An Intercalibration Study on Organobromine Compounds: Brominated Flame Retardants and Related Dioxin-Like Compounds in Waste TV Cabinet and Animal Fat

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Introduction

Recently, environmental problems relating to brominated flame retardants (BFRs) have become a matter of great concern due to their potential toxic risk on human and wildlife[1] and recent increase in levels of polybrominateddiphenyl ethers (PBDEs)[2-4]. International intercalibration studies on the analysis of these compounds have been conducted[5-7]. Recent interlaboratory studies[7,8] showed analytical improvement of PBDEs, particuraly for decabrominateddiphenylether (BDE209). However, other higher brominated congeners such as octa- and nonabromodiphenylethers have been determined scarcely due to problems in the availability of standards. Moreover, results on BFRs other than PBDEs, e.g., tetrabromobisphenol A (TBBPA), tribromophenol (TBP) and hexabromocyclododecane (HBCD), are very much limited[7].

Another concern has been related to the thermal breakdown products of BFRs such as polybrominateddibenzo-*p*-dioxins and dibenzofurans (PBDDs/DFs). Considerable levels of PBDDs/DFs were detected in waste television cabinets and other flame-retarded plastics[2]. The Ministry of the Environment, Japan has conducted surveys on halogenated dioxins in the environment[9]. PBDDs/DFs and monobromo-polychlorodibenzo-*p*-dioxins and dibenzofurans (MoBPCDDs/DFs) were found in various environmental media with BFRs[2,9]. Although commercially available standards for these compounds are still limited, development of a good QA/QC system has become imperative.

To evaluate the accuracy and reliability in the analysis for organobromine compounds, an intercalibration study in which 13 laboratories in Japan participated was initiated since April, 2003. Following the results on PBDD/DFs, MoBPCDDs/DFs and PBDEs in 'Mixed Standard Solutions' and 'Air-Dried Sediment', that were presented in the last DIOXIN symposium 2004[8], the new results on 'Waste TV Cabinet' and 'Animal Fat' are reported in this presentation.

Methods and Materials

Four groups of organobromine compounds were selected as target compounds; 1) PBDDs/DFs 2) MoBPCDDs/DFs, 3) PBDEs, and 4) TBBPA, TBP and HBCD. To compare with organobromine target compounds, polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/DFs) and coplanar PCBs (Co-PCBs) were also required to determine in some samples (i.e. 'Air-Dried Sediment' and 'Animal Fat' described below).

Four 'InterLab Samples' were designed in this study; 1) Mixed Standard Solutions, 2) Air-Dried Sediment, 3) Waste TV Cabinet, and 4) Animal Fat. The results and details of the samples 1) and 2) were reported in the previous paper[8]. The sample 'Waste TV Cabinet' was made from 50 cabinets (approx. 80 kg) collected from disused television in a home appliance recycle plant. All the cabinets were crushed into particle and homogenized by large volume mixer. A portion of the particle sample was solved into toluene, and then the toluene solution was dried on glass plate forming thin plastic plate. The thin plate sample was cut to small pieces and packed into 50 bottles. Homogeneity of the sample was tested by analyzing several elements by ICP-AES and X-ray fluorescence spectrometer (XRF). Although up to 6.7 % of inhomogeneity between the samples was observed by XRF, this is much smaller than the results of analytical errors for PBDEs. The sample 'Animal Fat' was made from the blubber (approx. 3.4 kg) of a dead body of finless porpoise (adult male) stranded along Seto-Inland Sea, Japan, in 2003.

Frozen blubber was cut and homogenized by GrindMix 200 (Retsch Co., Ltd.), and then the samples were pooled and filtered by 0.2 mm meshed screen to remove fibrous tissue. The filtered sample was well homogenized again and immediately packed into each sample bottle. Total 90 bottles of the sample were kept at -20°C. Homogeneity of this sample was tested by analyzing arsenic, which is one of fat affinitive element, by ICP-AES. The test result was indicated no inhomogeneity of the sample.

The participants were asked to analyze the samples using their own analytical method(s). Triplicate results for each sample were requested to evaluate variations or errors within each laboratory. All the participants sent the description of their method and representative chromatograms along with results for each compound in each sample to the coordinator. Guidelines for avoiding specific errors during analysis were provided to all the participants by the coordinator. For examples the participants were asked to 1) follow the QA/QC guidelines for the dioxin analysis suggested by JIS and the Ministry of the Environment, Japan, 2) examine all the analytical processes under 'UV cutoff' condition, 3) prepare blank by using exactly same method followed for the samples, 4) use proper standards, in particular for the analysis of high brominated compounds, 5) check well the linearity of the calibration curves, 6) confirm whether interference by PBDEs appear in the PBDF analysis, and 7) avoid thermal breakdown of high brominated compounds during sample pretreatment and GC analysis, as far as possible. During this study, several meetings were held between participants and coordinator to improve the methodology and to develop better guidelines for the analysis.

