Results from the Second Round of the International Intercalibration Study on PCDDs, PCDFs and planar PCBs in a Fly Ash Extract

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1. Introduction

PCDDs and PCDFs are known to be present on municipal solid waste incinerator fly ash and flue gases since the end of the seventies [1]. Nowadays many governments around the world have strict regulation for the emission of such compounds to the environment. Most regulations apply the TEQ concept in which the different PCDDs and PCDFs are given a toxicity factor relative to the most toxic dioxin 2,3,7,8-TCDD [2]. Recently toxic equivalent factors for the three planar PCBs, IUPAC number #77, #126 and #169 were also established. These PCBs were also found to be present in the emission of municipal waste incinerators by several authors in the end of the eighties [3].

In order to control the analytical performance of different laboratories an intercalibration study was conducted among laboratories which perform dioxin analyses around the world. This study, of which the first round took place in 1993/94, was reported upon at Dioxin'94. In the first round nine laboratories participated. For the second round more than 30 laboratories showed interest to participate. This showed that there is a large interest in comparing analytical results by means of an intercalibration study. This kind of comparison studies among analytical laboratories allow QA/QC, when performed on a regular basis and if organised globally, make it possible to compare the reported emission levels of the different countries in a more accurate way.

In the second round of the International Intercalibration six fly ash extracts were distributed to 30 participants and all laboratories were asked to report the TEQs, all 2,3,7,8-substituted dioxins and furans (17), the three planar PCBs (#77, #126, #169) plus the total dioxin and furan levels at each chlorination level. All participants were encouraged to submit results by electronic mail, which would avoid laborious entering of the results in a data base and this way reducing the time between analysis and the evaluation of the results.

2. Experimental

100 grams of fly ash (MSWI Ålidhem, Umeå, Sweden) was soxhlet extracted with toluene in portions of 10 gram. All extracts were combined and the total volume was reduced to 100 mL, from this two dilutions were made. In this way three extract were obtained extract A , the undiluted fly ash extract, extract B the diluted fly ash extract and extract C which was fortified with the different compounds mentioned in Table 1. Aliquots of 1 mL of the extracts in toluene, were transferred to glass ampoules and weighed. The glass ampoules were sealed in a flame and their weight was established again.

Each participant received 3 ampoules at two different times, the first batch containing an ampoule with extract A and two times an ampoule with extract B. The second batch, distributed two months later, contained one ampoule with extract and two ampoules with extract C. All laboratories were asked to report the amounts of 2,3,7,8- substituted dioxin and furan isomers, the three planar PCBs, the I-TEQs and the total PCDFs and PCDDs at each chlorination level. The participants were advised to use two different GC columns, i.e. one with a polar and one with a non-polar stationary phase. All laboratories used their own internal standards and clean up procedures.

PCDF		PCDD	
2,3,7,8-TCDF	1.8 ng	2,3,7,8-TCDD	0.1
2,3,4,8-TCDF	1.8 ng	1,2,3,7,8-PeCDD	0.1
1,2,3,7,8-PeCDF	1.8 ng	1,2,3,4,7,8-HxCDD	0.1
2,3,4,7,8-PeCDF	1.8 ng	1,2,3,6,7,8-HxCDD	0.1
1,2,3,4,8-PeCDF	1.8 ng	1,2,3,7,8,9-HxCDD	0.1
1,3,4,8,9-PeCDF	1.8 ng	1,2,3,4,6,7,8-HpCDD	0.1
1,2,3,4,7,8-HxCDF	1.8 ng	OCDD	0.1
1,2,3,6,7,8-HxCDF	1.8 ng	1,2,3,7/1,2,3,8-TCDD	1.4
1,2,3,7,8,9-HxCDF	1.8 ng		
2,3,4,6,7,8-HxCDF	1.8 ng	PCB	
1,2,3,4,6,7-HxCDF	1.8 ng	PCB #77	3
1,2,3,6,7,8-HxCDF	1.8 ng	PCB #110	3
1,2,3,4,6,7,8-HpCDF	1.8 ng	PCB #126	3
1,2,3,4,7,8,9-HpCDF	1.8 ng	PCB #128	3
OCDF	1.8 ng	PCB #169	3

