

## Calibration Study of Dioxin Analysis for Japanese Tap Water

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### Introduction

In Japan, dioxin monitoring for tap water (raw and treated water) have been carried out by a official manual “Dioxins Monitoring Manual for Raw and Treated Water of Tap Water (Ministry of Health and Welfare, Sep.1999)”. This manual includes sampling, chemical pretreatment, HRGC/HRMS measurement and quality management. Regarding “*in situ*”-sampling, large volume pre-concentration system is prescribed in order to collect 2000L (2m<sup>3</sup>) water sample (in case of treated water). As dioxin concentration of treated water extremely low (femto gram-TEQ/L level). It is indispensable to execute quality management for all steps (from sampling to GC/MS determination) for monitoring survey.

Calibration study (Proficiency Testing) for ultra-low concentration of dioxins was performed with an eye to QA/QC of dioxin analysis for Japanese tap water. Total of 17 laboratories have participated in the program.

### Materials and Methods

The four test samples were synthetically prepared by spiking standard solutions of known concentrations (Non Certified Reference Material) of dioxins into an ample (2 samples, each 1mL, including PCDDs/PCDFs) and polyurethane form plug (1 sample, 90mmID, 100mm height, including PCDDs/PCDFs and Dioxin like PCBs extracted from environmental medium) containing approximately low pg absolute value. Another 1 sample for blank test was prepared by no-spiking polyurethane form plug (not disclosed to participating laboratories).

### Results

Statistical evaluations were followed by a manner of ISO Guide 43. Robust statistical approach which uses z-scores, by Quartile Deviation (NIQR: normalized interquartile range) and Median was used to evaluate the participating laboratory's performance. Results are shown in *Table-1* (Standard solution in ample), *Table-2* (polyurethane form plug) and *Figure-1* (z-score for polyurethane form plug). Main reason of “z-score>2” in 2 or 3 laboratories were caused by lack of GC/MS sensitivity and calculation mistakes. Although concentration levels were extremely low, the “Robust coefficient variations” of almost congeners were below 10%, and z-score of each congener reported from participated laboratories within 2.

Table-1. Summary of statistical values for tow testing samples (standard solution in ample).

