

## STRATEGY FOR THE ANALYSIS OF PCDD/Fs AND DL-PCBs IN FLY ASHES AND EMISSIONS FROM STATIONARY SOURCES.

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### Abstract

The analysis of PCDD/Fs and DL-PCBs in emissions and solid residues from incinerators will be mandatory in the near future. European standard EN-1948 is being updated adding the 12 DL-PCBs to the 17 2,3,7,8-PCDD/F congeners. Therefore, a comprehensive method covering such 29 compounds has to be developed or broaden the existing PCDD/F analytical procedure including the DL-PCBs. In this sense, this work opted for the latter approach modifying the PCDD/F methodology particularly in the fractionation step to have Dioxins and DL-PCBs in separate fractions ready to be injected in the HRGC/HRMS system. Results obtained from the analysis of different fly ashes proved that the methodology is appropriate for the determination of these compound families according to the new European standard EN-1948.

### Introduction

EN1948 European standard is being updated and will include a new Part 4 concerning the determination of dioxin-like PCBs (DL-PCBs: PCB-77, PCB-81, PCB-105, PCB-114, PCB-118, PCB-123, PCB-126, PCB-156, PCB-157, PCB-167, PCB-169, PCB-189). As a result, analysis laboratories will need a comprehensive strategy for the analysis of such compounds together with the PCDD/Fs.

The lack of stack emission reference material makes the fly ash the most appropriate matrix to validate an analytical method for the determination of PCDD/Fs and DL-PCBs in emissions from stationary sources. Typically, the same interferences are present in both matrices and therefore a similar analytical strategy would be suitable for that purpose.

Frequently DL-PCBs are analyzed separately from PCDD/Fs or although being extracted simultaneously the fractionation and clean-up of the extract have not always been performed optimizing the overall analysis time. Usually, PCDD/F and coplanar PCBs (PCB-77, PCB-81, PCB-126, PCB-169) behave in a similar way during the fractionation and clean-up procedures and as a consequence they are collected in the same fraction, while the mono-ortho PCBs occur in another fraction. This fact makes the analysis time even longer than it is, since it is necessary to do three HRGC-HRMS determination per sample.

In this work an exhaustive simultaneous extraction of PCDD/Fs and DL-PCBs is proposed followed by a clean-up and fractionation scheme where PCDD/Fs are collected in a fraction separated from DL-PCBs and the latter can be analyzed by means of a single injection in an HRGC-HRMS system.

### Material and Methods

Fly ash samples were spiked with a 15 <sup>13</sup>C- PCDD/F mixture (EPA-1613LCS, Wellington Laboratories, Canada) and 12 <sup>13</sup>C- DL-PCBs mixture (WP-LCS, Wellington Laboratories, Canada). Two hours later spiked samples were digested with 3M HCl and in a permanent stirring and slight temperature for two hours. The solid fraction of the digested samples was separated from the supernatant by centrifugation and was Soxhlet extracted with toluene for 48h (2 x 24 h). A dicloromethane liquid-liquid extraction was carried out to the supernatant and this extract was mixed with the Soxhlet one.

The clean-up procedure consists of a sequential array of the three different Teflon preppacked columns: multilayer silica, alumina and PX-21 carbon adsorbents, respectively (FMS Inc, Boston, USA)<sup>1</sup> In this case, a eluants modification in the alumina column was introduced in order to perform a fractionation where all DL-PCBs could

be collected in a single fraction. For this purpose, the fraction 98:2 (hexane: dichloromethane) was substituted by a 90:10 (hexane: dichloromethane).

Instrumental PCDD/F analyses were performed on a Agilent gas chromatograph fitted with a DB-5ms (40m x 0.18 mm i.d. x 0.18µm film thickness) fused silica column (J&W Scientific, CA, USA) connected through a heated transfer line kept at 280°C to a Waters AutoSpec Ultima NT high resolution mass spectrometer<sup>2</sup> operated in SIM mode at 10 000 resolving power (10% valley definition) and using the isotopic dilution as the quantification method. DL-PCBs were analyzed in the same HRGC/HRMS system but using a DB-XLB fused silica column (60m x 0.25 mm i.d. x 0.25 µm film thickness) from J&W Scientific. CP-SIL 88 and DB-5 columns were also used to resolve the target compound the DB-5ms couldn't.

