Results from the Third Round of the International Intercalibration Study on PCDDs, PCDFs and planar PCBs: Part 1 Incineration.

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Introduction

For the third time an international intercalibration study was organised on the determination of PCDDs, PCDFs and planar PCBs in incineration samples. Several new extraction techniques for example SFE, ASE and micro wave assisted extraction have been introduced recently for the analysis of PCDDs, PCDF and PCBs from solid matrices. In the first two studies several fly ash extracts were distributed. This time also three 'real' fly ash samples were distributed in addition to three extracts and a standard solution.

Material and Methods

The participants received three fly ash samples, three incineration related extracts and a standard solution at two different times. Fly ash A and B came from the same batch and contained relatively high amounts of lime, fly ash C contained no lime. The extracts (D, E, and F) originated from a combined extract but different interference's (PCB oil, tar oil) were added. All participants were asked to consider the samples as routine samples and use their own extraction and clean up protocols and quantification standards.

Results and Discussion

In total 34 labs participated of which 30 were able to submit the results before the expiration of the set dead line. The results for the best performing labs for the three ash samples are given in Table 1. The inter-laboratory variation between the samples from the same batch (A and B) was small compared to the variation between the different laboratories. The inter-laboratory variation was somewhat larger for the ash samples than for the extracts in this study and extracts distributed in the first and second round. This indicates that extraction is a crucial step in the analysis of PCDDs, PCDFs and planar PCBs for ash samples. The RSD between the 21 best performing labs is reasonable (23%-33%) but leaves room for improvement. As seen in the previous rounds the RSD for 1,2,3,7,8,9-HxCDF is larger than the other 2,3,7,8-substituated congeners. Fragmentation from partly co-eluting hepta isomers might be a cause for this.

Table 1 The results of intercalibration 1 Fly Ash (Part 1)

Fly Ash A
(Statistics of the results of the 22 best performing labs out of a total of 30)

	Average	Median	Min	Max	RSD	%RSD
2,3,7,8-TeCDD	0.034	0.037	0.011	0.060	0.012	36%
1,2,3,7,8-PeCDD	0.13	0.14	0.04	0.22	0.05	40%
1,2,3,4,7,8-HxCDD	0.16	0.17	0.04	0.23	0.06	39%
1,2,3,6,7,8-HxCDD	0.55	0.62	0.22	0.78	0.19	34%
1,2,3,7,8,9-HxCDD	0.35	0.36	0.13	0.57	0.11	31%
1,2,3,4,6,7,8-HpCDD	5.86	6.18	2.00	9.93	2.07	35%
OCDD	14	16	4.0	23	5.0	38%
2,3,7,8-TeCDF	0.22	0.19	0.05	0.80	0.16	73%
1,2,3,7,8-PeCDF	0.35	0.37	0.09	0.71	0.16	47%
2,3,4,7,8-PeCDF	0.49	0.52	0.02	0.84	0.21	42%
1,2,3,4,7,8-HxCDF	0.61	0.58	0.19	1.40	0.26	43%
1,2,3,6,7,8-HxCDF	0.69	0.71	0.24	1.13	0.23	34%
1,2,3,7,8,9-HxCDF	0.31	0.12	0.02	1.18	0.37	121%
2,3,4,6,7,8-HxCDF	0.83	0.93	0.03	1.49	0.44	54%
1,2,3,4,6,7,8-HpCDF	2.7	2.7	0.8	4.3	0.9	33%
1,2,3,4,7,8,9-HpCDF	0.6	0.7	0.3	1.0	0.2	35%
OCDF	3.1	3.3	1.2	5.1	1.2	38%
PCB #77	0.32	0.23	0.07	0.80	0.21	65%
PCB #126	0.33	0.30	0.15	0.83	0.16	48%
PCB #169	0.25	0.22	0.09	0.52	0.11	43%
TEQ	**0.84**	**0.89**	**0.40**	**1.26**	**0.28**	**33%**

Fly Ash B
(Statistics of the results of the 22 best performing labs out of a total of 30)

