

Results from the 1st round of the international intercalibration study for PBDD/DF and mixed PC/BDD/DF in standard solutions and incineration samples

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Introduction

Already in 1986 the formation of PBDD/DF from technical brominated diphenyl ethers (BDEs) was shown by Buser et al.ⁱ Further evidence of the formation of PBDD/DFs from BDEs was presented by Thomaⁱⁱ and Luijkⁱⁱⁱ and from Tetrabromobisphenol-A (TBBP-A) by Thoma^{iv} and Dumler^v. These small scale laboratory experiments, often performed in quartz vials or tubes at elevated temperatures (600-900 °C), show that formation of PBDD/DF is favoured from the Penta BDE formulation. Also the technical Deca BDE formulation generates considerable amounts of PBDD/DFs while formation from TBBP-A is somewhat lower as recently reviewed by Weber^{vi}. In pilot scale incineration of BFRs alone or together with municipal solid waste, formation of PBDD/DFs and mixed PC/BDD/DFs has been shown^{vii,viii}. Under normal operating conditions the formation of the mixed PC/BDD/DFs is favoured through 'De Novo' synthesis in the cooling zone of the incinerator as with chlorinated PCDD/DFs. Other thermal processes during production (extrusion, moulding)^{ix,x} might result in PBDD/DF formation. In addition products with BFRs, such as rear covers of TV sets, can contain relatively high levels of PBDD/DFs as was recently shown in a Japanese study^{xi}. Although only limited data are available and no Toxic Equivalent Factors (TEF) have been assigned, there is strong proof for dioxin-like toxicity of both PBDD/DF and the mixed Cl/Br dioxins and furans as recently reviewed by Birnbaum^{xii} et al. Several methods for brominated dioxins, adapted from the analysis of chlorinated dioxins, have been published in the past^{xiii,xiv,xv}. But recently there seem to be a new interest for the analysis of PBDD/DF^{xvi,xvii}. Problems with interferences of BDEs during clean up and extraction or high resolution GC/MS analysis are known. In addition to thermal breakdown of higher brominated PBDD/DFs or decomposition of Deca BDE to PBDFs. While new data is expected to come out, intercalibration of the methods used by different laboratories is of course an important QA/QC feature. Here we present the first results of an international intercalibration on the analysis of PBDD/DFs and mixed Cl/Br containing dioxins and furans.

Methods and materials

Two fly ash samples and two standard solutions were sent to 25 laboratories for the analysis of both PBDD/DF and mixed Cl/Br dioxins and furans. The laboratories were asked to analyse the compounds listed in Table 1 using their own extraction and clean up procedures and use their own standard solutions for quantification. Sample A consisted of a pooled cyclone ash made available

by Dr. Gunilla Söderström containing both PBDD/DFs and mixed Br/Cl dioxins and furans after incineration of BFRs in a pilot incinerator. Sample B consisted of a fly ash made available by Dr. Roland Weber containing low levels of PBDD/DFs but somewhat higher levels of mixed Cl/Br compounds. Standard solution A was a dilution of mix DF-2046A made available by Cambridge Isotope Laboratories and contained a mixture of 9 Tetra- through Hexa PBDD/DFs at a concentration of 10-1000 pg/ul. The other solution was a mixture of mixed Cl/Br dioxins and furans at a concentration of 10-50 pg/ul donated by Wellington Laboratories.

Results

Of the total of 25 participants 12 were able to report results before the set deadline. The report frequency of 48% is significantly lower than similar studies on the chlorinated homologues were report frequencies are normally over 80%. Also the variation in the data of a standard solution is larger up to 115%. However good results were obtained for several compounds resulting in RSDs between 16 and 39% for the brominated dioxins and furans. Two of the HxBDD were co-eluting on the column used by most of the participants and results were reported for the sum of the two isomers. From the results for the 6 mixed Cl/Br dioxins and furans standard solutions it showed that this analysis was somewhat more difficult and a lower number of participants (8) were able to report levels. In addition a larger RSD was seen for the 5 compounds. All values were in reasonable agreement with the designed values.

Table 1. Results from the 2 standard solutions A and B. All levels in pg/ul.

