EVALUATION OF INTERLABORATORY STUDY ON PCDD, PCDF AND DIOXIN LIKE PCB IN THE REFERENCE MATERIAL IN JAPAN (9TH ROUND FY 2011 RESEARCH GROUP ON ULTRA TRACE ANALYSES, JEMCA, JAPAN)

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Introduction

Inter-laboratory round robin is available for maintaining the quality/skills of dioxin analysis through testing bycertified laboratories. There are over 100 accredited Laboratories for dioxin by MLAP (Specified Measurement Laboratory Accreditation Program) system of Ministry of Economy Trade and Industry (METI) in Japan.Ministry of Environment (MOE) has another program for examining the order of competence also. But it is more important to maintain QA/QC system and evaluate quality of daily analysis data continuously. There are some official proficiency tests for dioxin analysis by JSAC (The Japan Society for Analytical Chemistry), MOE and METI in Japan.

Research Group on Ultra Trace Analyses (UTA) which is accompanying organization of Japan Environmental Measurement & Chemical Analysis Association (JEMCA) established in 2003. The UTA consists of 63 private dioxin testing laboratories in 2011 and is responsible for developing the analytical potential of not only dioxins but also other trace level analysis of well known POPs in the environment. UTA carried out inter-laboratory round robin studies annually since 2003, R-1:flyash extract in 2003, R-2:soil in 2004, R-3:PUF fortified extract in 2005, R-4:soil in 2006, R-5:soil in 2007, R-6:flyash in 2008 ,R-7:sediment in 2009, R-8:sediment in 2010, and R-9:flyash in 2011 for polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs). This paper summarizes the recent inter-laboratory study (R-9, FY 2011) conducted by UTA group for PCDDs, PCDFs and DL- PCBs in sediment sample.

Materials and methods

The flyash reference material the ninth round robin study (R-9) was sent to 63 laboratories. The flyash reference material was collected, dried, milled, homogenized and packed in 25 g portions.

All member laboratories were asked to report all 2,3,7,8-substituted PCDD/DFs congeners, homologues and 12 DL-PCBs. A special result form was sent to all members in which, the following details were requested; 1. The analytical results obtained, including recovery percentage, 2. Complete analytical procedure followed and 3. SIM Chromatograms of each sample. Results of these studies are evaluated for median, normalized interquartile range (NIQR), coefficient of variation by Robust method (CV % rob) for each PCDDs, PCDFs and DL-PCBs. Furthermore Z-score was calculated and evaluated by ISO/IEC 17043(JIS Q 17043). Laboratories, which exceed >±3 of Z-score were required cause analysis and report of corrective action.

Results and discussion:

The results of the ninth round robin study on an isomer/congener specific basis with median, and their NIQR and CV % rob are summarized in Table 1. Every data set was used to identify obvious outliers. Obvious outliers were defined as having each Z-score over 3.

As our earlier report, significant differences were observed between laboratories, in particular for 1,2,3,7,8-PeCDF and 1,2,3,4,7,8-HxCDF, depending upon the capillary column that was used for the analysis. The main causes of these differences are due to co-eluting congeners in polar GC phase (SP-2331 or CP-Sil88) (ex. 1,2,3,7,8-PeCDF co-eluting 1,2,3,4,8-PeCDF, 1,2,3,4,7,8-HxCDF co-eluting 1,2,3,4,7,9-HxCDF). During combined data processing for these congeners, the CV % rob value were clearly increased.

The CV % rob in R-9 ranged from 4.9% to 9.8% for PCDDs/DFs congeners, 4.4 % to 9.1 % for DL-PCBs. and 3.83% for TEQ (not indicated in the table).

Table 1. Statistical analysis of the 9th round robin (R-9, 2011) study results of PCDDs/PCDFs and DL-PCBs.

