Evaluation of interlaboratory study for PCDDs,PCDFs and Dioxin like PCBs in the soil reference material

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Introduction

Inter-laboratory round robin is available for maintaining dioxin analytical quality/skills by testing or certified laboratories. There are over 150 dioxin testing laboratories available in Japan consequently, Ministry of Environment (MOE) and Ministry of Economy Trade and Industry (METI) have began to investigate quality of dioxin testing laboratory and to upgrade their skills with in 4 years. On the other hand, Research Group for Dioxin Analysis which have technical experts from 33 private dioxin testing laboratories had carried out inter-laboratory round robin 4 times since 1998 to 2002. These studies has been transferred to new research group namely, Research Group on Ultra Trace Analyses (UTA) which is accompanied organization of Japan Environmental Measurement & Chemical Analysis Association (JEMCA) in 2003. The UTA consists 84 private dioxin testing laboratories and has been subjected to grow up the technical potential not only for dioxins but other trace level analysis of well known POPs, endocrine disrupting chemicals (EDCs) and ubiquitous contaminants in the environment. UTA carried out first round studies (R-1) in 2003 and second round studies (R-2) in 2004, respectively for polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs).

Methods and Materials

On the first round robin study (R-1), one fly ash extract solution and standard solution was sent to 83 members. On the second round robin study (R-2), one soil sample and standard solution was sent to 84 members. Soil samples had been dried, sieved, grinded, and checked homogeneity for particle size and inorganic component analysis, further more packed in to 200-g portions while, fly ash extracts has been packed into two 1-mL ampoules. All member laboratories were ask to consider the samples as a routine analysis with two extraction and clean up individually in addition to duplicate HRGC-HRMS analysis of sample vial. They were asked to adapt QA/QC procedures that they follow regularly. All member laboratories were asked to report all 2,3,7,8-substituted PCDD/DFs, congeners and the 12 DL-PCBs. A special result form was sent to all members in which, the following details were requested from each laboratories includes; 1. The obtained analytical data, 2. Complete analytical procedure that each laboratory follows and 3. Chromatograms of each sample.

Results of these studies are evaluated for median, normalized interquartile range (NIQR), relative standard deviations (RSD) for each polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs). Furthermore calculate Z-score and evaluate by ISO/IEC Guide 43-1 (JIS Q 0043-1). Laboratories, which exceed >3 of Z-score were required cause analysis and report of corrective action.

Results and Discussion

The results for the first robin study (R-1) were presented on isomer/congener specific basis with median, normalized semi-interquartile range (NIQR) and relative standard deviations (RSD) are summarized in Table 1. Every data set were used to identify obvious outliers. Obvious outliers were defined as having each Z-score over 2.

Table 1 Median, normalized interquartile range (NIQR) and RSD of round robin study.

	first round robin study (R-1) fly ash extract solution 2003, 83 labs.			second round robin study (R-2) soil sample 2004, 84 labs.		
	Median (pg/ml)	NIQR	RSD(%)	Median (pg/g)	NIQR	RSD(%)
2,3,7,8-TeCDD	40	3.4	8.5	0.74	0.12	16.5
1,2,3,7,8-PeCDD	170	11	6.2	6	0.87	14.5
1,2,3,4,7,8-HxCDD	94	9.7	10.3	5.6	0.87	15.4
1,2,3,6,7,8-HxCDD	130	10	8.1	10	1.6	15.9
1,2,3,7,8,9-HxCDD	120	9.6	8.2	10	1.8	17.2
1,2,3,4,6,7,8-HpCDD	380	23	6.1	53	8.8	16.5
OCDD	280	24	8.6	90	10	11.2
2,3,7,8-TeCDF	240	22	9.2	2.2	0.39	17.8
1,2,3,7,8-PeCDF	670	60	8.9	4.6	1.1	23.3
2,3,4,7,8-PeCDF	600	37	6.2	5.4	0.69	12.7
1,2,3,4,7,8-HxCDF	660	40	6	6.5	0.96	14.8
1,2,3,6,7,8-HxCDF	640	38	5.9	6.8	0.72	10.7
1,2,3,7,8,9-HxCDF	54	6.7	12.4	0.7	0.17	24.2
2,3,4,6,7,8-HxCDF	440	30	6.9	8.2	0.85	10.4
1,2,3,4,6,7,8-HpCDF	1,000	78	7.4	23	2.4	10.4
1,2,3,4,7,8,9-HpCDF	150	11	7.3	3.7	0.41	11.1
OCDF	240	17	7.1	11	1.2	10.6
344'5-TeCB(#81)	30	3.1	10.4	4.1	0.53	13
33'44'-TeCB(#77)	190	16	8.3	69	5.7	8.3
33'44'5-PeCB(#126)	130	11	8.3	6.8	0.57	8.4
33'44'55'-HxCB(#169)	52	4.4	8.4	1.3	0.3	23.2
2'344'5-PeCB(#123)	20	2.1	10.8	7.3	0.77	10.5
23'44'5-PeCB(#118)	460	30	6.6	350	27	7.8
233'44'-PeCB(#105)	260	22	8.5	170	14	8.1
2344'5-PeCB(#114)	27	2.5	9.4	11	1.3	11.8
23'44'55'-HxCB(#167)	38	3	7.8	23	2	8.4
233'44'5-HxCB(#156)	100	6.9	6.9	62	5.2	8.4
233'44'5'-HxCB(#157)	45	3.9	8.7	14	1.6	11.5
233'44'55'-HpCB(#189)	65	4.5	6.9	6.5	0.62	9.5
TEQ	50	3.3	6.50%	-	-	-