Compounds	Sample-A (Mixed Standard Solution)						Sample-B (Mixed Standard Solution)						
	Average (pg/uL)	Median (pg/uL)	Lower Quartile (pg/uL)	Upper Quartile (pg/uL)	Normalized IQR (pg/uL)	Robust CV (%)	Prepared Conc. (pg/uL)	Average (pg/uL)	Median (pg/uL)	Lower Quartile (pg/uL)	Upper Quartile (pg/uL)	Normalized IQR (pg/uL)	Robust CV (%)
2,3,7,8-TeCDD	0.48	0.40	0.36	0.44	0.054	13.4	0.20	0.18	0.19	0.17	0.20	0.019	10.0
TeCDDs	5.8	6.0	5.4	6.3	0.61	10.3	60	61	60	58	65	4.6	7.7
1,2,3,7,8-PeCDD	0.82	0.82	0.78	0.86	0.057	7.0	0.20	0.17	0.17	0.16	0.20	0.030	17.4
PeCDDs	2.3	2.3	2.2	2.4	0.13	5.6	0.20	0.19	0.18	0.17	0.20	0.022	12.4
1,2,3,4,7,8-HxCDD	0.36	0.38	0.34	0.40	0.043	11.4	0.40	0.36	0.38	0.35	0.40	0.041	10.9
1,2,3,6,7,8-HxCDD	0.73	0.72	0.66	0.79	0.095	13.1	0.40	0.40	0.40	0.37	0.42	0.033	8.3
1,2,3,7,8,9-HxCDD	0.37	0.38	0.35	0.41	0.039	10.4	0.20	0.18	0.18	0.18	0.20	0.015	8.2
HxCDDs	1.8	1.7	1.6	1.8	0.15	9.0	1.0	1.0	0.95	0.92	1.0	0.063	6.6
1,2,3,4,6,7,8-HpCDD	1.9	1.9	1.8	2.0	0.13	6.8	1.0	0.97	0.99	0.93	1.0	0.050	5.1
HpCDDs	1.9	2.0	1.8	2.1	0.17	8.6	1.0	0.97	1.0	0.93	1.0	0.050	5.0
OCDD	9.9	9.8	9.7	10	0.22	2.3	50	4.7	4.8	4.5	50	0.35	7.4
Total PCDDs	22	22	21	23	0.93	4.2	67	68	67	65	72	4.6	6.9
2,3,7,8-TeCDF	2.0	2.0	1.9	2.1	0.11	5.6	2.0	1.8	1.9	1.7	2.0	0.20	10.7
TeCDFs	6.1	6.2	5.7	6.4	0.56	9.0	2.0	2.0	2.0	1.9	2.0	0.074	3.7
1,2,3,7,8-PeCDF	0.66	0.68	0.57	0.74	0.13	18.7	4.0	3.9	4.0	3.6	4.1	0.41	10.3
2,3,4,7,8-PeCDF	0.53	0.54	0.50	0.56	0.039	7.3	0.40	0.40	0.41	0.38	0.45	0.052	12.7
PeCDFs	2.1	2.1	2.0	2.2	0.15	7.2	0.80	0.80	0.82	0.72	0.86	0.10	12.4
1,2,3,4,7,8-HxCDF	1.1	1.1	0.97	1.2	0.17	15.3	0.40	0.39	0.39	0.38	0.41	0.020	5.2
1,2,3,6,7,8-HxCDF	0.50	0.51	0.47	0.52	0.035	7.0	0.40	0.34	0.36	0.33	0.39	0.043	11.8
1,2,3,7,8,9-HxCDF	0.40	0.39	0.36	0.43	0.046	11.9	0.20	0.16	0.15	0.14	0.18	0.024	16.1
2,3,4,6,7,8-HxCDF	0.89	0.96	0.87	0.98	0.080	8.3	0.60	0.52	0.52	0.48	0.56	0.057	11.2
HxCDFs	3.9	3.9	3.8	4.0	0.15	3.8	1.6	1.5	1.5	1.4	1.6	0.11	7.7
1,2,3,4,6,7,8-HpCDF	2.0	2.0	1.9	2.0	0.074	3.7	1.0	0.91	0.92	0.88	0.96	0.056	6.0
1,2,3,4,7,8,9-HpCDF	0.38	0.39	0.38	0.41	0.022	5.7	0.40	0.34	0.34	0.31	0.38	0.046	13.6
HpCDFs	2.4	2.4	2.3	2.6	0.19	7.7	1.4	1.3	1.3	1.2	1.3	0.074	5.7
OCDF	2.0	2.0	1.9	2.0	0.074	3.7	1.0	0.99	0.98	0.94	1.0	0.043	4.4
Total PCDFs	17	17	16	17	0.74	4.5	8.8	8.5	8.5	7.8	8.8	0.72	8.5
Total (PCDDs+PCDFs)	38	38	37	39	1.5	3.9	76	76	76	73	81	5.4	7.1

## References

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Table-2. Summary of statistical values for one testing sample (spiked polyurethane form plug).