PCDDs/DFs, DL-PCB	MEDIAN (pg/g)	NIQR	CV% rob	MIN (pg/g)	MAX (pg/g)	MEAN (pg/g)	SD	N
2378-TeCDD	41	2.93	7.1	28	49	41	3.85	63
12378-PeCDD	211	14.1	6.7	177	261	210	16.2	63
123478-HxCDD	233	17.4	7.5	191	304	232	19.5	63
123678-HxCDD	836	47.8	5.7	652	1030	830	60.5	63
123789-HxCDD	726	41.9	5.8	577	897	727	54.4	63
1234678-HpCDD	2438	166	6.8	2035	3110	2436	174	63
OCDD	977	87.7	9.0	785	1120	968	83.0	63
2378-TeCDF	455	36.0	7.9	355	582	456	43.7	63
12378-PeCDF	345	121	35.1	279	581	400	93.3	63
12378-PeCDF(※a)	337	16.5	4.9	279	459	336	27.3	41
12378-PeCDF(※b)	529	36.0	6.8	445	581	520	35.9	22
23478-PeCDF	442	24.8	5.6	330	492	438	28.1	63
123478-HxCDF	261	40.4	15.5	199	363	271	39.0	63
123478-HxCDF(※a)	253	17.0	6.7	199	363	249	26.6	41
123478-HxCDF(※b)	311	21.5	6.9	278	354	313	20.2	22
123678-HxCDF	262	13.0	5.0	217	299	260	16.4	63
123789-HxCDF	39	3.8	9.8	26	58	40	6.0	62
234678-HxCDF	265	24.1	9.1	215	320	268	25.3	63
1234678-HpCDF	481	25.2	5.2	409	578	481	32.5	63
1234789-HpCDF	104	8.75	8.4	83	126	105	9.69	63
OCDF	268	23.8	8.9	215	327	267	24.2	63
344'5-TeCB(#81)	119	5.19	4.4	101	137	118	7.27	63
33'44'-TeCB(#77)	489	25.6	5.2	380	558	484	34.4	63
33'44'5-PeCB(#126)	183	14.5	7.9	139	240	184	19.4	63
33'44'55'-HxCB(#169)	40	3.0	7.6	32	119	41	10.6	63
2'344'5-PeCB(#123)	75	5.2	6.9	60	104	76	7.11	63
23'44'5-PeCB(#118)	1625	125	7.7	1188	2050	1636	147	63
233'44'-PeCB(#105)	733	61.5	8.4	612	877	744	58.5	63
2344'5-PeCB(#114)	85	7.75	9.1	66	111	85	8.23	63
23'44'55'-HxCB(#167)	123	8.25	6.7	98	152	124	10.8	63
233'44'5-HxCB(#156)	319	24.1	7.6	250	369	319	25.5	63
233'44'5'-HxCB(#157)	99	8.01	8.1	82	111	99	7.15	63
233'44'55'-HpCB(#189)	78	4.15	5.3	61	91	78	5.06	63

Used GC column for 1,2,3,7,8-PeCDF and 1,2,3,4,7,8-HxCDF analysis

(※a) BPX-DXN, DB-5, BPX-5, RH-12ms etc.: separate single peak

(※b) SP-2331, CP-Sil88 etc.: including co-elute congeners

Table 2 describes the trends of CV % rob from the 1st to 9th round robin study. It seems better CV% rob result for 9th round robin study as compared with the result of the past. These results indicate appreciable improvement of the analytical techniques and systems of UTA individual laboratories every year. They have gradually increased number of laboratories to use GC columns that can separate other congeners in the analysis of 1,2,3,7,8- PeCDF and 1,2,3,4,7,8-HxCDF. (e.g. during R-9 study the use of such columns is 65% while it was only 24% during R-1).

Table 2. Trends of the round robin study results (CV % rob)