Results and Discussion

All participants that reported results used HRGC-HRMS(EI) or HRGC- LRMS(EI) and isotope-labeled standards for the determination of target compounds. The triplicate results from each laboratory were averaged, then the average concentrations and relative standard deviations (RSDs) between the laboratories were calculated and summarized for each compounds in 'Waste TV Cabinet' (Table 1) and 'Animal Fat' (Table 2).

Table 1. Summary of results on 'Waste TV Cabinet'

Compounds	a	Ave. Conc.	%RSD
PBDDs/DFs		ng/g	
2,3,7,8-TeBDD	6	—	—
1,2,3,7,8-PeBDD	6	—	—
1,2,3,4,7,8-/1,2,3,6,7,8-HxBDD	6	—	—
1,2,3,7,8,9-HxBDD	6	—	—
OBDD	6	86	33
2,3,7,8-TeBDF	6	3.8	30
1,2,3,7,8-PeBDF	6	4.1	21
2,3,4,7,8-PeBDF	6	6.3	30
1,2,3,4,7,8-HxBDF	6	61	12
1,2,3,4,6,7,8-HxBDF	6	260	25
OBDF	6	1300	17
TeBDDs	6	6.2	23
PeBDDs	6	—	—
HxBDDs	6	—	—
HxBDDs	6	7.7	24
TeBDFs	6	140	16
PeBDFs	6	340	16
HxBDFs	6	1100	14
HxBDFs	6	2600	25
PBDEs		ng/g	
2,4,4'-TrBDE (#28)	4	0.024	19
2,2',4,4'-TeBDE (#47)	4	1.3	16
2,2',4,4',6-PeBDE (#99)	4	3.2	27
2,2',4,4',5-PeBDE (#100)	4	1.1	33
2,2',4,4',5,6'-HxBDE (#153)	4	620	25
2,2',4,4',5,6'-HxBDE (#154)	4	66	22
2,2',3,4,4',5',6-HxBDE (#183)	4	3700	21
2,2',3,3',4,4',6,6'-OBDE (#196)	2	810	—
2,2',3,3',4,4',5,6'-OBDE (#197)	2	2100	—
2,2',3,3',4,4',5,6,6'-NoBDE (#206)	2	3000	—
2,2',3,3',4,4',5,6,6'-NoBDE (#207)	2	1860	—
DeBDE (#209)	4	9900	18
TrBDFs	4	0.068	7
TeBDFs	4	1.4	14
PeBDFs	4	6.3	26
HxBDFs	4	620	24
HxBDFs	4	3700	21
OBDFs	4	3000	26
NoBDFs	4	4300	18
Other BFRs		ng/g	
TBBPA	7	6800	11
2,4,6-Tribromophenol (TBP)	2	6	44
HBCD	2	11	—

a: number of data. %RSD: relative standard deviation in %.
—: Less number of results reported or more than a half of data reported below the detection/quantification limits.

Table 2. Summary of results on 'Animal Fat'

