Results from an International Intercalibration Study on PCDDs and PCDFs in a Fly Ash Extract.

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INTRODUCTION

In order to estimate the reliability of data on the emission of PCDDs and PCDFs from incineration sources an interlaboratory calibration on the analysis of these compounds in a fly ash extract was organised.

Intercalibration studies on PCDDs and PCDFs in different matrices have been organised by a number of organisations. The World Health Organisation coordinated an intercalibration study on PCDDs, PCDFs and PCBs in human milk and human blood showing the difficulties of ultra trace analysis on levels in the low ppt range (TEQ on fat basis)[1-3]. Clement et al.[4] reported on the analysis of an ambient air extract containing 2,3,7,8-TCDD in a concentration of approximately 50 pg per sample and a total PCDD/PCDF concentration of 35 ng. In both studies calibration, internal and recovery standards were supplied by the coordinating organisation. In an intercalibration organised by the BCR[5], a department of the European Union, a raw fly ash extract was used (35 ng/ml 2,3,7,8-TCDD) but no standards were supplied, all participants used own standards and spiking procedures.

In the presented study a fly ash extract was used to evaluate the performance of nine different laboratories (six Japanese, an American, a Finnish and a Swedish). The aspect of the presence of interfering compounds in a fly ash extract was given more weight than the limits of detection for the target compounds. Sample clean up and sufficient mass resolution during GC/MS analysis consequently becoming important for good performance.

EXPERIMENTAL

50 grams of fly ash (MSWI Ålidhem, Umeå, Sweden) was soxhlet extracted with toluene in portions of 10 gram. All extracts were combined and the amount of toluene was reduced to 50 ml, this 50 ml was further divided in a 30 ml extract A, a 10 ml extract B and a 10 ml extract C. Extract B and C were fortified with different PCDD and PCDF isomers to complicate analysis, the congeners and amounts are given in table 1. The congeners used for fortification were chosen for different reasons, added non 2,3,7,8-substituted congeners were known to co-elute on frequently used polar columns, whereas 2,3,7,8,-substituted isomers were only added to increase the total concentration of this congener. Aliquots of 1 ml toluene were transferred to glass ampoules and the ampoules were sealed. Each laboratory received one ampoule of extract A, B and C and was asked to report the amounts of 2,3,7,8-substituted congeners per sample as well as the total TEQs calculated from these amounts. All laboratories used own calibration, internal and recovery standards and clean up procedures. All participants used HRGC/HRMS to analyse the extracts after extensive sample clean up. Nearly all laboratories were able to inject the samples on two different columns, one with a polar and one non-polar stationary phase.

Table 1 Congeners used for fortification of fly ash extracts B and C.

Extract B[1]		Extract C[1]	
2,3,7,8-TCDD	1 ng	1,2,3,7,8-PCDF	0.5 ng
1,2,3,4,8-PCDF	1 ng	2,3,4,7,8-PCDF	1 ng
1,2,3,7,8-PCDF	0.5 ng	1,2,3,4,7,8-HxCDF	1 ng
1,2,3,4,7,9-HxCDF	1 ng	1,2,3,7,8,9-HxCDF	1 ng
1,2,3,7,8,9-HxCDF	1 ng	1,2,3,4,7,8-HxCDF	1 ng
OCDF	15 ng	OCDD	32 ng

[1] ng/sample

RESULTS AND DISCUSSION

Eight of the nine participating laboratories were able to report their results. The results of the analyses of all three extracts are given in table 2. The amounts of the 2,3,7,8-substituted congeners(ng/sample) together with the GC-columns used by the different laboratories, the average for each congener, the %RSD and the TEQ value calculated from the I-TEFs are reported. One laboratory was not able to report a value for 1,2,3,4,7,8,9-HpCDF due to interferences.
An %RSD of only 23% for extract A and C and 20% for extract B between TEQ values of the 8 laboratories is very promising. All participating laboratories show good agreement reporting TEQs. Looking closer at the %RSD of the specific congeners shows that the %RSD for 1,2,3,7,8,9-HxCDF is significantly higher than the %RSD for the other reported congeners. This congener showed also higher %RSD in other intercalibrations[4,5], no direct explanation for this large variance could be found. Further exploration of table 2 shows that the variation within laboratories is smaller than differences between the different participants. The laboratories can be divided in three groups with two (5 ,8) on the low side and two (1,6) on the high side, and four (3,4,7,9) very close to the mean value.
All 2,3,7,8-substituted fortifications are revealed by increasing the mean concentration of the original congener, except for the fortification of 1,2,3,7,8,9-HxCDF. The large %RSD as discussed above hides the small change in average concentration. The two non 2,3,7,8-substituted fortifications, 1,2,3,4,8-PCDF and 1,2,3,4,7,9-HxCDF did not have any effect on the mean values and were not experienced as problems by the participants.

