QUALITY CONTROL FOR THE OFFICIAL TEST FACILITY OF DIOXINS IN KOREA

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Introduction

In Korea, The concentration of dioxins from flue gases of municipal waste incineration facilities with capacities over 50 tons/day has been regulated by the guideline: 0.1 ng-TEQ/Nm^3 for new facilities, and 0.5 ng-TEQ/Nm^3 for existing facilities and it will be strengthened to 0.1 ng-TEQ/Nm^3 until year 2002. Dioxins from these incineration facilities have to be measured more than 2 times annually by the Official Test Facility of Dioxins[1].
Six institutions have been certified so far as the Official Test Facility of Dioxins. These facilities have to be evaluated by the quality control program provided by National Institute of Environmental Research every year[2].
In 1999, quality control for evaluation of sampling and analyzing ability of dioxins was carried out for 4 institutions certified in 1998.

Materials and Methods

To evaluate the sampling and analyzing ability, each institution took a flue gas sample from identical stack of M incineration facility and analyzed dioxins by Certified Air Pollution Testing Method[3]. This method is similar with USEPA method 1613 and method 23. The results of sampling and analysis of dioxins have to be submitted to National Institute of Environmental Research for quality control.
The result of dioxin sampling has to be meet the parameter of the isokinetic coefficient of 95 ~110%, and the results of dioxins analysis have to be meet the parameters of resolution over 10,000, mass calibration within ±5ppm, ion abundance ratio within 15%, and the recovery of 50~ 120%

Results

The sampling results for each institution are shown in Table 1. The isokinetic coefficients were 100.9%, 102%, 102.1% and 99.2%, respectively.

Table 1. Results of dioxins sampling for 4 institutions.

	A			B			C			D		
	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
Isokinetic coefficient(%)	104.3	98.5	99.9	102.9	102.8	101.6	103.6	103.3	99.3	102.8	97.9	96.8
O_2 Conc.(%)	8.1	8.6	8.5	8.2	8.8	8.4	8.6	8.7	8.8	8.5	8.6	9.6
CO_2 Conc.(%)	10.5	10.4	9.5	12.4	11.9	12.2	6.9	6.8	6.2	8.8	8.1	7.4
CO Conc.(ppm)	51.1	17.7	16.1	36.1	24.1	25.0	23.9	12.3	17.7	21.3	17.4	20.4
Water(%)	29.1	28.0	29.6	25.8	26.7	25.2	28.3	28.5	26.1	29.1	29.3	29.2
Sampling time	240	240	240	240	240	240	240	240	240	240	240	240
Amount(Nm^3)	3.20	3.12	3.12	3.96	3.68	4.13	3.83	3.92	3.68	3.92	3.47	3.63
Flow rate(m/sec)	19.5	19.6	19.8	19.2	18.9	19.9	18.6	19.1	18.2	19.6	18.4	19.5

Table 2. Recovery of internal standard for 4 institutions. unit:%

		A			B			C			D		
		1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
Furan	^{13}C-2,3,7,8-TCDF	92.7	84.3	86.6	108.8	103.8	99.3	82.3	90.9	79.6	92.2	84.3	80.4
	^{13}C-1,2,3,7,8-PeCDF	92.7	87.0	89.0	90.8	91.8	81.8	81.5	92.3	75.8	103.0	105.9	99.3
	^{13}C -2,3,4,7,8-PeCDF	90.5	82.3	84.4	105.7	108.1	99.8	79.1	92.6	75.7	88.8	80.8	86.9
	^{13}C-1,2,3,4,7,8-HxCDF	86.5	83.0	85.2	102.1	101.1	99.6	89.3	94.8	85.9	91.0	87.3	75.1
	^{13}C-1,2,3,6,7,8-HxCDF	88.5	88.9	87.6	103.7	100.4	97.6	89.5	95.0	87.8	91.7	89.5	77.9
	^{13}C-2,3,4,6,7,8-HxCDF	89.9	82.6	85.7	120.3	120.6	117.9	85.2	98.6	78.8	86.8	76.9	79.2
	^{13}C-1,2,3,7,8,9-HxCDF	96.8	86.8	94.2	123.4	122.7	121.1	86.5	93.7	82.3	85.2	78.9	79.8
	^{13}C-1,2,3,4,6,7,8-HpCDF	82.5	81.4	83.1	117.6	115.1	113.1	79.9	92.1	74.4	90.8	87.5	71.4
	^{13}C-1,2,3,4,7,8,9-HpCDF	80.4	78.8	84.0	117.2	115.8	111.6	86.2	96.6	82.0	87.1	79.3	90.3
Dioxin	^{13}C-2,3,7,8-TCDD	90.8	88.9	84.8	99.2	94.9	95.1	82.8	89.3	75.2	101.3	99.2	95.5
	^{13}C-1,2,3,7,8-PeCDD	88.3	88.7	89.0	72.2	71.7	62.9	100.0	113.9	94.9	113.6	112.4	115.0
	^{13}C-1,2,3,4,7,8-HxCDD	83.5	84.8	85.2	99.1	95.1	95.8	88.8	90.7	85.1	100.6	94.7	98.1
	^{13}C-1,2,3,6,7,8-HxCDD	87.9	88.5	88.1	101.6	94.2	98.9	88.3	89.1	86.2	103.5	97.2	100.2
	^{13}C-1,2,3,4,6,7,8-HpCDD	89.0	88.4	87.9	107.4	105.6	100.5	85.4	94.7	85.3	106.2	101.5	102.7
	^{13}C- OCDD	77.0	79.2	80.0	112.5	113.9	103.7	96.9	86.4	94.4	97.9	96.7	99.1
^{13}C-1,2,3,4-TCDD		96.5	90.9	88.2	62.4	62.3	101.2	101.0	96.2	99.0	89.9	87.8	92.3

