Intercalibration Study on PCDD, PCDF and planar PCBs for Standard Solutions and Flyash Sample in Japan

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Introduction

Quality assurance (QA) and quality control (QC) in Dioxin analysis is most important, since the analysis of dioxin request not only ultra trace analysis but also extremely high accuracy and precision. Accordingly, all the process ranging from sampling, extraction, clean up, GC-MS analysis, identification, to quantification shall be conducted under identical and strict quality control.
Several interlaboratory calibration studies have been carried out for environmental, industrial samples and commercially available dioxin standards 1,2,3,4,5).
The only available standard reference material (SRM) is 2,3,7,8-TCDD and 13C12-2,3,7,8-TCDD from NIST SRM1614. Cambridge Isotope Laboratories (USA) and Wellington Laboratories (Canada) mainly produce commercially available native and isotope labeled standard in ±10% deviation of guarantied concentration. Certified reference materials (CRMs) in environmental samples are also available.
For the QA/QC program in dioxin analysis each laboratory should record and report about required matters if necessary. These are followings, record of procedures (sampling, extraction, clean up and GC-MS measurement, determination), record of chromatograms including separation of target isomers, fluctuation in sensitivity of instrument and instrument calibration reports at high resolution, record of preparation of standard and their traceability, results of minimum method detection and determination limits, validation results of internal standard recovery, isotope ratio, method blank and reproducibility data.
From the reported result of standard solutions and fly ash extracts by several laboratories most of results are within 25% in relative standard deviation especially for total TEQ, but each congener has still problems.

Materials and Methods

Standard solution mixture of PCDDs/PCDFs and coplanar PCBs were provided by Wellington laboratories. Individual congener(crystaline and solution) were provided by Cambridge Isotope Laboratories (USA) and Wellington Laboratories (Canada). Three kinds of flyash sample were selected for intercalibration in which one was carbon-splayed flyash.
Each laboratory uses their own standard both native and isotope labeled. Analytical method by HRGC-HRMS were according to Japanese method (i.e. JIS 0311). Each laboratory should report four data including duplicate analysis and duplicate extraction of sample. Additionally recovery, fortification level and kinds of labeled internal standard were reported.

Results and Discussion

Standard solution

From the results of standard solution, RSD(%) were around 10 % which is in the same level of to the deviation of guarantied concentration. Relatively RSD(%) of coplanar PCB were in the wide range of 10-17%. Reproducibility in each laboratory was within 3%. This indicate that analytical error of instrument were very small. Also each laboratories use their own standard solution in difference of providing company, kinds of labeled congener, lot, dilution method and calibration method.

Flyash sample

From the results of flyash sample RSD(%) of total WHO-TEQ were within 8-12.4%. The deviation of coplanar PCB were relatively big. These results indicate that the difference of deviation arises from extraction efficiency, presence of interferences, capability of isomer separation in GC column. Reproducibility in each laboratory was within 10%.

The main factor of analytical error were discussed and summarized as followings.

1. Easy mistake of input information.
2. Mistake of calculations and insufficient confirmation.
3. Error of small volume sampling of solution.
4. Difference of native standard solution in providing company, lot, and preparation or dilution method and calibration method.
5. Difference of internal standard solution in providing company, kinds of labeled congener and fortification level.
6. Difference of capability of isomer separation in GC column.
7. Difference of presence of interference from insufficient clean up method.
8. Difference of extraction efficiency for flyash.
9. Unsuitable instrument operation.
10. Deviation and linearity of calibration curve.
11. Reproducibility of analysis.
12. Mistake of identification of target isomer.