Table 1. Fortification levels of extract C

3. Results

25 of 30 participating laboratories were able to report before the set dead line, two more participants reported after their dead line had expired. The results of these two laboratories will be included in the final report of the intercalibration results, but are not included in the results presented here. The average, mean, minimum, maximum, standard deviation and the percentual standard deviation are given in Table 2. Selecting the 21 best results from a total of 25 participants, the results are very good with a relative standard deviation of 11 %, 15% and 12 % for the TEQs of extract A, B and C respectively. It should however be considered that the TEQs are a weighed mean of the summation of the results of the 17 PCDD and PCDF congeners and the 3 planar PCBs. The relative standard deviation for the most toxic dioxin, 2,3,7,8-TCDD, is still around 30 %. Five participants were not able to analyse the three planar PCBs, but the result of the other laboratories with a relative standard deviation between 20 and 30 % is promising for this newly included compound class. The participants who ran samples on two different columns did not experience any problems with the fortifications of interfering non 2,3,7,8-substituted congeners.

Table 2. The results of the intercalibration on a fly ash extract.

Fly Ash Extract A
(Statistics of the results of the 21 best results out of total of 25)

	Average	Median	Min	Max.	RSD	%RSD
2,3,7,8-TeCDD	0.049	0.043	0.026	0.125	0.019	39
1,2,3,7,8-PeCDD	0.23	0.23	0.11	0.40	0.05	22
1,2,3,4,7,8-HxCDD	0.36	0.34	0.26	0.59	0.08	23
1,2,3,6,7,8-HxCDD	0.97	0.93	0.74	1.61	0.18	19
1,2,3,7,8,9-HxCDD	0.64	0.57	0.40	1.20	0.20	31
1,2,3,4,6,7,8-HpCDD	9.1	8.9	7.2	13.5	1.2	13
OCDD	18.9	19.0	8.4	33.1	4.3	23
2,3,7,8-TeCDF	0.24	0.21	0.14	0.57	0.09	39
1,2,3,7,8-PeCDF	0.63	0.55	0.39	1.00	0.18	28
2,3,4,7,8-PeCDF	0.77	0.76	0.58	1.12	0.13	16
1,2,3,4,7,8-HxCDF	1.2	1.1	0.8	2.4	0.3	29
1,2,3,6,7,8-HxCDF	1.3	1.2	0.9	2.2	0.2	18
1,2,3,7,8,9-HxCDF	0.22	0.18	0.10	0.77	0.15	66
2,3,4,6,7,8-HxCDF	1.4	1.4	0.4	2.2	0.3	21
1,2,3,4,6,7,8-HpCDF	4.6	4.6	3.0	6.4	0.7	16
1,2,3,4,7,8,9-HpCDF	0.9	1.0	0.2	1.4	0.2	20
OCDF	4.6	4.7	2.0	6.9	1.0	23
PCB #77	0.39	0.38	0.21	1.09	0.14	35
PCB #126	0.59	0.62	0.13	0.80	0.13	23
PCB #169	0.40	0.41	0.24	0.66	0.10	24
TEQ	**1.4**	**1.4**	**1.2**	**1.9**	**0.2**	**11%**

Fly Ash Extract B
(Statistics of the results of the 21 best results out of total of 25)

	Average	Median	Min	Max.	RSD	%RSD
2,3,7,8-TeCDD	0.014	0.013	0.008	0.03	0.005	35
1,2,3,7,8-PeCDD	0.07	0.07	0.02	0.14	0.02	34
1,2,3,4,7,8-HxCDD	0.11	0.10	0.04	0.30	0.04	40
1,2,3,6,7,8-HxCDD	0.28	0.27	0.14	0.40	0.06	21
1,2,3,7,8,9-HxCDD	0.19	0.20	0.03	0.35	0.07	35
1,2,3,4,6,7,8-HpCDD	2.6	2.5	2.0	4.2	0.5	18
OCDD	5.7	5.4	2.9	12.8	1.6	28
2,3,7,8-TeCDF	0.07	0.06	0.03	0.13	0.02	34
1,2,3,7,8-PeCDF	0.18	0.18	0.11	0.39	0.06	32
2,3,4,7,8-PeCDF	0.23	0.22	0.14	0.40	0.06	25
1,2,3,4,7,8-HxCDF	0.3	0.3	0.2	0.7	0.1	27
1,2,3,6,7,8-HxCDF	0.4	0.3	0.3	0.6	0.1	18
1,2,3,7,8,9-HxCDF	0.07	0.05	0.02	0.39	0.07	100
2,3,4,6,7,8-HxCDF	0.5	0.4	0.3	1.3	0.2	35
1,2,3,4,6,7,8-HpCDF	1.3	1.3	0.8	3.1	0.3	27
1,2,3,4,7,8,9-HpCDF	0.3	0.3	0.1	0.5	0.1	27
OCDF	1.3	1.3	0.7	3.6	0.4	34
PCB #77	0.10	0.11	0.02	0.17	0.03	33
PCB #126	0.17	0.17	0.04	0.25	0.04	26
PCB #169	0.12	0.12	0.03	0.30	0.05	44
TEQ	**0.4**	**0.4**	**0.3**	**0.5**	**0.1**	**15%**