Table 3. Concentration of 2,3,7,8-substituted congeners for 4 institutions. unit:pg/Nm^3

		A			B			C			D		
		1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
Furan	2,3,7,8-TCDF	2.235	1.917	1.845	2.405	2.930	3.875	2.735	2.613	1.520	1.797	2.437	1.950
	1,2,3,7,8-PeCDF	8.497	6.352	6.045	8.424	8.218	11.389	4.204	4.199	2.739	4.030	6.953	4.310
	2,3,4,7,8-PeCDF	8.226	5.912	6.342	6.787	7.743	9.481	6.944	9.206	5.637	3.493	6.127	4.067
	1,2,3,4,7,8-HxCDF	9.781	9.106	7.093	8.932	8.712	10.580	5.240	3.698	3.064	4.460	7.683	5.153
	1,2,3,6,7,8-HxCDF	10.043	7.206	7.315	8.370	8.747	10.621	9.093	9.274	7.651	4.853	8.570	5.293
	2,3,4,6,7,8-HxCDF	12.885	9.149	9.248	3.651	3.455	3.159	12.381	12.645	6.327	6.947	11.567	7.720
	1,2,3,7,8,9-HxCDF	1.056	0.774	0.515	10.198	12.296	13.044	-	-	-	-	-	-
	1,2,3,4,6,7,8-HpCDF	28.980	18.859	20.578	22.285	19.092	19.533	26.586	24.134	16.651	15.200	23.700	17.600
	1,2,3,4,7,8,9-HpCDF	5.989	3.569	4.592	7.5069	5.491	7.379	-	-	-	3.713	4.373	3.257
	OCDF	9.573	5.512	5.083	21.500	16.658	19.387	-	-	-	121.47	54.167	32.633
Dioxin	2378-TCDD	1.007	1.066	1.097	3.183	2.158	2.384	0.790	1.828	1.177	0.700	0.899	0.877
	12378-PeCDD	8.487	7.691	7.788	6.359	8.322	10.461	2.031	7.093	3.125	6.733	8.683	8.090
	123478-HxCDD	19.746	14.689	15.829	9.147	10.333	13.235	21.425	20.208	10.945	6.280	9.707	7.537
	123678-HxCDD	66.120	53.394	56.694	23.284	31.970	44.740	67.557	59.150	38.353	23.833	36.100	30.367
	123789-HxCDD	41.108	33.808	33.631	12.606	19.735	25.814	39.033	37.882	22.539	10.867	17.767	14.833
	1234678-HpCDD	714.56	519.83	524.18	225.94	340.21	483.25	543.97	525.03	248.24	191.00	298.00	219.00
	OCDD	681.29	502.32	508.96	245.95	332.10	446.55	500.02	497.21	246.38	172.33	281.33	183.00
Total (PCDFs + PCDDs)		1629.6	1199.1	1216.8	630.48	838.17	1134.9	1242.1	1214.2	614.36	613.82	826.69	545.90
Mean Conc.		1348.49			867.85			1023.54			662.14		

Table 4. Mean conc.(pg/Nm^3) and %RSD of 2,3,7,8-substituted congeners for 4 institutions