Compounds	a	Ave. Conc.	%RSD
PBDEs		pg/g	
2,4,4'-TrBDE (#28)	10	23000	17
2,2',4,4'-TeBDE (#47)	10	200000	20
2,2',4,4',6-PeBDE (#99)	10	33000	17
2,2',4,4',5-PeBDE (#100)	10	36000	14
2,2',4,4',5,6'-HxBDE (#153)	10	84000	11
2,2',4,4',5,6'-HxBDE (#154)	10	110000	21
2,2',3,4,4',5',6-HpBDE (#183)	10	6700	23
2,2',3,3',4,4',5,6'-OBDE (#196)	6	190	18
2,2',3,3',4,4',5,6,6'-OBDE (#197)	7	1900	14
2,2',3,3',4,4',5,5',6,6'-NoBDE (#206)	7	28	—
2,2',3,3',4,4',5,6,6'-NoBDE (#207)	6	130	16
DeBDE (#209)	2	360	27
TrBDEs	7	23000	10
TeBDEs	7	260000	18
PeBDEs	7	140000	23
HxBDEs	7	340000	18
HpBDEs	7	47000	13
OBDEs	7	23000	19
NoBDEs	7	4700	12
Other BFRs		ng/g	
TBBPA	2	—	—
2,4,6-Tribromophenol (TBP)	2	440	68
HBCD	2	54000	—
PCDDs/DFs		ng/g	
2,3,7,8-TeCDD	7	—	—
1,2,3,7,8-PeCDD	7	2.1	10
1,2,3,4,7,8-HxCDD	7	4.3	11
1,2,3,6,7,8-HxCDD	7	4.3	16
1,2,3,7,8,9-HxCDD	7	0.81	10
1,2,3,4,6,7,8-HpCDD	7	21	6
OCDD	7	76	9
2,3,7,8-TeCDF	7	1.6	50
1,2,3,7,8-PeCDF	6	1.6	36
2,3,4,7,8-PeCDF	7	6.8	28
1,2,3,4,7,8-HxCDF	7	6.8	18
1,2,3,6,7,8-HxCDF	6	1.8	33
1,2,3,7,8,9-HxCDF	7	3.1	12
2,3,4,6,7,8-HxCDF	7	3.6	80
1,2,3,4,6,7,8-HpCDF	7	4.7	9
1,2,3,4,7,8,9-HpCDF	7	0.26	—
OCDF	7	—	—
TeCDDs	7	4.8	44
PeCDDs	7	3.4	21
HxCDDs	7	1.4	18
HpCDDs	7	2.1	8
TeCDFs	7	16	61
PeCDFs	7	31	86
HxCDFs	7	49	46
Co-PCBs		kg/g	
HxCDFs	7	5.4	11
3,4,4',5-TeCB (#81)	7	66	16
3,3',4,4'-TeCB (#77)	7	730	62
3,3',4,4',5-PeCB (#126)	7	110	28
3,3',4,4',5,5'-HxCB (#169)	7	120	13
2',3,4,4',5-PeCB (#123)	7	2300	16
2,3',4,4',5-PeCB (#118)	7	1000000	18
2,3,3',4,4'-PeCB (#105)	7	110000	12
2,3,4,4',5-PeCB (#114)	7	3700	23
2,3',4,4',5,5'-HxCB (#167)	7	99000	14
2,3,3',4,4',5-HxCB (#156)	7	27000	20
2,3,3',4,4',5'-HxCB (#157)	7	17000	10
2,3,3',4,4',5,5'-HpCB (#189)	7	4200	8

The results on 'Waste TV Cabinet' showed that the concentrations of BDE209 in this sample were in percent levels (9% of the averaged concentration). TBBPA was also contained at relatively high concentrations. In addition, the concentrations of some PBDFs were up to ppm levels. On the other hand, the reported concentrations of MoBPCDDs/DFs were below the detection limits. These results reported in this study are almost identical with those

found in an earlier study which analyzed PBDEs and PBDDs/DFs in waste TV casing[2]. The RSDs for PBDDs/DFs and PBDEs ranged from 14-33% and 10-39%, respectively. The ranges of RSDs were almost similar to those reported on 'Air-Dried Sediment' in our previous paper[8]. Higher variability found in the result of OBDD than the other PBDDs/DFs reflects analytical difficulty in the determination of highly brominated dioxins at low concentrations. Despite of this, the results of PBDDs/DFs in 'Waste TV Cabinet' are better than those reported in an earlier intercalibration study on halogenated dioxins in fly ash samples[10]. This may due to some improvements applied in our studies[8] (e.g., optimization of RRFs in the quantification of highly brominated dioxins, etc.). The highest RSD was observed in the result of BDE100 because of co-elution of this isomer with other isomer peak(s) during GC separation as noted in our previous report on 'Air-Dried Sediment'[8].

In the sample 'Animal Fat', BFRs such as PBDEs, TBP and HBCD were detected, while the concentrations of PBDDs/DFs and MoBPCDDs/DFs were reported to be below the detection limits by all the participants. In addition to BFRs, Co-PCBs and PCDDs/DFs were detected and quantified in this sample. The concentrations of BDE47 (200 ng/g of averaged concentration) was the highest among PBDEs detected. BDE209 was also detected by many participants although the concentrations were lower than those of other congeners. The concentrations and composition of PBDEs found in the 'Animal Fat' (homogenized blubber of finless porpoise) were similar to those observed in the blubber of coastal cetaceans in Japanese waters[11]. The RSDs for PBDEs ranged from 11-33%, which is almost same as the reported range in 'Air-Dried Sediment' in our previous paper[8]. On the other hand, the variation in the results of some Co-PCBs and PCDFs were over 50%RSD. This is different from those reported on 'Air-Dried Sediment'[8] in which the RSDs for chlorinated dioxins were smaller than those for PBDEs and PBDDs/DFs. Detail analysis of these chlorinated dioxins conducted by a participant indicated possible interferences by PCBs and polychlorinated diphenylethers (PCDEs) in the determination of Co-PCBs and PCDFs.

This study contributes to establish a better QA/QC system for the analysis of BFRs and related dioxin-like compounds as well as other potential POPs candidates.

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