

EVALUATION OF INTERLABORATORY STUDY FOR PCDDs, PCDFs AND DIOXIN LIKE PCBs IN ENVIRONMENTAL SAMPLE IN JAPAN.

Takumi TAKASUGA¹⁾, Kenji Otsuka²⁾, Tadashi Mochizuki²⁾, Kazuo IWAKI³⁾, Kiichiro TANAKA⁴⁾, Toru MIYAZAKI⁵⁾

Research Group on Ultra Trace Analyses, Japan Environmental Measurement & Chemical Analysis Association (JEMCA)

1) Shimadzu Techno Research, #1, Nishinokyo-Shimoaicho, Nakagyo-ku, Kyoto 604-8436, Japan, 2) JFE Techno Research, 3) Ohu University, 4) Toray Research Center, 5) Nittech Research

Introduction

Inter-laboratory round robin is available for maintaining dioxin analytical quality/skills by testing or certified laboratories. There are over 140 accredited Laboratory 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 examination program for order competence also. But it is more important to maintain QA/QC system and evaluate quality of daily analysis data continuously. There are some proficiency test for dioxin analysis by JSAC (The Japan Society for Analytical Chemistry), MOE and METI officially.

On the other hand, Research Group for Dioxin Analysis, which has 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, second round studies (R-2) in 2004 and third round studies (R-3) in 2005, respectively for polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs). This paper summarizes and evaluate of recent interlaboratory study for PCDDs,PCDFs and Dioxin like PCBs in environmental sample.

Materials and Methods

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 and standard solution has been packed into two 1-mL ampoules. On the third round robin study (R-3), polyurethane foam (PUF) fortified fly ash extract was sent to 82 members. All member laboratories were ask to consider the samples as a routine analysis by official Japanese analytical method for dioxins with 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 calculated Z-score and evaluated 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 round robin study were presented on isomer/congener specific basis with median, NIQR and RSD are summarized in Table 1. Every data set was 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.

PCDDs/DFs , DL-PCB	1st round robin study (R-1) fly ash extract, 2003, 83 lab.			2nd round robin study (R-2) soil sample, 2004, 84 lab.			3rd round robin study (R-3) PUFsample, 2005, 82 lab.		
	Median (pg/mL)	NIQR	RSD(%)	Median (pg/g)	NIQR	RSD(%)	Median (pg/total)	NIQR	RSD(%)
2378-TeCDD	39.9	3.4	8.5%	0.8	0.1	15.8%	121.5	9.1	7.5%
12378-PeCDD	172.8	10.8	6.3%	6.0	1.0	16.7%	321.0	18.9	5.9%
123478-HxCDD	94.4	9.7	10.3%	5.6	0.9	15.8%	153.5	13.0	8.5%
123678-HxCDD	125.0	10.9	8.7%	10.2	1.7	16.6%	156.5	15.2	9.7%
123789-HxCDD	117.5	9.7	8.3%	10.2	1.8	17.5%	214.0	14.1	6.6%
1234678-HpCDD	374.8	23.6	6.3%	53.5	8.8	16.5%	443.5	40.0	9.0%
OCDD	279.0	23.7	8.5%	90.4	10.4	11.5%	174.0	11.1	6.4%
2378-TeCDF	241.8	22.0	9.1%	2.2	0.4	17.9%	249.0	22.6	9.1%
12378-PeCDF	669.3	67.0	10.0%	4.6	1.1	23.4%	287.0	31.9	11.1%
23478-PeCDF	596.0	36.2	6.1%	5.4	0.7	13.7%	245.5	15.2	6.2%
123478-HxCDF	656.0	41.0	6.3%	6.5	1.0	15.2%	157.5	14.1	8.9%
123678-HxCDF	635.8	39.9	6.3%	6.8	0.7	10.7%	175.5	16.3	9.3%
123789-HxCDF	54.3	7.0	12.9%	0.7	0.1	17.4%	19.7	2.0	10.3%
234678-HxCDF	433.8	28.8	6.6%	8.2	0.8	10.4%	111.0	11.1	10.0%
1234678-HpCDF	1045.0	77.3	7.4%	23.0	2.4	10.5%	154.5	12.2	7.9%
1234789-HpCDF	152.3	11.4	7.5%	3.7	0.4	11.5%	32.8	3.3	10.2%
OCDF	241.0	16.8	7.0%	11.3	1.2	10.7%	29.0	3.4	11.6%
344'5'-TeCB(# 81)	30.2	3.5	11.5%	4.1	0.5	12.9%	10.7	1.0	9.0%
33'44'-TeCB(# 77)	188.3	15.5	8.2%	69.0	5.7	8.3%	78.8	7.3	9.3%
33'44'5'-PeCB(# 126)	130.5	11.2	8.6%	6.8	0.6	8.9%	44.1	4.1	9.4%
33'44'55'-HxCB(# 169)	52.3	4.4	8.4%	1.3	0.3	23.1%	9.6	1.8	18.7%
2'344'5'-PeCB(# 123)	19.5	2.2	11.2%	7.3	0.8	10.7%	9.2	0.9	10.0%
23'44'5'-PeCB(# 118)	461.8	31.8	6.9%	344.3	28.7	8.3%	46.0	8.3	18.1%
233'44'-PeCB(# 105)	262.8	21.9	8.3%	168.3	14.1	8.4%	37.0	6.8	18.5%
2344'5'-PeCB(# 114)	26.9	2.6	9.8%	11.0	1.3	12.2%	5.3	1.1	20.6%
23'44'55'-HxCB(# 167)	38.6	3.1	8.1%	23.4	1.9	8.3%	16.2	1.6	9.8%
233'44'5'-HxCB(# 156)	100.4	8.3	8.3%	61.7	5.1	8.2%	22.5	2.0	8.9%
233'44'5'-HxCB(# 157)	45.6	4.0	8.8%	14.0	1.6	11.5%	14.1	1.4	9.9%
233'44'55'-HpCB(# 189)	65.2	4.7	7.2%	6.5	0.6	9.8%	12.6	1.0	7.7%
TOTAL TEQ	808.2	36.7	4.5%	16.4	2.3	14.0%	716.5	35.3	4.9%