		A		B		C		D	
		Mean Conc.	%RSD	Mean Conc.	%RSD	Mean Conc.	%RSD	Mean Conc.	%RSD
Furan	2,3,7,8-TCDF	1.999	10.4	3.070	24.3	2.289	29.2	2.061	16.2
	1,2,3,7,8-PeCDF	6.968	19.2	9.344	19.0	3.714	22.7	5.098	31.6
	2,3,4,7,8-PeCDF	6.827	18.0	8.004	17.1	7.262	24.9	4.562	30.4
	1,2,3,4,7,8-HxCDF	7.993	19.4	9.408	10.9	4.001	28.0	5.765	29.4
	1,2,3,6,7,8-HxCDF	8.188	19.6	9.155	13.9	8.6673	10.3	6.239	32.6
	2,3,4,6,7,8-HxCDF	10.427	20.4	3.422	7.2	10.451	34.2	8.745	28.3
	1,2,3,7,8,9-HxCDF	0.782	34.6	11.846	12.5	0.000	0.0	0.000	0.0
	1,2,3,4,6,7,8-HpCDF	22.806	23.7	20.303	8.5	22.481	23.2	18.833	23.3
	1,2,3,4,7,8,9-HpCDF	4.717	25.8	6.792	16.6	0.000	0.0	3.781	14.8
	OCDF	6.723	36.9	19.182	12.7	0.000	0.0	69.422	66.8
ioxin	2378-TCDD	1.057	4.3	2.560	20.0	1.265	41.5	0.825	13.2
	12378-PeCDD	7.989	5.4	8.381	24.5	4.083	65.2	7.835	12.8
	123478-HxCDD	16.755	15.8	10.905	19.3	17.526	32.7	7.841	22.1
	123678-HxCDD	58.736	11.2	33.330	32.4	55.020	27.3	30.100	20.4
	123789-HxCDD	36.182	11.8	19.385	34.1	33.151	27.8	14.489	23.9
	1234678-HpCDD	586.188	19.0	349.799	36.9	439.078	37.7	236.000	23.5
	OCDD	564.194	18.0	342.869	28.8	414.539	35.1	212.222	28.3

Table 5. TEQ concentration of 2,3,7,8-substituted congeners for 4 institutions. unit:pg-TEQ/Nm^3

		A			B			C			D		
		1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
Furan	2,3,7,8-TCDF	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	1,2,3,7,8-PeCDF	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	2,3,4,7,8-PeCDF	0.003	0.002	0.002	0.002	0.003	0.003	0.003	0.003	0.002	0.001	0.002	0.002
	1,2,3,4,7,8-HxCDF	0.000	0.000	0.000	0.001	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000
	1,2,3,6,7,8-HxCDF	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.001	0.000
	2,3,4,6,7,8-HxCDF	0.001	0.001	0.001	0.000	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001
	1,2,3,7,8,9-HxCDF	0.000	0.000	0.000	0.001	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000
	1,2,3,4,6,7,8-HpCDF	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	1,2,3,4,7,8,9-HpCDF	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000
	OCDF	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Dioxin	2378-TCDD	0.001	0.001	0.001	0.002	0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.001
	12378-PeCDD	0.003	0.003	0.003	0.002	0.003	0.004	0.001	0.003	0.001	0.002	0.003	0.003
	123478-HxCDD	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.002	0.001	0.001	0.001	0.001
	123678-HxCDD	0.005	0.004	0.004	0.002	0.002	0.003	0.005	0.004	0.003	0.002	0.003	0.002
	123789-HxCDD	0.003	0.002	0.002	0.001	0.001	0.002	0.003	0.003	0.002	0.001	0.001	0.001
	1234678-HpCDD	0.005	0.004	0.004	0.002	0.002	0.003	0.004	0.004	0.002	0.001	0.002	0.002
	OCDD	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total(PCDDs+PCDFs)		0.023	0.019	0.019	0.015	0.018	0.022	0.021	0.022	0.014	0.010	0.015	0.013
Mean TEQ Conc.		0.020			0.018			0.019			0.013		

The analysis results of dioxins are shown in Table 2, 3 and 4. The recoveries were as follows; institution A:77.0-96.7%, B:62.3-123.4%, C:74.4-113.9% D:71.4-115.0%. Institution B exceeded the recovery of two HxCDFs slightly. The concentrations of 2,3,7,8-substituted congeners for 4 institutions are shown in Table 3. Institution C did not detect 1,2,3,7,8,9-HxCDF, 1,2,3,4,7,8,9-HpCDF and OCDF. Institution D did not detect 1,2,3,7,8,9-HxCDF. TEQ concentrations for 4 institutions were similar, but a little lower in institution D.

Conclusion

The following results could be drawn from the quality control study performed in 1999 for 4 institutions certified in 1998. The isokinetic coefficient, the parameter for evaluation of dioxin sampling ability was excellent for all 4 institutions. The parameters for evaluation of dioxin analysis ability were good for all 4 institutions. But institutions C and D showed low sensitivity for high chlorinated dioxins and institution B exceeded the range of recovery slightly.

These results demonstrate that the Korean official method is a promising method to manage quality control of facility doing dioxin analysis. Further study should be made for validating the Korean method by comparing with the proven methods and experience labs internationally.

References

1. Enforce regulation of section 1 of article 24 of Waste Management, 1997, MOE(Korea)
2. Established rule of National Institute of Environmental Research, 1997, NIER(Korea)
3. Korean Certified Air Pollution Testing Method, 1996, MOE(Korea)