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Table 1. Results of Standard Solutions in interlaboratories(19 Lab)

PCDD,PCDF ampoule unit□pg/uL	Designed Value	AVRAGE	MEDIAN	MIN	MAX	STDEV	RSD %
2,3,7,8-TeCDD	2	1.95	1.97	1.21	2.58	0.287	14.67
1,2,3,7,8-PeCDD	5	4.95	5.01	4.32	5.93	0.404	8.17
1,2,3,4,7,8-HxCDD	5	4.79	4.84	3.82	5.88	0.455	9.50
1,2,3,6,7,8-HxCDD	5	4.75	4.67	3.84	6.18	0.494	10.41
1,2,3,7,8,9-HxCDD	5	4.83	4.92	4.20	6.56	0.538	11.13
1,2,3,4,6,7,8-HpCDD	5	5.22	5.29	4.17	5.84	0.432	8.29
OCDD	10	10.05	10.19	8.56	11.15	0.857	8.53
2,3,7,8-TeCDF	2	1.97	2.00	1.47	2.42	0.206	10.47
1,2,3,7,8-PeCDF	5	4.73	4.68	3.80	5.44	0.394	8.34
2,3,4,7,8-PeCDF	5	4.70	4.69	3.82	6.28	0.549	11.68
1,2,3,4,7,8-HxCDF	5	4.86	4.89	3.89	5.94	0.488	10.04
1,2,3,6,7,8-HxCDF	5	4.78	4.82	3.68	5.55	0.511	10.69
1,2,3,7,8,9-HxCDF	5	4.68	4.63	3.84	5.46	0.469	10.02
2,3,4,6,7,8-HxCDF	5	4.85	4.95	3.78	5.63	0.480	9.90
1,2,3,4,6,7,8-HpCDF	5	5.09	5.13	4.26	5.54	0.355	6.99
1,2,3,4,7,8,9-HpCDF	5	4.84	4.97	4.12	5.17	0.311	6.43
OCDF	10	9.63	9.71	8.68	10.88	0.602	6.25
COPCB ampoule unit□pg/uL							
3,4,4',5-TeCB (# 81)	10	9.75	9.62	7.97	11.93	1.081	11.09
3,3',4,4'-TeCB (# 77)	10	9.81	9.90	7.46	11.90	1.193	12.16
3,3',4,4',5-PeCB (#126)	10	9.64	9.61	7.75	13.50	1.686	17.49
3,3',4,4',5,5'-HxCB(#169)	10	9.81	9.96	7.61	14.20	1.471	15.00
2',3,4,4',5-PeCB (#123)	10	9.75	9.49	8.09	15.00	1.564	16.04
2,3',4,4',5-PeCB (#118)	10	9.90	9.41	8.03	13.90	1.504	15.19
2,3,3',4,4'-PeCB (#105)	10	9.89	9.95	8.11	12.83	1.360	13.76
2,3,4,4',5-PeCB (#114)	10	9.72	9.58	7.08	13.50	1.589	16.36
2,3',4,4',5,5'-HxCB (#167)	10	9.67	9.91	6.65	11.78	1.125	11.64
2,3,3',4,4',5-HxCB (#156)	10	9.69	9.88	6.60	12.93	1.305	13.47
2,3,3',4,4',5'-HxCB (#157)	10	9.49	9.60	7.58	12.33	1.040	10.96
2,3,3',4,4',5,5'-HpCB (#189	10	9.85	9.56	7.46	12.90	1.383	14.05
2,2',3,4,4',5,5'-HpCB(#180	10	9.78	9.57	6.89	14.33	1.629	16.66
2,2',3,3',4,4',5-HpCB(#170	10	10.23	10.02	7.58	13.90	1.758	17.18