	1	2	3	4	5	6	7	8	9	10	11	12	Mean	RSD	%RSD
2,3,7-TrBrDD	NA	NA	NA	NA	NA	ND	< 0.06	< 0.2	NA	NA	< 0.6	NA	ND	ND	ND
2,3,7,8-TeBrDD	36	15	10	10	14	10	14	10	9	9	9	10	13	8	59%
1,2,3,7,8-PeBrDD	234	51	50	78	84	51	61	50	50	62	29	55	71	53	74%
1,2,3,4,7,8-HxBrDD**	NA	485	510	334	989	500	505	490	513	382	540	710	542	175	32%
1,2,3,6,7,8-HxBrDD**	NA	485	510	334	989			490	513	382	540	710	550	195	35%
1,2,3,7,8,9-HxBrDD	NA	164	240	248	337	240	224	280	263	279	470	270	274	78	28%
2,3,7,8-TeBrDF	263	141	110	118	142	120	167	100	79	120	68	120	129	50	39%
1,2,3,7,8-PeBrDF	2105	533	510	558	548	470	531	530	528	567	540	550	664	455	68%
2,3,4,7,8-PeBrDF	2391	502	510	487	527	470	624	490	504	560	490	530	674	542	81%
1,2,3,4,7,8-HxBrDF	NA	353	400	NA	485	420	584	400	403	420	885	480	483	155	32%
1,2,3,4,6,7,8-HpBrDF	NA	NA	1000	NA	1423	930	1004	970	1050	1236	NA	NA	1088	178	16%
2-Br-7,8-CIDD	NA	9	NA	NA	36	9	15	9	NA	NA	8	NA	14	11	75%
2-Br-3,7,8-CIDD	4	9	10	NA	23	11	25	9	NA	NA	11	NA	13	7	57%
2,3-Br-7,8-CIDD	8	9	11	NA	89	52	11	9	NA	NA	15	NA	26	29	115%
2-Br-1,3,7,8-CIDD	41	52	NA	NA	21	10	68	53	NA	NA	36	NA	40	20	50%
2-Br-7,8-CIDF	NA	10	NA	NA	46	10	9	10	NA	NA	9	NA	16	15	98%
2-Br-6,7,8-CIDF	10	9	NA	NA	39	10	12	9	NA	NA	21	NA	16	11	71%

** Co-eluting isomers on DB-% like columns.

In Table 2 the results from the analysis of fly ash sample A is shown. The sample contained reasonable amounts of PBDD/DFs but relatively low levels of the mixed Br/Cl homologues. The results for both 2,3,7,8- TeBDD and 2,3,7,8-TeBDF are in reasonable agreement, but these results are still not as good as the results achieved with their chlorinated homologues in other studies. The

mixed Cl/Br dioxins and furans were present at a much lower level but were nevertheless detected by 7 of the participants. The agreement of the analysis of both 2-Br-3,7,8-CIDD and 2-Br-6,7,8-CIDF at the low level of 0.01-0.09 ng/g was reasonable good (66-68%). Problems quantifying the totals of the mixed compounds were reported due to large number of congeners and interferences at the different Br/Cl masses monitored. Fly ash B, results not shown here, contained very low levels of PBDD/DFs. The levels of mixed Br/Cl dioxins and furans were in the same low range as fly ash A. To obtain results from the limited amount of fly ash available (3-5g) was a real challenge in this case.

