.583	87.403
Total DL- PCBs	**44281.532**		**1260.828**	
TOTAL WHO-TEQ (pg/g)			**188512,538**	

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