Compounds		Prepared Conc. (pg/L)	Average (pg/L)	Median (pg/L)	Lower Quartile (pg/L)	Upper Quartile (pg/L)	Normalaized IQR (pg/uL)	Robust CV (%)
P C D D s	1,3,6,8-TeCDD	0.012	0.012	0.012	0.010	0.013	0.0020	17.7
	1,3,7,9-TeCDD	0.0060	0.0056	0.0056	0.0052	0.0060	0.00061	11.0
	2,3,7,8-TeCDD	0.00040	0.00047	0.00050	0.00040	0.00058	0.00013	26.7
	TeCDDs	0.025	0.023	0.023	0.021	0.025	0.0033	14.5
	1,2,3,7,8-PeCDD	0.0014	0.0012	0.0012	0.0009	0.0014	0.00032	26.7
	PeCDDs	0.024	0.019	0.020	0.018	0.022	0.0028	13.9
	1,2,3,4,7,8-HxCDD	0.0014	0.0014	0.0012	0.0011	0.0014	0.00022	18.5
	1,2,3,6,7,8-HxCDD	0.0027	0.0024	0.0024	0.0020	0.0026	0.00044	18.5
	1,2,3,7,8,9-HxCDD	0.0023	0.0021	0.0022	0.0018	0.0024	0.00044	20.7
	HxCDDs	0.033	0.028	0.030	0.027	0.031	0.0028	9.4
	1,2,3,4,6,7,8-HpCDD	0.017	0.017	0.017	0.016	0.017	0.00074	4.4
	HpCDDs	0.034	0.033	0.034	0.031	0.034	0.0020	6.1
	OCDD	0.075	0.075	0.075	0.071	0.079	0.0059	7.9
Total PCDDs		0.191	0.178	0.180	0.170	0.190	0.0148	8.2
P C D F s	1,2,7,8-TeCDF	0.0017	0.0014	0.0016	0.0013	0.0018	0.00035	22.7
	2,3,7,8-TeCDF	0.0017	0.0017	0.0017	0.0015	0.0019	0.00026	15.3
	TeCDFs	0.039	0.033	0.035	0.029	0.038	0.0065	18.5
	1,2,3,7,8-PeCDF	0.0021	0.0025	0.0023	0.0021	0.0028	0.00048	20.9
	2,3,4,7,8-PeCDF	0.0026	0.0027	0.0027	0.0024	0.0029	0.00041	15.1
	PeCDFs	0.041	0.031	0.035	0.027	0.038	0.0083	24.2
	1,2,3,4,7,8-HxCDF	0.0030	0.0031	0.0032	0.0028	0.0034	0.00043	13.5
	1,2,3,6,7,8-HxCDF	0.0034	0.0029	0.0032	0.0030	0.0034	0.00030	9.4
	1,2,3,7,8,9-HxCDF	0.00080	0.00079	0.0006	0.0003	0.0008	0.00032	54.8
	2,3,4,6,7,8-HxCDF	0.0041	0.0041	0.0043	0.0040	0.0047	0.00052	12.2
	HxCDFs	0.034	0.030	0.032	0.029	0.034	0.0039	12.2
	1,2,3,4,6,7,8-HpCDF	0.013	0.012	0.012	0.012	0.013	0.00074	6.2
	1,2,3,4,7,8,9-HpCDF	0.0020	0.0020	0.0020	0.0018	0.0022	0.00030	14.8
	HpCDFs	0.021	0.021	0.021	0.020	0.023	0.0022	10.6
OCDF		0.011	0.0104	0.010	0.0091	0.011	0.0014	13.9
Total PCDFs		0.146	0.125	0.130	0.113	0.140	0.0204	15.7
Total (PCDDs+PCDFs)		0.337	0.30	0.31	0.27	0.33	0.041	13.2
DL   P C B s	3,3',4,4'-TeCB (#77)	0.013	0.016	0.017	0.015	0.017	0.0015	8.7
	3,4,4',5'-TeCB (#81)	0.0024	0.0031	0.002	0.0018	0.0025	0.00052	25.9
	3,3',4,4',5'-PeCB (#126)	0.0065	0.0055	0.0053	0.0049	0.0062	0.0010	18.2
	3,3',4,4',5,5'-HxCB (#169)	0.0025	0.0018	0.0019	0.0016	0.0022	0.00044	23.4
	Total non-ortho PCBs	0.0244	0.0259	0.0260	0.0240	0.0270	0.00222	8.6
	2,3,3',4,4'-PeCB (#105)	0.024	0.025	0.026	0.024	0.028	0.0030	11.4
	2,3,4,4',5'-PeCB (#114)	0.0022	0.0068	0.0027	0.0023	0.0035	0.00089	32.9
	2,3',4,4',5'-PeCB (#118)	0.055	0.059	0.058	0.055	0.064	0.0067	11.5
	2',3,4,4',5'-PeCB (#123)	0.0031	0.0030	0.0027	0.0026	0.0031	0.00037	13.7
	2,3,3',4,4',5'-HxCB (#156)	0.012	0.011	0.011	0.010	0.012	0.0016	14.8
	2,3,3',4,4',5'-HxCB (#157)	0.0055	0.0053	0.0049	0.0045	0.0051	0.00044	9.1
	2,3',4,4',5,5'-HxCB (#167)	0.0070	0.0060	0.0060	0.0056	0.0064	0.00059	9.9
	2,3,3',4,4',5,5'-HpCB (#189)	0.0039	0.0032	0.0030	0.0026	0.0033	0.00052	17.3
Total mono-ortho PCBs		0.112	0.119	0.120	0.110	0.130	0.0148	12.4
Total DL-PCBs		0.136	0.144	0.140	0.130	0.150	0.0148	10.6
Total TEQ (pg-TEQ/L)		0.00617	0.00594	0.00608	0.00556	0.00652	0.000710	11.7