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) 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-3 ranged from 8.7% (5.9% to 11.6%) for PCDDs/DFs, 12.5% (7.7% to 20.6%) for DL-PCBs and 4.9% for TEQ. The RSD(%) result in R-3 shows a little bigger to R-1 but more smaller to R-2. Possible explanation for slightly higher RSD (%) in R-2 calibration probably due to extraction difference for low level soil sample.

In order to evaluate the reproducibility, TEQ values and typical congeners obtained by multiple analysis were compared and plotted in Fig.1 for R-3.

Fig. 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)

The number of laboratories which presented report of corrective action >3 of Z-score, were 31 lab./83 lab. (total) for R-1, 30 lab./81 lab.(total) for R-2 and 33 lab./78 lab.(total) for R-3.

Literature Cited

1. Takuya Shiozaki, Takumi Takasuga, Kazuo Iwaki, Tadashi Mochiduki, Toru Miyazaki, Kiichiro Tanaka, Research Group on Ultra trace Analyses : Evaluation of Interlaboratory Round Robin Study (2000-2002). *J. Organohalogen. Compd, Dioxin* 2004
2. Takumi TAKASUGA, Kiichiro TANAKA, Kazuo IWAKI, Tadashi Mochizuki, Toru MIYAZAKI: Evaluation of interlaboratory study for PCDDs, PCDFs and Dioxin like PCBs in the soil reference material. *J. Organohalogen. Compd, Dioxin* 2005

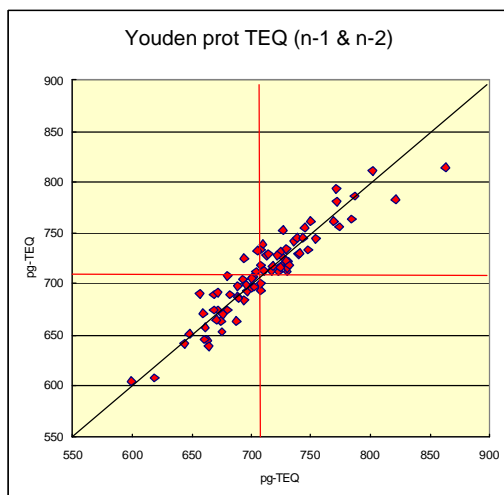


Fig. 1 Youden plot for TEQ in R-3 study
Cross point of each axis indicate median of each injection