## Results and Discussion

In order to test the procedure previously described, it was indispensable to facing the lack of fly ash with certified values for PCDD/Fs and DL-PCBs. So, two steps were necessary to validate the methodology. First, the Certified Reference Material (CRM) number 615 was used for the dioxin analysis. The results showed in Table 1 were obtained after running the sample through three different columns (DB-5ms, CP-SIL 88, and DB-5). Typical coelution occurred in DB-5ms, which was not able to resolve the 2,3,4,7,8-PeCDF and 1,2,3,7,8,9-HxCDF from interferences found in samples related to combustion process. The analysis of the CRM-615 using the methodology proposed here reveals very good results since the target compound concentration have been found to be in the certified range (table 1).

Table 1. Analysis of CRM-615 using the proposed analytical procedure (n=5).

	concentration			v. ref. pg/g	Uncertainty pg/g
	pg/g	SD	RSD		
<b>2,3,7,8-TCDF</b>	87.34	12.99	14.87	86	28
<b>1,2,3,7,8-PeCDF</b>	148.19	20.58	13.89	176	26
<b>2,3,4,7,8-PeCDF</b>	124.980	5.796	4.638	125	20
<b>1,2,3,4,7,8-HxCDF</b>	198.60	18.31	9.22	203	21
<b>1,2,3,6,7,8-HxCDF</b>	209.89	16.46	7.84	204	23
<b>2,3,4,6,7,8-HxCDF</b>	138.631	12.131	8.751	130	15
<b>1,2,3,7,8,9-HxCDF</b>	16.297	1.274	7.820	13.3	2
<b>1,2,3,4,6,7,8-HpCDF</b>	679.53	47.18	6.94	750	90
<b>1,2,3,4,7,8,9-HpCDF</b>	55.17	2.94	5.32	61	6
<b>OCDF</b>	250.24	26.97	10.78	290	40
<b>2,3,7,8-TCDD</b>	31.89	4.90	15.37	27	5
<b>1,2,3,7,8-PeCDD</b>	103.58	8.02	7.74	92	12
<b>1,2,3,4,7,8-HxCDD</b>	75.20	10.44	13.89	74	12
<b>1,2,3,6,7,8-HxCDD</b>	109.56	7.23	6.60	103	13
<b>1,2,3,7,8,9-HxCDD</b>	120.68	16.12	13.36	108	16
<b>1,2,3,4,6,7,8-HpCDD</b>	808.78	92.08	11.39	870	130
<b>OCDD</b>	1719.82	318.95	18.55	1750	200

The second step for the validation of this methodology was to analyze DL-PCBs in fly ash samples. A participation in an interlaboratory exercise was used for that purpose (Table 2). As it can be seen in table 2, the results obtained present a z-score lower than  $\pm 2$  for all cases but PCB-156 in the hazardous waste incinerator fly

ash. This fact could be caused by a coelution with the PCB-172<sup>3</sup>. In the same way, good or very good recovery rates were obtained for the congeners analyzed in both fly ashes.

Table 2 Results of the DL-PCBs analysis in fly ash samples in the frame of an interlaboratory exercise.