	Average	Median	Min	Max	RSD	%RSD
2,3,7,8-TeCDD	0.033	0.037	0.011	0.050	0.012	35%
1,2,3,7,8-PeCDD	0.13	0.15	0.04	0.23	0.05	40%
1,2,3,4,7,8-HxCDD	0.17	0.17	0.05	0.31	0.06	38%
1,2,3,6,7,8-HxCDD	0.57	0.58	0.18	0.83	0.20	34%
1,2,3,7,8,9-HxCDD	0.36	0.36	0.10	0.71	0.14	39%
1,2,3,4,6,7,8-HpCDD	6.06	6.20	1.70	9.20	2.23	37%
OCDD	15	16	3.0	26	6.0	41%
2,3,7,8-TeCDF	0.24	0.19	0.07	0.91	0.17	73%
1,2,3,7,8-PeCDF	0.36	0.34	0.09	0.72	0.17	47%
2,3,4,7,8-PeCDF	0.51	0.54	0.02	0.83	0.21	41%
1,2,3,4,7,8-HxCDF	0.64	0.58	0.14	1.90	0.36	56%
1,2,3,6,7,8-HxCDF	0.72	0.74	0.20	1.14	0.26	36%
1,2,3,7,8,9-HxCDF	0.31	0.13	0.02	1.14	0.37	121%
2,3,4,6,7,8-HxCDF	0.86	1.00	0.03	1.60	0.48	56%
1,2,3,4,6,7,8-HpCDF	2.7	2.8	0.7	4.3	0.9	34%
1,2,3,4,7,8,9-HpCDF	0.7	0.7	0.2	1.1	0.2	35%
OCDF	3.4	3.3	0.8	5.6	1.3	39%
PCB #77	0.31	0.23	0.05	0.70	0.21	66%
PCB #126	0.36	0.32	0.16	0.76	0.17	48%
PCB #169	0.23	0.23	0.05	0.47	0.12	54%
TEQ	**0.89**	**0.94**	**0.35**	**1.28**	**0.28**	**31%**

Table 1 Continued.

Fly Ash C
(Statistics of the results of the 25 best performing labs out of a total of 30)

	Average	Median	Min	Max	RSD	%RSD
2,3,7,8-TeCDD	0.076	0.082	0.027	0.120	0.023	30%
1,2,3,7,8-PeCDD	0.20	0.21	0.07	0.47	0.08	41%
1,2,3,4,7,8-HxCDD	0.16	0.17	0.07	0.22	0.04	28%
1,2,3,6,7,8-HxCDD	0.25	0.25	0.08	0.49	0.09	37%
1,2,3,7,8,9-HxCDD	0.27	0.27	0.12	0.54	0.10	36%
1,2,3,4,6,7,8-HpCDD	2.26	2.27	0.85	3.73	0.77	34%
OCDD	7.0	7.0	3.0	11	2.0	33%
2,3,7,8-TeCDF	0.42	0.32	0.15	1.25	0.30	70%
1,2,3,7,8-PeCDF	0.51	0.52	0.09	0.87	0.19	36%
2,3,4,7,8-PeCDF	0.54	0.56	0.02	0.83	0.18	33%
1,2,3,4,7,8-HxCDF	0.98	0.85	0.29	1.89	0.40	41%
1,2,3,6,7,8-HxCDF	0.89	0.86	0.35	2.26	0.39	43%
1,2,3,7,8,9-HxCDF	0.38	0.13	0.04	1.40	0.48	126%
2,3,4,6,7,8-HxCDF	1.20	1.31	0.03	4.70	0.95	79%
1,2,3,4,6,7,8-HpCDF	4.8	5.0	1.8	6.7	1.3	26%
1,2,3,4,7,8,9-HpCDF	0.5	0.5	0.2	0.8	0.1	28%
OCDF	3.6	3.7	1.4	5.4	1.2	34%
PCB #77	0.20	0.13	0.08	0.86	0.20	98%
PCB #126	0.13	0.12	0.07	0.28	0.05	39%
PCB #169	0.07	0.07	0.03	0.13	0.03	37%
TEQ	**1.02**	**0.99**	**0.54**	**1.39**	**0.23**	**23%**

Conclusions

Intercalibration of 'real' fly ash samples showed somewhat larger variation than fly ash extracts or standard solutions. This indicates that extraction is a crucial step in the analysis of PCDDs, PCDFs and planar PCBs in incineration related samples. The overall results are promising when the results are summarised as TEQ showing a RSD of 23%-33% for the best performing laboratories. The variation for the individual congeners 1,2,3,7,8,9-HxCDF and 2,3,7,8-TCDF is significantly larger. Even though most participants measured the samples on two different GC- columns, with a polar or a non-polar phase. The variance in the results for the planar PCBs, although not reported by all participants, is similar to the results for the PCDDs and PCDFs. The levels of PCBs for incineration samples contribute only marginaly to the total TEQ.

Intercalibration exercises are an essential tool in the assurance of the quality of dioxin analysis. This kind of studies enables laboratories to improve their analytical capacity or confirm their capability. This way data acquired by different laboratories will be directly compatible, both form a scientific and a legislative point of view.

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Table 2. Participants in the third round of the International Intercalibration

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