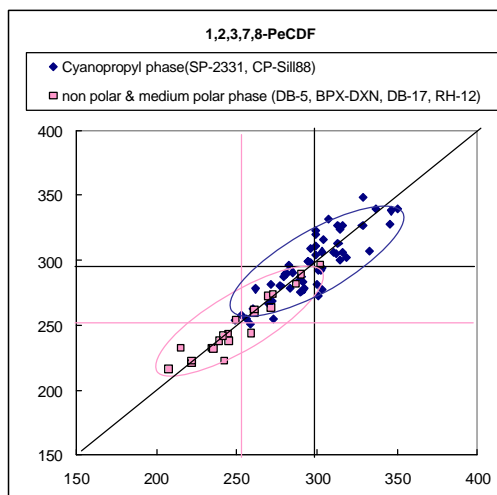


Fig. 2 Youden plot for 1,2,3,7,8-PeCDF in R-3.
Cross point of each axis indicate median of each injection

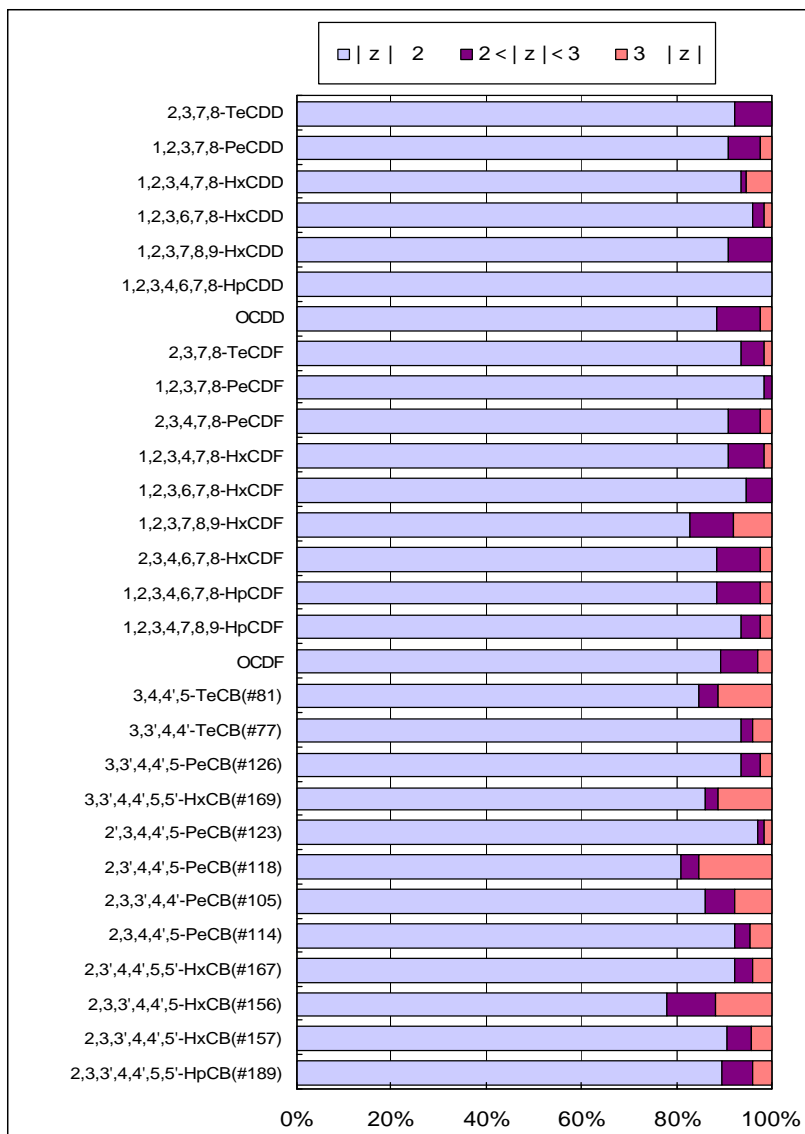


Fig. 3 Relative percentage of Z-score results in R-3 round robin study.