Table 2. Results Fly Ash A, all values in ng/g

	1	2	3	4	5	6	7	8	9	10	11	12	Mean	RSD	%RSD
2,3,7-TrBrDD	NA	NA	NA	NA	NA	0.11	0.069	0.17	NA	NA	0.062	NA	0.10	0.05	48%
2,3,7,8-TeBrDD	0.57	ND	0.035	0.14	0.27	0.21	< 0.095	0.13	0.1	0.05	0.30	0.21	0.20	0.16	77%
1,2,3,7,8-PeBrDD	1.14	0.98	0.60	0.33	0.34	0.48	0.624	0.58	0.1	0.63	0.19	0.33	0.53	0.30	58%
1,2,3,4,7,8-HxBrDD**	NA	1.01	1.8	0.88	0.69	1.1	0.727	1.2	0.71	0.89	1.1	1.9	1.09	0.41	38%
1,2,3,6,7,8-HxBrDD**	NA	1.01	1.8	0.88	0.69			1.2	0.71	0.89	1.1	1.9	1.13	0.44	39%
1,2,3,7,8,9-HxBrDD	NA	ND	0.49	0.56	0.15	0.69	0.471	0.85	0.46	0.73	1.2	0.52	0.61	0.28	46%
2,3,7,8-TeBrDF	7.13	3.40	0.91	2.02	2.39	5.0	1.32	0.8	1.3	0.49	1.9	3.3	2.50	1.96	78%
1,2,3,7,8-PeBrDF	12.21	1.27	1.0	1.78	2.11	3.9	1.23	2.8	3.3	1.95	2.1	2.8	3.04	3.02	99%
2,3,4,7,8-PeBrDF	22.52	4.35	3.4	4.75	2.01	3.7	3.26	3.3	2.4	4.69	2.6	3.5	5.04	5.57	111%
1,2,3,4,7,8-HxBrDF	NA	27.03	15	NA	21.6	30	29.2	29	8.6	33.6	NA	32	25.1	8.41	33%
1,2,3,6,7,8-HxBrDF	0.068	NA	NA	NA	NA	NA	NA	NA	4	NA	NA	NA	2.03	2.78	137%
1,2,3,7,8,9-HxBrDF	0.054	NA	NA	NA	NA	NA	< 0.10	NA	0.6	NA	NA	NA	0.33	0.39	118%
2,3,4,6,7,8-HxBrDF	0.090	NA	NA	NA	NA	NA	0.54	NA	3.5	NA	NA	NA	1.38	1.85	135%
1,2,3,4,6,7,8-HpBrDF	NA	NA	220	NA	191.9	150	117	170	84	161	NA	NA	156	45.4	29%
Total TriBrDD	NA	NA	NA	NA	NA	0.38	0.28	0.65	NA	NA	0.20	NA	0.38	0.20	52%
Total TeBrDD	ND	NA	1.2	NA	NA	1.5	1.39	1.8	1.25	NA	1.4	NA	1.42	0.21	15%
Total PeBrDD	10.6	NA	4.5	NA	NA	4.0	4.62	3.6	1.34	NA	1.8	NA	4.35	3.05	70%
Total HxBrDD	NA	NA	16	NA	NA	10	7.59	12	8.1	NA	27	NA	13.4	7.31	54%
Total TriBrDF	NA	NA	NA	NA	NA	29	23	17	NA	NA	19	NA	22	5	24%
Total TeBrDF	NA	NA	47	NA	NA	65	59.2	67	24.4	NA	25	NA	48	19	40%
Total PeBrDF	1141	NA	110	NA	NA	130	102	180	123	NA	130	NA	274	383	140%
Total HxBrDF	NA	NA	250	NA	NA	250	181	270	109	NA	320	NA	230	74	32%
2-Br-7,8-CIDD	NA	ND	NA	NA	0.022	N.D.	< 0.004	0.0061	NA	NA	< 0.002	NA	0.01	0.01	80%
2-Br-3,7,8-CIDD	ND	ND	ND	NA	0.018	N.D.	< 0.004	0.0066	NA	NA	< 0.01	NA	0.01	0.01	66%
2,3-Br-7,8-CIDD	0.007	ND	0.0036	NA	0.28	N.D.	< 0.004	0.0059	NA	NA	0.017	NA	0.06	0.12	194%
2-Br-1,3,7,8-CIDD	0.070	ND	NA	NA	NA	N.D.	< 0.004	<0.0002	NA	NA	< 0.02	NA	0.07	NA	NA
2-Br-7,8-CIDF	NA	ND	NA	NA	0.28	0.01	0.033	0.038	NA	NA	0.033	NA	0.08	0.11	143%
2-Br-6,7,8-CIDF	0.098	0.114	NA	NA	0.19	0.036	0.028	0.068	NA	NA	< 0.01	NA	0.09	0.06	68%
Total TriBrCIDD	NA	NA	ND	NA	NA	N.D.	4.79	0.15	NA	NA	< 0.3	NA	2.47	3.28	133%
Total TeBrCIDD	0.46	NA	ND	NA	NA	0.032	NA	0.096	NA	NA	0.24	NA	0.21	0.19	92%
Total PeBrCIDD	0.29	NA	0.12	NA	NA	0.091	NA	0.10	NA	NA	0.251	NA	0.17	0.09	54%
Total TriBrCIDF	NA	NA	0.18	NA	NA	0.34	NA	1.7	NA	NA	3.8	NA	1.51	1.68	111%
Total TeBrCIDF	2.19	NA	0.32	NA	NA	0.45	NA	3.4	NA	NA	10.3	NA	3.33	4.10	123%
Total PeBrCIDF	0.16	NA	0.89	NA	NA	0.38	NA	6.6	NA	NA	7.59	NA	3.12	3.65	117%

** Co-eluting isomers on DB-% like columns.

Conclusion

Of the participating laboratories 48% were able to report the PBDD/DF or the mixed Br/CIDD/DFs on both the fly ash samples and the two standard solutions. The results for the standard solutions were good for many congeners, the fly ash samples were a bigger challenge due to the limited

amount of material available for analysis. A follow up study with more material or material with higher concentrations of the target compounds would be more feasible.

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