Table 2. Continued

Fly Ash Extract C (Statistics of the results of the 21 best results out of total of 25)	Average	Median	Min	Max.	RSD	%RSD
2,3,7,8-TeCDD	0.161	0.150	0.095	0.312	0.043	27
1,2,3,7,8-PeCDD	0.22	0.22	0.14	0.30	0.04	18
1,2,3,4,7,8-HxCDD	0.23	0.22	0.12	0.60	0.07	32
1,2,3,6,7,8-HxCDD	0.39	0.39	0.29	0.57	0.06	14
1,2,3,7,8,9-HxCDD	0.34	0.34	0.26	0.46	0.06	18
1,2,3,4,6,7,8-HpCDD	2.1	2.1	1.7	2.5	0.2	10
OCDD	4.3	4.1	2.1	7.6	1.0	22
2,3,7,8-TeCDF	2.14	2.01	1.40	5.13	0.71	33
1,2,3,7,8-PeCDF	2.43	2.26	1.80	3.40	0.47	19
2,3,4,7,8-PeCDF	2.17	2.05	1.26	3.23	0.42	19
1,2,3,4,7,8-HxCDF	2.2	2.1	1.4	3.2	0.4	17
1,2,3,6,7,8-HxCDF	2.3	2.2	1.5	3.4	0.4	17
1,2,3,7,8,9-HxCDF	1.76	1.73	0.78	2.30	0.25	14
2,3,4,6,7,8-HxCDF	2.1	2.1	1.4	2.7	0.3	14
1,2,3,4,6,7,8-HpCDF	2.7	2.7	1.7	4.1	0.4	17
1,2,3,4,7,8,9-HpCDF	1.8	1.9	0.3	2.7	0.4	24
OCDF	1.0	1.1	0.6	1.7	0.3	25
PCB #77	3.76	3.69	1.80	6.32	0.91	24
PCB #126	3.30	3.50	1.09	4.79	0.71	22
PCB #169	3.38	3.18	2.10	6.84	1.00	30
TEQ	**3.0**	**3.0**	**2.3**	**3.8**	**0.4**	**12%**

4. Conclusion

The second round of the International Intercalibration showed good agreement in the analysis of the TEQs of 3 different fly ash extract between laboratories around the world. The results of the inter-calibration indicated analytical problems for some of the participants, but confirmed the analytical capacity of most of the laboratories. The RSD of the TEQ was below 15% comparing the results of the 21 best performing laboratories out of a total of 25.

The results encourage the organising committee to organise a third round of the studies in order to ensure a continues means of QA/QC for the participants of the first and second round as well as for new participants in 1997/98. The organising committee is also planning an intercalibration on a sewage sludge and sediment samples in 1996/97. At the moment it seems that the PCDD and PCDF problems for sewage sludge have not been completely recognized.

5. Acknowledgement

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Table 3. Participants in the second round of the International Intercalibration.

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6. References

1. Olie K., P.L. Vermeulen, and O. Hutzinger (1977): PCDDs and PCDFs are trace compounds of fly ash and flue gas of some municipal incinerators in The Netherlands. Chemosphere **8**, 455-459.
2. Safe S. (1990): PCBs, PCDDs PCDFs and related compounds: Environmental and mechanistic considerations which support the development of TEFs. CRC Crit. Rev. Toxicol. **21**, 51-88.
3. Sakai S., M. Hiraoka, N. Takeda and K. Shiozaki (1993): Coplanar PCBs and PCDDs/PCDFs in municipal waste incineration. Chemosphere **27**, 233-240.