EVALUATION OF INTERLABORATORY STUDY FOR PCDDs,PCDFs AND DIOXIN LIKE PCBs IN THE SOIL REFERENCE MATERIAL.

OTSUKA K[1)], TAKASUGA T [2)], IWAKI K[3)], TANAKA K[4)], MIYAZAKI T[5)]
Research Group on Ultra Trace Analyses, Japan Environmental Measurement & Chemical Analysis Association (JEMCA)
1) JFE Techno Research, 1-1,minami-watarida-cho, kawasaki-ku, kawasaki, kanagawa 210-855, Japan,   2) Shimadzu Techno Research, 3) Ohu University, 4) Toray Research Center, 5) Nittech Research

Abstract

In Research Group on Ultra Trace Analyses(UTA), "Dioxin fourth round robin study (R-4)" were conducted by use of the paddy soil sample in 2006 Japan. Results of these studies were evaluated based on ISO/IEC Guide43-1(JIS Q 0043-1) including Z-score value by the organizer. CV % rob in R-4 ranged from 15.8 %(9.7 % to 24.8 %) for PCDDs/DFs, 13.5 %(8.2 % to 21.5 %) for DL-PCBs and 12.4 % for TEQ.

Introduction

Inter-laboratory round robin is available for maintaining dioxin analytical quality/skills by testing or certified laboratories. The UTA consists 81 private dioxin analytical 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), one fly ash extract solution and standard solution for 83 members in 2003, second round studies (R-2), one soil sample for 84 members in 2004, third round studies (R-3) polyurethane foam sample fortified extract for 82 members in 2005 and fourth round studies (R-4) in 2006, respectively for polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs).

Materials and Methods

On the fourth round robin study (R-4), one paddy soil sample was sent to 79 members. The soil sample distributed the paddy soil and after the air drying, crushing, and division of the riddle, the sample to which the mixture making was done by V type Brenda was distributed. 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 PCDDs/DFs congeners and the 12 DL-PCBs additionally PCDDs/DFs homologue. 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 PCDDs/DFs and 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 round robin study were presented on isomer/congener specific basis with median, 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 2.

CV % rob in R-4 ranged from 15.8 %(9.7 % to 24.8 %) for PCDDs/DFs, 13.5 %(8.2 % to 21.5 %) for DL-PCBs and 12.4 % for TEQ. This CV % rob result in R-4 shows a little bigger compare to past results with PCDDs/DFs, DL-PCBs and Total TEQ. Possible explanation for slightly higher CV % rob in R-4 due to wide ranged concentration between congeners, and in particular, as for 2,3,7,8-TeCDD (CV % rob=24.8 %) which deviation was relatively big because of low concentration, and, as for this, a factor to be different from OCDD (CV % rob=13.9 %) which was highest concentration around 20ng/g.

Table 1 Statistical analysis of the analytical results of PCDD/PCDF and DL-PCB isomers