Table 2. Results of Fly ash sample(A,B,C)in interlaboratories□(unit:ng/g(dry)□

	Flyash A		Flyash B		Flyash C	
Lab. No.	1,2,3,4,5,6,7 (n=7)		8,9,10,11,12,13,14 (n=7)		16,17,18,19,20 (n=5)	
Flyash	A		B		C	
	AVRAGE	RSD %	AVRAGE	RSD %	AVRAGE	RSD %
2,3,7,8-TeCDD	0.0408	11.62	0.051	17.87	0.192	10.94
1,2,3,7,8-PeCDD	0.212	16.90	0.294	11.56	0.605	14.23
1,2,3,4,7,8-HxCDD	0.27	12.85	0.403	14.23	0.814	16.09
1,2,3,6,7,8-HxCDD	2.53	8.15	1.56	16.78	1.51	13.19
1,2,3,7,8,9-HxCDD	1.69	12.85	0.843	12.09	1.03	20.38
1,2,3,4,6,7,8-HpCDD	33.1	17.40	10.1	14.28	15.8	25.97
OCDD	63.2	23.34	19.3	13.14	39.4	30.12
2,3,7,8-TeCDF	0.216	31.74	0.371	10.20	0.845	6.67
1,2,3,7,8-PeCDF	0.814	22.14	1.14	18.68	1.63	17.83
2,3,4,7,8-PeCDF	1.07	9.05	1.16	8.09	1.38	11.67
1,2,3,4,7,8-HxCDF	2.03	11.66	1.63	23.63	1.79	20.32
1,2,3,6,7,8-HxCDF	2.26	14.10	1.82	21.74	1.95	17.44
1,2,3,7,8,9-HxCDF	0.391	16.66	0.142	37.93	0.154	34.75
2,3,4,6,7,8-HxCDF	5.7	16.23	2.35	15.95	2.85	18.53
1,2,3,4,6,7,8-HpCDF	15.4	19.05	6.97	13.73	9.29	19.81
1,2,3,4,7,8,9-HpCDF	4.83	13.68	0.95	20.75	1.14	27.40
OCDF	29.7	19.70	3.8	14.81	5.27	27.36
TeCDDs	51.9	18.52	8.24	15.83	3.49	12.51
PeCDDs	61.3	9.77	14.2	12.62	7.74	15.31
HxCDDs	270	12.41	27.1	18.22	17.1	12.43
HpCDDs	68	18.44	19.9	11.97	29.8	24.82
OCDD	63.2	23.34	19.3	13.14	39.4	30.12
PCDDs	514	11.79	88.4	10.11	97.4	22.67
TeCDFs	15.8	8.07	13.4	10.52	21.9	9.37
PeCDFs	20.9	11.01	14	6.21	19.8	14.84
HxCDFs	30.5	7.12	15.5	16.67	18.9	16.67
HpCDFs	37.8	13.14	10.6	14.67	14.4	18.95
OCDF	30.1	19.70	3.8	14.81	5.27	27.36
PCDFs	135	9.88	57.3	8.73	80.2	13.32
PCDDs+PCDFs	649	10.73	146	8.44	178	17.58
3,4,4',5-TeCB (# 81)	0.173	12.29	0.312	13.68	0.135	7.15
3,3',4,4'-TeCB (# 77)	0.269	19.10	0.457	11.86	0.379	16.36
3,3',4,4',5-PeCB (#126)	0.467	9.39	0.801	20.68	0.474	9.91
3,3',4,4',5,5'-HxCB(#169)	0.312	6.62	0.573	24.87	0.259	15.44
2',3,4,4',5-PeCB (#123)	0.0584	22.82	0.146	17.27	0.0317	56.19
2,3',4,4',5-PeCB (#118)	0.51	10.99	0.322	23.48	0.193	23.03
2,3,3',4,4'-PeCB (#105)	0.468	10.14	0.455	26.54	0.235	23.53
2,3,4,4',5-PeCB (#114)	0.0929	34.30	0.128	22.74	0.0361	15.19
2,3',4,4',5,5'-HxCB (#167)	0.344	99.27 #128	0.25	30.01	0.0902	8.73
2,3,3',4,4',5-HxCB (#156)	0.56	26.26	0.498	23.59	0.262	41.30
2,3,3',4,4',5'-HxCB (#157)	0.371	31.86	0.467	22.46	0.131	13.92
2,3,3',4,4',5,5'-HpCB (#189)	0.638	11.21	0.598	21.51	0.194	34.79
2,2',3,4,4',5,5'-HpCB(#180)	0.319	25.97	0.155	58.58	0.132	67.37
2,2',3,3',4,4',5-HpCB(#170)	1.84	14.53	0.473	49.30	0.334	18.78
PCDD+PCDF I-TEQ	2.86	7.60	1.95	8.71	2.67	12.92
PCDD+PCDF WHO-TEQ	2.88	6.84	2.08	8.93	2.93	12.18
COPCB WHO-TEQ	0.0505	8.96	0.0866	19.95	0.0503	8.97
PCDD+PCDF+COPCB WHO-TEQ	2.9	7.02	2.2	7.29	3	12.78