Prepared Conc. (pg/L): absolute value in polyurethane form plug / 2000L

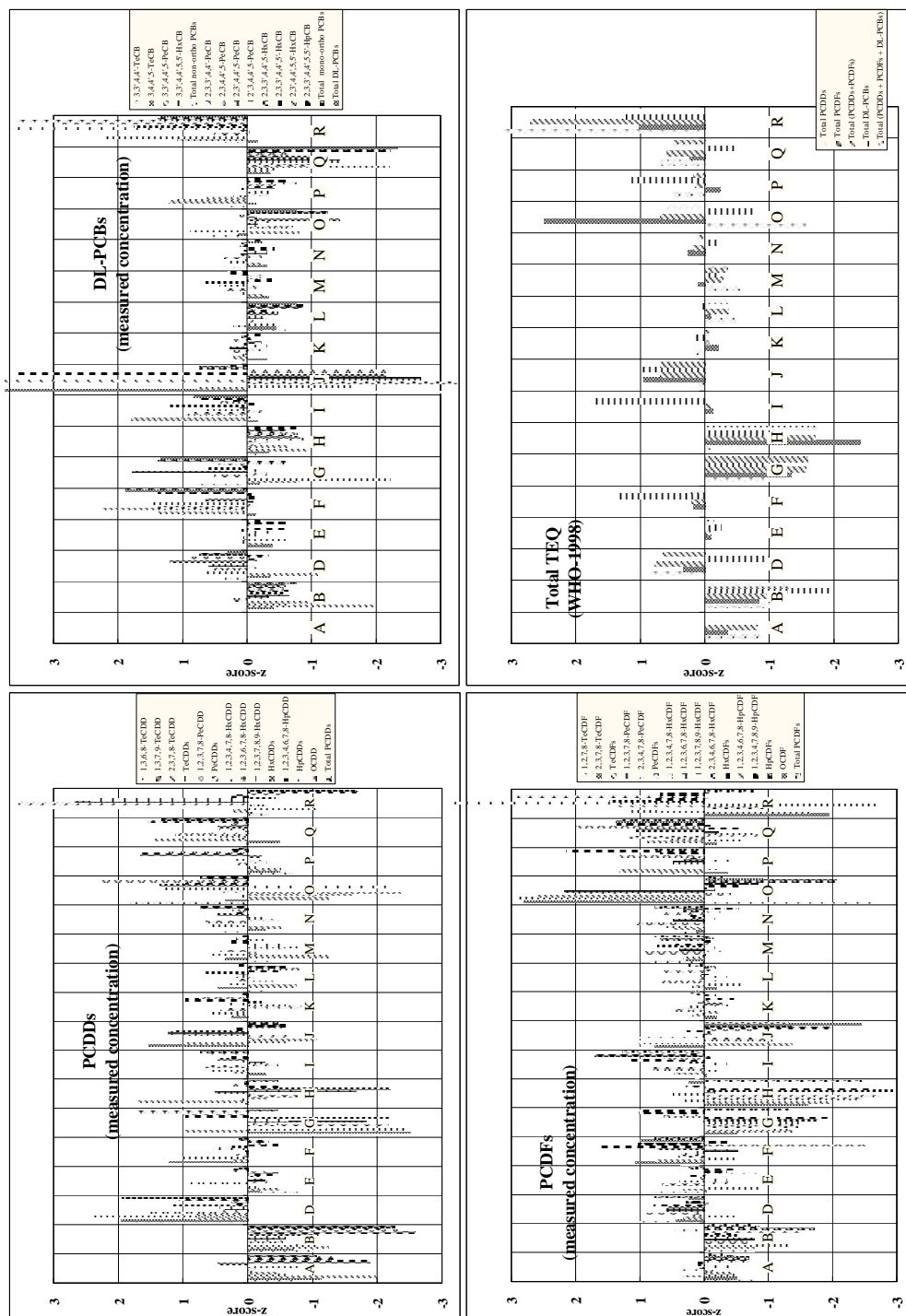


Figure-1. Z-score bar chart for one testing sample (spiked polyurethane form plug).