| PCDDs/DFs	Median (pg/g)	NIQR	CV%rob	DL-PCB	Median (pg/g)	NIQR	CV%rob
2378-TeCDD	1.0	0.3	24.8	344'5-TeCB(#81)	3.5	0.6	16.1
12378-PeCDD	8.3	1.4	16.6	33'44'-TeCB(#77)	78.1	9.0	11.6
123478-HxCDD	12.2	2.0	16.2	33'44'5-PeCB(#126)	7.4	1.2	16.7
123678-HxCDD	37.2	4.9	13.3	33'44'55'-HxCB(#169)	1.3	0.2	18.5
123789-HxCDD	27.1	3.6	13.4	2'344'5-PeCB(#123)	7.7	1.1	14.8
1234678-HpCDD	1158.8	178.4	15.4	23'44'5-PeCB(#118)	308.2	40.1	13.0
OCDD	19587.5	2715.0	13.9	233'44'-PeCB(#105)	152.5	20.2	13.2
2378-TeCDF	3.9	0.6	15.5	2344'5-PeCB(#114)	3.3	0.7	21.5
12378-PeCDF	9.0	2.0	22.2	23'44'55'-HxCB(#167)	20.8	2.1	10.0
23478-PeCDF	5.6	0.5	9.7	233'44'5-HxCB(#156)	48.6	4.5	9.3
123478-HxCDF	42.6	4.9	11.5	233'44'5'-HxCB(#157)	14.2	1.3	9.4
123678-HxCDF	20.5	3.0	14.5	233'44'55'-HpCB(#189)	6.2	0.5	8.2
123789-HxCDF	4.5	0.8	16.9	—	—	—	—
234678-HxCDF	14.8	3.2	21.8	—	—	—	—
1234678-HpCDF	412.0	66.7	16.2	—	—	—	—
1234789-HpCDF	60.8	9.2	15.2	—	—	—	—
OCDF	1336.3	154.3	11.5	TOTAL TEQ	48.1	6.0	12.4
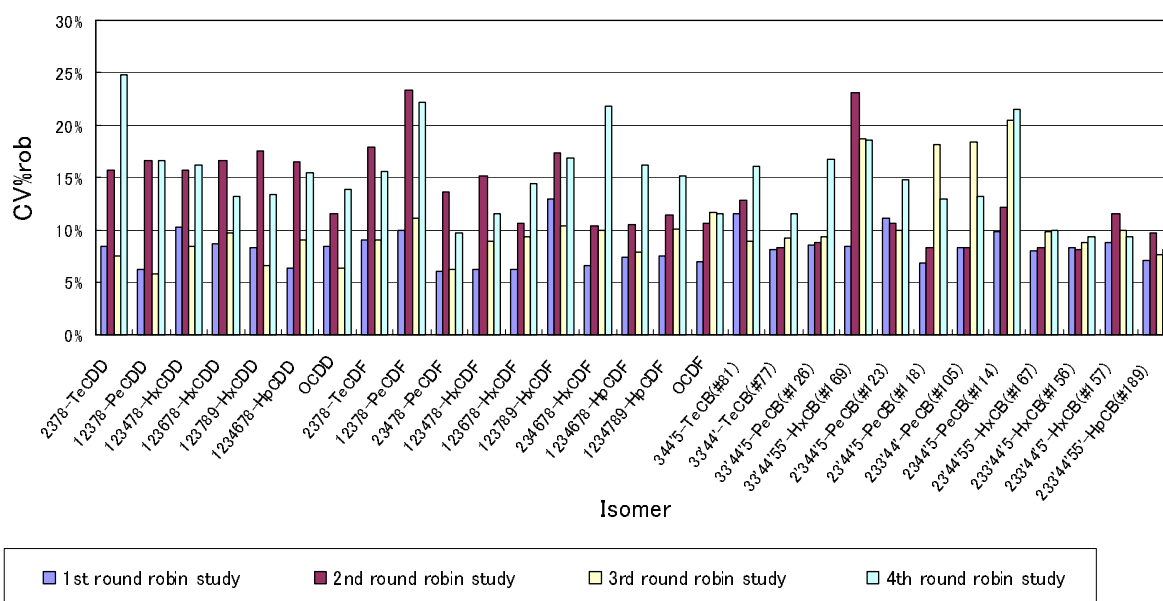
Fig. 1 Transition of the 4th round robin study result because of the 1st (CV % rob)

Additionally the specific evaluation was conducted between the differences of analytical results by GC phase column type, which shows different results due to co-eluting congeners for each GC phase.

In order to evaluate the reproducibility, TEQ values and typical congeners obtained by multiple analysis were compared and Youden plotted in Fig.2 for R-4.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 , 33 lab./78 lab.(total) for R-3 and 23 lab./75 lab.(total) for R-4. Figure 3 shows Z-score appearance rate of R-4 round robin study.