As mentioned earlier, R-1 study was carried out in 2003, and sample was distributed as an extracted solvent of fly ash. During that period, Japanese dioxin testing laboratory accreditation system (MLAP: Specified Measurement Laboratory Accreditation Program) has already been introduced. Probably, MLAP system might be possible explanation for the improvement and accuracy of dioxin analysis, since MLAP has required on-site audit and correction of improper process or quality system. RSD (%) in R-1 ranged from 5.9% to 12.4% for PCDDs/DFs, 6.9% to 10.8% for DL-PCBs and 6.5% for TEQ. RSD (%) in R-2 ranged from 10.4% to 24.2% for PCDDs/DFs, 7.8% to 23.2% for DL-PCBs. Possible explanation for slightly higher RSD (%) in R-2 calibration probably due to extraction difference. 1,2,3,7,8,9-HxCDF is relatively greater than other PCDDs/DFs, since several laboratory could not separate 1,2,3,7,8,9-HxCDF peaks from fragment ion of HpCDF. RSD (%) of DL-PCBs were almost same as those of PCDDs/DFs.

In order to evaluate the reproducibility, TEQ values and typical congeners obtained by multiple analysis were compared and plotted in Fig.1 for R-1 and Fig.2, respectively.

Table 1. GC column users among participants

GC column	Lab. number
SP-2331	56
CP-Si188	7
BPX-DXN	10
BPX-5	2
DB-5	19
BPX-50	7
DB-17	44
HT-8 PCB	56
RH-12	9
ENV-17	1
HP-50	2

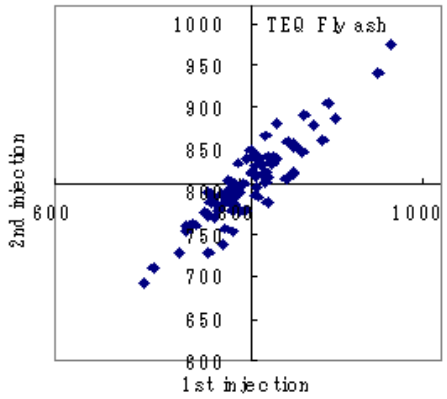

Fig. 1 Youden plot for first round robin study R-1
Cross point of each axis indicate median of each