CONCLUSIONS

The results of the analysis of three fly ash extracts by 8 different laboratories show a RSD of 25% for the calculated TEQs.
A RSD larger than 50% for 1,2,3,7,8,9-HxCDF indicates uncertainty in the quantification of this congener.
The interlaboratory calibration study was useful in evaluating the reliability of results produced by different laboratories and should be proceeded including the analysis of non-*ortho* PCBs, as these compounds have been assigned TEFs.

Table 2 Results of the analyses of fly ash extract A, B and C.

	Laboratory										
	1	3	4	5	6	7	8	9			
	GC Column										
	SP-2330 DB-5	SP-2331 Ultra#2	SP-2331 DB-5	SP-2331 SPB-5	SP2331 HP-5	SP-2331 DB-5	DB-DIOX	DB-5 DB-225			
Fly Ash Extract A[3]									**AVE**	**RSD**	**%RSD**
2,3,7,8-TCDD	**1.48**	**1.1**	**0.78**	**0.56**	**0.59**	**0.99**	**0.54**	**0.85**	**0.86**	**0.32**	**38%**
1,2,3,7,8-PCDD	5	3.4	3.35	2.1	4.3	5	4.5	3.2	3.86	1.01	26%
1,2,3,4,7,8-HxCDD	6.4	4.6	4.6	1.6	6.3	4.2	2.9	3.8	4.30	1.61	37%
1,2,3,6,7,8-HxCDD	10.7	8.2	7.6	4	12	8.4	6.3	6.2	7.93	2.56	32%
1,2,3,7,8,9-HxCDD	12.4	6.7	6.55	3.2	8.5	6.8	4.3	6.5	6.87	2.77	40%
1,2,3,4,6,7,8-HpCDD	122	82	91.5	90	110	80	50	75	87.56	21.93	25%
OCDD	345	200	255	285	290	140	156	230	237.63	70.19	30%
2,3,7,8-TCDF	3.9	3.5	2.35	2.2	3.4	2	2	3.2	2.82	0.76	27%
1,2,3,7,8-PCDF	4.1	8.4	6.5	6.3	14	10	4	5.6	7.36	3.36	46%
2,3,4,7,8-PCDF	8.7	8.1	5.65	7.6	12	8	6.6	8.3	8.12	1.86	23%
1,2,3,4,7,8-HxCDF	10	12	8.5	5.1[2]	16	8.9	7	22	11.19	5.47	49%
1,2,3,6,7,8-HxCDF	9	9.7	8.05	6.1	18	7.8	7	7.9	9.19	3.73	41%
1,2,3,7,8,9-HxCDF	1.4	4.9	3.2	0.98	2.9	1.6	0.6	0.47	2.01	1.54	77%
2,3,4,6,7,8-HxCDF	15.4	13	9.85	8	16	10	4.8	16	11.63	4.14	36%
1,2,3,4,6,7,8-HpCDF	69.5	56	54	42	71	51	37	37	52.19	13.30	25%
1,2,3,4,7,8,9-HpCDF	n.a.[1]	6.2	4.45	1.7	4.5	5.4	4	4.9	4.45	1.41	32%
OCDF	35	29	33.5	32	33	23	21	25	28.94	5.31	18%
I-TEQ	**18**	**15**	**12.5**	**10**	**20**	**14**	**11**	**15**	**14.44**	**3.37**	**23%**
Fly Ash Extract B[3]											
2,3,7,8-TCDD	3.59	2.3	2.1	1.8	1.6	2.3	1.4	2.1	2.15	0.67	31%
1,2,3,7,8-PCDD	5	3.6	3.7	2.8	4.2	3.9	4.4	3.3	3.86	0.68	18%
1,2,3,4,7,8-HxCDD	6.5	4.6	4.4	3.2	5.4	4.1	2.6	3.9	4.34	1.22	28%
1,2,3,6,7,8-HxCDD	10.7	7.4	7.7	4.1	11	7.5	6	6	7.55	2.35	31%
1,2,3,7,8,9-HxCDD	12	6.4	6.6	3.2	8.6	6.1	4	5.8	6.59	2.74	42%
1,2,3,4,6,7,8-HpCDD	120.9	76	83	211	100	77	49	72	98.61	50.03	51%
OCDD	353	190	250	318	260	120	146	223	232.50	80.11	34%
2,3,7,8-TCDF	4	3.5	2.3	2.4	3.1	2.6	1.8	3.1	2.85	0.71	25%
1,2,3,7,8-PCDF	4.5	8.9	8.1	7.6	13	8.5	4.3	6.2	7.64	2.79	36%
2,3,4,7,8-PCDF	8.3	7.7	9.2	7.3	9.8	6.3	6.5	7.9	7.88	1.22	15%
1,2,3,4,7,8-HxCDF	13.5	12	9.5	7.5[2]	17	12	6.6	21	12.39	4.82	39%
1,2,3,6,7,8-HxCDF	9.6	9.3	8	8.3	17	9.6	6.4	7.4	9.45	3.25	34%
1,2,3,7,8,9-HxCDF	2.7	5.5	3.5	1.4	3.2	2.6	1.2	1.2	2.66	1.46	55%
2,3,4,6,7,8-HxCDF	14.9	12	9.9	8.5	17	11	4.3	15	11.58	4.10	35%
1,2,3,4,6,7,8-HpCDF	68.9	55	50	78	57	46	35	34	52.99	15.31	29%
1,2,3,4,7,8,9-HpCDF	n.a.[1]	6	4.5	0.94	4.7	5.8	3.8	4.6	4.33	1.68	39%
OCDF	47	40	41	51	42	24	29	36	38.75	8.91	23%
I-TEQ	**21**	**16**	**16**	**14**	**20**	**15**	**11**	**16**	**16.13**	**3.18**	**20%**