PCDDs/DFs, DL-PCB	2003 (1st) flyash ext.	2004 (2nd) soil	2005 (3rd) PUF fortified	2006 (4th) soil	2007 (5th) soil	2008 (6th) flyash	2009 (7th) sediment	2010 (8th) sediment	2011 (9th) flyash
2378-TeCDD	8.5%	15.8%	7.5%	24.8%	15.4%	11.4%	15.0%	15.6%	7.1%
12378-PeCDD	6.3%	16.7%	5.9%	16.6%	10.3%	9.6%	9.3%	7.2%	6.7%
123478-HxCDD	10.3%	15.8%	8.5%	16.2%	10.7%	10.0%	7.6%	6.9%	7.5%
123678-HxCDD	8.7%	16.6%	9.7%	13.3%	10.4%	9.9%	6.9%	6.7%	5.7%
123789-HxCDD	8.3%	17.5%	6.6%	13.4%	6.8%	10.8%	8.0%	9.2%	5.8%
1234678-HpCDD	6.3%	16.5%	9.0%	15.4%	10.2%	8.9%	6.3%	6.4%	6.8%
OCDD	8.5%	11.5%	6.4%	13.9%	7.5%	8.3%	6.7%	8.5%	9.0%
2378-TeCDF	9.1%	17.9%	9.1%	15.6%	8.8%	13.8%	11.0%	10.7%	7.9%
12378-PeCDF	10.0%	23.4%	11.1%	22.2%	23.6%	38.8%	32.2%	27.1%	35.1%
12378-PeCDF(※a)			7.8%	14.1%	9.8%	12.6%	5.7%	9.7%	4.9%
12378-PeCDF(※b)			9.0%	16.2%	7.1%	9.8%	9.2%	9.4%	6.8%
23478-PeCDF	6.1%	13.7%	6.2%	9.7%	10.3%	9.2%	7.5%	11.6%	5.6%
123478-HxCDF	6.3%	15.2%	8.9%	11.5%	13.0%	10.8%	9.9%	8.8%	15.5%
123478-HxCDF(※a)			9.1%	9.9%	8.6%	9.2%	9.0%	8.1%	6.7%
123478-HxCDF(※b)			7.2%	13.2%	8.0%	10.8%	5.6%	9.9%	6.9%
123678-HxCDF	6.3%	10.7%	9.3%	14.5%	6.5%	10.6%	8.2%	9.4%	5.0%
123789-HxCDF	12.9%	17.4%	10.3%	16.9%	14.7%	15.8%	13.7%	12.3%	9.8%
234678-HxCDF	6.6%	10.4%	10.0%	21.8%	10.1%	10.3%	10.4%	10.0%	9.1%
1234678-HpCDF	7.4%	10.5%	7.9%	16.2%	10.1%	9.9%	9.1%	7.7%	5.2%
1234789-HpCDF	7.5%	11.5%	10.2%	15.2%	9.5%	9.8%	7.9%	7.3%	8.4%
OCDF	7.0%	10.7%	11.6%	11.5%	10.1%	10.2%	9.0%	6.6%	8.9%
344'5-TeCB(#81)	11.5%	12.9%	9.0%	16.1%	10.2%	10.0%	5.6%	11.9%	4.4%
33'44'-TeCB(#77)	8.2%	8.3%	9.3%	11.6%	5.7%	10.4%	6.2%	10.6%	5.2%
33'44'5-PeCB(#126)	8.6%	8.9%	9.4%	15.9%	9.6%	9.7%	8.9%	10.9%	7.9%
33'44'55'-HxCB(#169)	8.4%	23.1%	18.7%	18.5%	16.0%	7.6%	10.5%	15.0%	7.6%
2'344'5-PeCB(#123)	11.2%	10.7%	10.0%	14.8%	8.8%	12.9%	9.0%	7.3%	6.9%
23'44'5-PeCB(#118)	6.9%	8.3%	18.1%	13.0%	6.9%	20.1%	5.7%	7.1%	7.7%
233'44'-PeCB(#105)	8.3%	8.4%	18.5%	12.3%	8.7%	12.2%	6.2%	5.8%	8.4%
2344'5-PeCB(#114)	9.8%	12.2%	20.6%	19.0%	11.0%	12.6%	5.9%	10.9%	9.1%
23'44'55'-HxCB(#167)	8.1%	8.3%	9.8%	10.0%	10.8%	9.3%	7.5%	7.1%	6.7%
233'44'5-HxCB(#156)	8.3%	8.2%	8.9%	9.3%	7.2%	9.4%	6.2%	7.6%	7.6%
233'44'5'-HxCB(#157)	8.8%	11.5%	9.9%	9.4%	11.3%	7.6%	6.0%	5.0%	8.1%
233'44'55'-HpCB(#189)	7.2%	9.8%	7.7%	8.2%	9.0%	8.3%	7.1%	8.9%	5.3%
PCDDs/DFs			8.5%	15.4%	9.9%	10.6%	8.9%	9.1%	7.1%
DL-PCB			12.5%	13.2%	9.6%	10.9%	7.1%	9.0%	7.1%
PCDDs/DFs, DL-PCB			10.2%	14.5%	9.8%	10.7%	8.1%	9.1%	7.1%

Used GC column for 1,2,3,7,8-PeCDF and 1,2,3,4,7,8-HxCDF analysis

(※a) BPX-DXN, DB-5, BPX-5, RH-12ms etc.: separate single peak

(※b) SP-2331, CP-Sil88 etc.: including co-elute congeners

Figure 1 shows Z-sore exceed >±3 laboratory numbers in individual congeners in R-9 in 2011. Generally results from around 90% of the laboratories showed <±2 Z-score in individual congeners data. Furthermore, reproducibility data on extraction procedure (≦30 %) and injection (≦10 %) showed appreciable results from many laboratories.