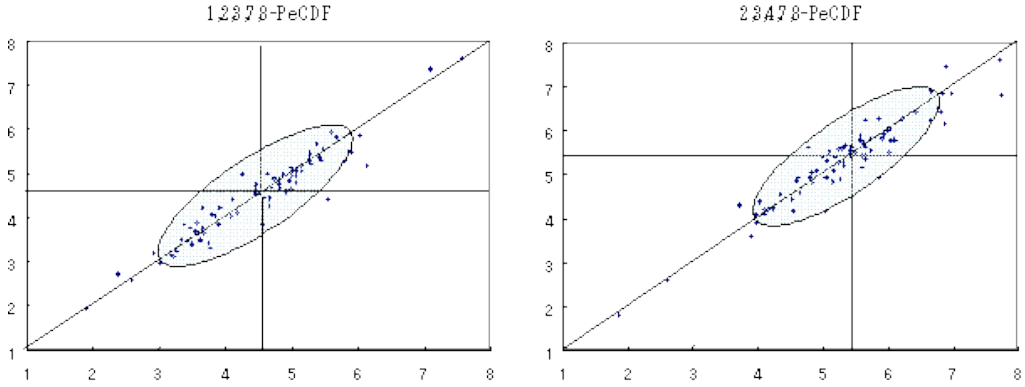

Fig. 2 Youden plot for second round robin study R-2
Cross point of each axis indicate median of each injection

Table 2. The table showing different results of 1,2,3,7,8-PeCDF when using different GC phase (e.g. polarity)

Type of GC column	Lab. No.	Average (pg/g)	SD	RSD%	MAX	MIN	Median	NIQR	CV% rob
SP-2331 CP-Si88	61	4.72	0.924	19.60%	7.59	1.92	4.8	0.719	15.0%
BPX-DXN DB-type, RH-	19	3.63	0.624	17.20%	5.11	2.55	3.54	0.389	11.0%

Table 2 shows the specific differences of analytical results for 1,2,3,7,8-PeCDF by GC column type. These results indicate that different GC phase shows different results especially for 1,2,3,7,8-PeCDF.

The main causes of these differences are due to co-eluting congeners for polar GC phase (SP-2331 or CP-Sil88)

Participants of these studies

List of members who have participated these studies was shown below.

Participants of Study R-2

BAB-Hitachi Industrial, BML, Chiba Prefectural Environment Foundation, Chugai Techinos, Dia Analysis Service,

Ebara Research, Environment and Biochemistry Research Institute, Environmental Control Center, Environmental Science Research Niigata, Environmental Technology Service, Fukuda Hydrologic Center, Fukui Environmental Analysis Center, Green Laboratory, Gumma Analysis Center, Hiroshima Environment and Health Association, Ibiden Engineering, Industrial Analysis Service, Izumitec, Japan Food Research laboratories, Japan Inspection, Joetsu Environmental Science Center, Kaneka Techno Research, KankyoGiken, Kankyo Kagaku Kenkyusyo, KankyoKogaiCenter, Kankyo Sogo Kenkyujo, Kankyo Sol-tech, Kankyo Techno, Kankyou Sogo KenkyuKiko, KankyoTechnos, Kawaju Techno Service, Kinki BunsekiCenter, Kishimoto Clinical Laboratory Group, KN Lab. Analysis, Kobelco Eco Solution, Kobelco Research Institute, JFE Technoresearch, Kyoto Microbiological Institute, Kyushu Environmental Evaluation Association, Kyushu Techno Research, Kureha Analytical center, Metocean Environment,

Mie Prefecture Environmental Conservation Agency, Mitsubishi Material, Mitsui Chemical Analysis and Consulting Service, Miura, Nature Environment Support, Nihon Environmental Services, Niigata Prefecture Environmental Analysis Center, Nittech Research, Nippon Total Science, North Techno Research, NS Kankyo, Okinawa Prefectural Environmental Science Center, Oyakama-ken KankyoHozenJigyodan, Riken Analysis Center, Ryomei Engineering, Ryonichi Engineering, Saga Prefectural Environmental Science Inspection Association, Seikan, Shimadzu Techno Research, Shinnikka Environmental Engineering, Shizuoka-ken Sangyo KankyoCenter, Sogo MizuKenkyujo, Sumiko Techno Research, Sumitomo Metal Technology, Tatsuta Environmental Analysis Center, Techno Chubu, Teijin Eco Science, Term, Toden Environmental Engineering, Toho Kaken, Toho Kako Kensetsu, Tohoku RyokkaKankyoHozen, Tokai Analytical Chemistry Institute, Tokai Technology Center, Tokai Techno, Tokyo Technical Service, Toray Research Center, Towa Kagaku, Unichemy, Unitika Environmental Technical Center, Yagai Kagaku,