Table 2 Continued.

	Laboratory										
	1	3	4	5	6	7	8	9			
	GC Column										
	SP-2330 DB-5	SP-2331 Ultra#2	SP-2331 DB-5	SP-2331 SPB-5	SP2331 HP-5	SP-2331 DB-5	DB-DIOX	DB-5 DB-225			
Fly Ash Extract C[3]									**AVE**	**RSD**	**%RSD**
2,3,7,8-TCDD	1.34	0.91	0.79	0.28	0.53	0.98	0.55	1.2	0.82	0.36	44%
1,2,3,7,8-PCDD	5.6	3.3	4.2	2.4	4.4	3.5	4.2	3.5	3.89	0.94	24%
1,2,3,4,7,8-HxCDD	8.0	5.5	5.5	2.5	6.5	9.1	3.7	5	5.73	2.15	38%
1,2,3,6,7,8-HxCDD	10.8	7.4	7.8	5.4	12	13	5.5	6.3	8.53	3.00	35%
1,2,3,7,8,9-HxCDD	10.1	6.7	6.6	3.4	9.7	10	4	5.4	6.99	2.69	39%
1,2,3,4,6,7,8-HpCDD	108	82	82	88	120	79	51	75	85.63	20.94	24%
OCDD	289	220	350	356	350	140	163	215	260.38	87.58	34%
2,3,7,8-TCDF	3.5	3.4	2.4	1.4	3.2	2.6	2	3.1	2.70	0.74	27%
1,2,3,7,8-PCDF	7.6	8.9	8.5	5.6	12	8.6	4.4	6.5	7.76	2.33	30%
2,3,4,7,8-PCDF	9.4	8.6	13	6.2	11	7	7	9.2	8.93	2.27	25%
1,2,3,4,7,8-HxCDF	15	14	11	7.2[2]	17	14	8.3	24	13.81	5.31	38%
1,2,3,6,7,8-HxCDF	11.9	9.5	7.9	6.8	14	10	6.4	7.7	9.28	2.63	28%
1,2,3,7,8,9-HxCDF	3.5	5.9	3.9	1.3	3.3	2.7	1.4	1.5	2.94	1.57	54%
2,3,4,6,7,8-HxCDF	15.8	12	11	7	14	8.8	4.9	15	11.06	3.91	35%
1,2,3,4,6,7,8-HpCDF	68.9	54	39	64	62	46	35	35	50.49	13.62	27%
1,2,3,4,7,8,9-HpCDF	n.a.[1]	5.9	3.5	1.3	4.9	6.4	3.7	4.7	4.34	1.71	39%
OCDF	32.9	27	33	32	32	22	19	24	27.74	5.54	20%
TEQ	**20**	**15**	**17**	**10**	**19**	**15**	**11**	**16**	**15.38**	**3.50**	**23%**

[1] not analysed due to artifact interference
[2] 1,2,3,4,7,8-/1,2,3,4,7,9-HxCDF
[3] ng/sample

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