<b>Hazardous Waste Incinerator Fly ash</b>				
<b>Compunds</b>	Mean n=2		Exercise	z-score
	concentration ng/g	Recovery C <sup>13</sup> (%)	average value ng/g	
PCB #77	0.086	69	0.064	1.51
PCB #81	0.039	69	0.035	1.02
PCB #105	0.117	60	0.078	1.
PCB #114	0.020	61	0.016	1.22
PCB #118	0.304	64	0.162	1.41
PCB #123	0.043	63	0.021	1.63
PCB #126	0.079	56	0.071	0.52
PCB #156	0.088	82	0.042	7.42
PCB #157	0.033	79	0.026	1.35
PCB #167	0.039	82	0.026	1.56
PCB #169	0.040	76	0.031	0.46
PCB #189	0.041	75	0.037	1.63
<b>Sampling Stnd.</b>				
<sup>13</sup> C PCB #60		108		
<sup>13</sup> C PCB #127		97		
<sup>13</sup> C PCB #159		107		
<b>Municipal Solid Waste Incinerator Fly ash</b>				
<b>Compunds</b>	Mean n=2		Exercise	z-score
	concentration ng/g	Recovery C <sup>13</sup> (%)	average value ng/g	
PCB #77	4.719	86	4.63	0.92
PCB #81	0.840	85	0.81	0.75
PCB #105	1.957	71	1.90	0.54
PCB #114	0.438	70	0.47	-0.01
PCB #118	1.763	73	1.91	0.01
PCB #123	1.291	73	0.65	1.48
PCB #126	5.108	67	5.10	0.33
PCB #156	2.621	90	2.48	0.98
PCB #157	1.286	90	1.24	0.72
PCB #167	1.027	91	1.02	0.49
PCB #169	2.082	87	2.10	0.29
PCB #189	2.186	87	2.07	0.7
<b>Sampling Stnd</b>				
<sup>13</sup> C PCB #60		102		
<sup>13</sup> C PCB #127		102		
<sup>13</sup> C PCB #159		106		

The final step of this work was to apply the analytical procedure to real samples. PCDD/Fs and PCBs were analyzed in another two fly ashes (Table 3). Recovery rates were satisfactory in all cases ranging from 78 to 102 in the HWI fly ash and 64 to 93 in MSWI fly ash.

Table 3 Application of the method to another two fly ash samples

PCDD/Fs	HWI Fly ash		MSWI Fly ash	
	Mean (n=2)		Mean (n=2)	
	concentration ng/g	Recovery C <sup>13</sup> (%)	concentration ng/g	Recovery C <sup>13</sup> (%)
2,3,7,8-TCDF	0.218	85	0.150	85
1,2,3,7,8-PeCDF	0.415	92	0.192	93
2,3,4,7,8-PeCDF	0.770	91	0.193	90
1,2,3,4,7,8-HxCDF	0.979	80	0.210	81
1,2,3,6,7,8-HxCDF	1.277	79	0.215	82
2,3,4,6,7,8-HxCDF	2.323	78	0.199	78
1,2,3,7,8,9-HxCDF	0.083	84	0.016	84
1,2,3,4,6,7,8-HpCDF	6.675	85	0.539	82
1,2,3,4,7,8,9-HpCDF	0.834	85	0.085	86
OCDF	4.996	n.p.	0.228	n.p.
2,3,7,8-TCDD	0.027	86	0.025	87
1,2,3,7,8-PeCDD	0.142	95	0.056	93
1,2,3,4,7,8-HxCDD	0.166	81	0.044	81
1,2,3,6,7,8-HxCDD	0.264	81	0.082	81
1,2,3,7,8,9-HxCDD	0.217	n.p.	0.061	n.p.
1,2,3,4,6,7,8-HpCDD	2.637	85	0.679	87
OCDD	8.758	81	1.588	83
PCB-81	0.078	101	0.046	64
PCB-77	0.2	102	0.056	64
PCB-126	0.237	87	0.044	64
PCB-169	0.117	91	0.020	80
PCB-123	0.096	78	0.035	68
PCB-118	0.306	80	0.215	67
PCB-114	0.033	80	0.031	67
PCB-105	0.211	82	0.098	64
PCB-167	0.061	83	0.026	84
PCB-156	0.161	82	0.062	80
PCB-157	0.098	81	0.022	80
PCB-189	0.133	94	0.034	74

The analytical procedure presented in this work proved to be appropriate for the simultaneously analysis of PCDD/Fs and DL-PCBs allowing the Laboratories to have an effective tool for the implementation of the coming upgraded EN-1948 European Standard.

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### References

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