The trends number of laboratories whose results exceeded >±3 of Z-score of at least one data in individual congeners, were 20 / 77 (total) for R-1, 27 / 83 (total) for R-2, 33 / 78 (total) for R-3, 23 / 75 (total) for R-4, 32 / 77 (total) for R-5, 20 / 77 (total) for R-6, 11 / 70 (total) for R-7 ,32 / 66 (total) for R-8 and 25/ 63(total) for R-9. These trends indicate that individual laboratories maintain QA/QC systems for Z-score in inter-laboratory round robin study.

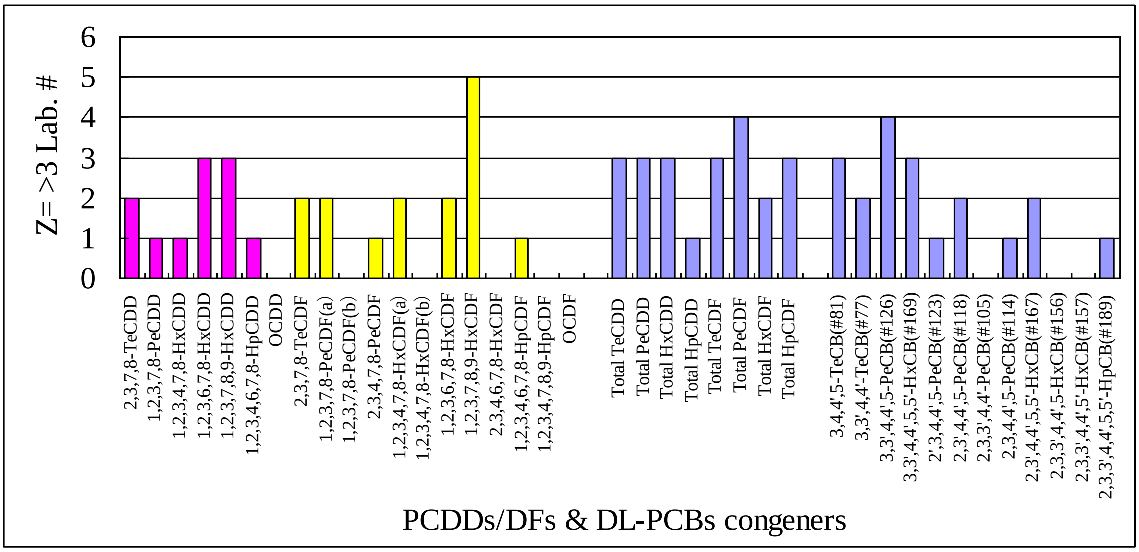

Fig. 1. Z-score exceed >±3 laboratory numbers in individual congeners (total 63 laboratories R-9 in 2011).

Used GC column for 1,2,3,7,8-PeCDF and 1,2,3,4,7,8-HxCDF analysis

(※a) BPX-DXN, DB-5, BPX-5, RH-12ms etc.: separate single peak

(※b) SP-2331, CP-Sil88 etc.: including co-elute congeners

References:

1. Shiozaki T, Takasuga T, Iwaki K, Mochizuki T, Miyazaki T, Tanaka K, (2004): *Organohalogen Compounds*, 66, 510-515.
2. Takasuga T, Tanaka K, Iwaki K., Mochizuki T, Miyazaki T, (2005): *Organohalogen Compounds*, 67, 408-411. Organohalogen Compounds, 67, 408-411 (2005).
3. Takasuga T, Otsuka K, Mochizuki T, Iwaki K, Tanaka K, Miyazaki T, (2006): *Organohalogen Compounds*, 68:1402.
4. Otsuka K, Takasuga T, Iwaki K, Tanaka K, Miyazaki T, (2007): *Organohalogen Compounds*, 69: 1272-1275.
5. Takasuga T, Otsuka K, Iwaki K, Tanaka K, Miyazaki T, (2008): *Organohalogen Compounds*, 70: 2268-2271.
6. Takasuga T, Otsuka K, Funakoshi K, Iwaki K, Matsumura T, (2009): *Organohalogen Compounds*, 71: 1548-1551.
7. Takasuga T, Miyazaki T, Kuroiwa T, Iwaki K, Ohtsuka K, Funakoshi K, Matsumura T, (2010): *Organohalogen Compounds*, 72: 1609-1612.
8. Takasuga T, Miyazaki T, Kuroiwa T, Iwaki K, Ohtsuka K, Funakoshi K, Matsumura T,(2011): *Organohalogen Compounds*, 73: 2017-2173.