References

1. Takuya Shiozaki, Takumi Takasuga, Kazuo Iwaki, Tadashi Mochiduki, Toru Miyazaki, Kiichiro Tanaka: :*Organohalogen Comp* 2004;66:519.
2. Takumi TAKASUGA, Kiichiro TANAKA, Kazuo IWAKI, Tadashi Mochizuki, Toru MIYAZAKI: *Organohalogen Comp* 2005; 67:408.
3. Takumi TAKASUGA, Kenji OTSUKA, Tadashi MOCHIZUKI, Kazuo IWAKI, Kiichiro TANAKA, Toru MIYAZAKI:*Organohalogen Comp* 2006; 68:1402.
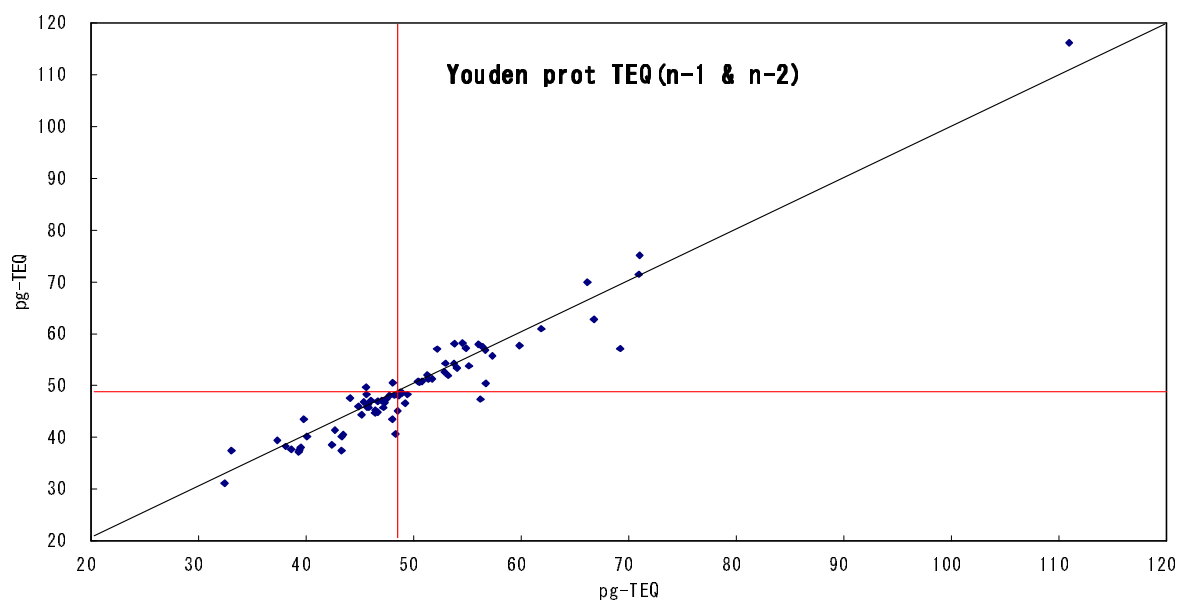
Fig. 2 Youden plot for TEQ in R-4 study
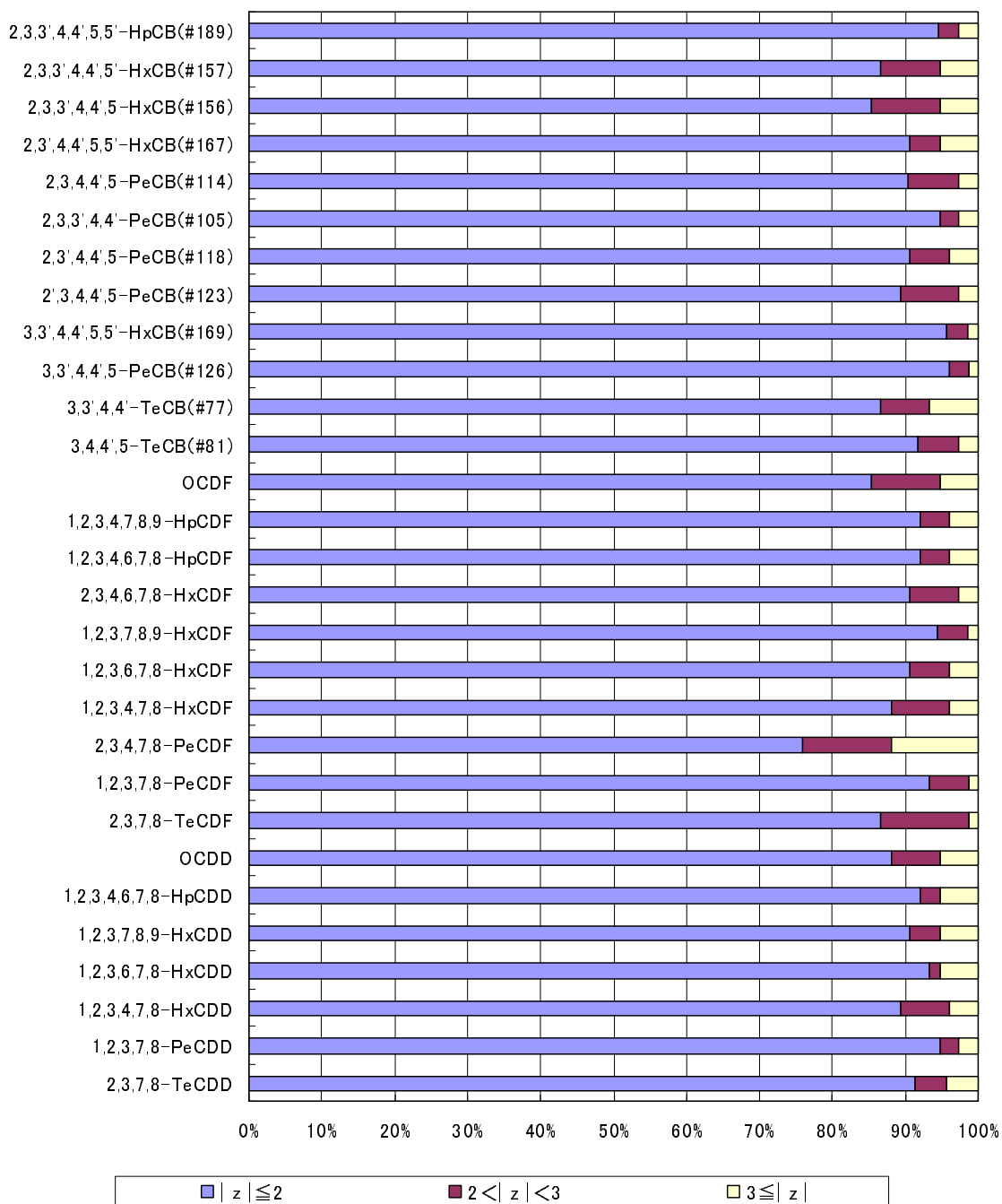Cross point of each axis indicate median of each injection

Fig. 3 Relative percentage of Z-score results in R-4 round robin study.