Fly-ash Extract-A Proposed Reference Material for PCDDs and PCDFs

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Introduction

The use of certified reference material (CRM) is a method of choice to validate analytical method and to control analytical quality. The National Institute of Environmental Studies (NIES) produced and distributed a series of CRMs for trace elements (NIES No.1 - No.10) and now producing new series of CRMs for chemical speciation and trace organics (NIES No.11 - No.20). Extract from municipal incinerator fly-ash is a candidate CRM as it contains significant amount of PCDDs and PCDFs as well as other chlorinated compounds. In the present paper, analytical result of a candidate reference material prepared from incinerator fly-ash is discussed. Reference material is required for PCDDs and PCDFs determination as those chemicals are potentially hazardous to human health through environmental pollution.

Experimental

Preparation of Reference Material

fly-ash sample (3 kg) collected in municipal incinerator was extracted by using Soxhlet extractor with toluene for 24 hours. Toluene extract was made up to 1,000 ml and an aliquot (2ml) was sealed into 500 ampules, under nitrogen. The material was stored in refrigerator at - 20℃.

Determination of PCDD and PCDF isomers.

Determination of PCDD and PCDF isomers was made by using capillary gaschro-matography - high resolution mass spectrometry in cooperation with five laboratories. The internal standards (I.S.) obtained from Cambridge Isotope Labs were added to the extracted and subjected to analysis. Internal standards used here are as follows. (Table 1) Resolution of mass spectrometry was set to 10,000. The capillary column (SP2331,60m, 0.25 ϕ , 0.1 μ ,thickness) is used for separation. Because reference material contains significant amount of PCDDs and PCDFs with low extent of interferents, PCDDs and PCDFs were determined either by direct injection to GC / MS or by injection after cleaning - up using H_2SO_4 partition / Al_2O_3 column chromatography.

Table 1 Internal standard used for spike

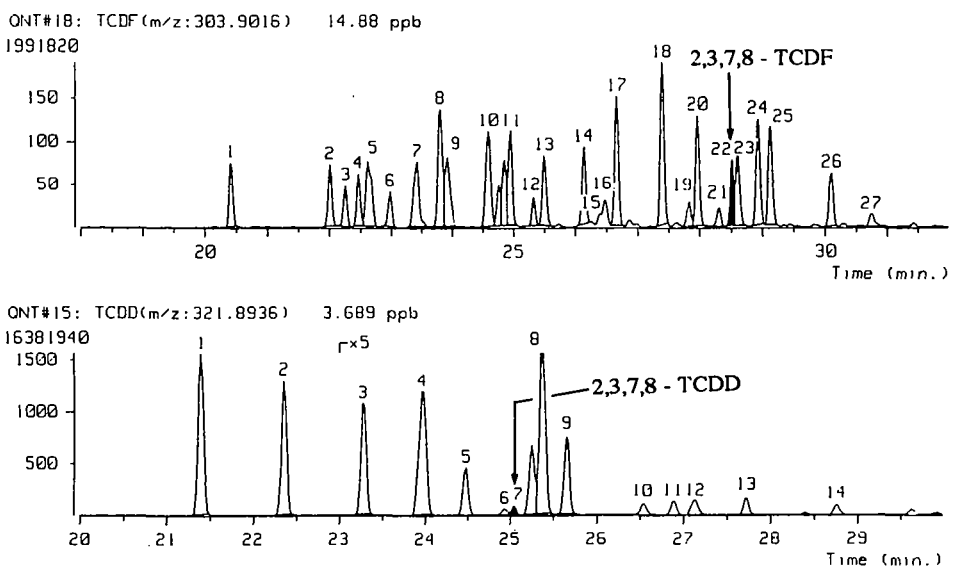
Compound	Internal standard
2, 3, 7, 8 - TCDD	13C - 2, 3, 7, 8 - TCDD
1, 2, 3, 7, 8 - PeCDD	13C - 1, 2, 3, 7, 8 - PeCDD
1, 2, 3, 4, 7, 8 - HxCDD	13C - 1, 2, 3, 6, 7, 8 - HxCDD
1, 2, 3, 6, 7, 8 - HxCDD	13C - 1, 2, 3, 6, 7, 8 - HxCDD
1, 2, 3, 7, 8, 9 - HxCDD	13C - 1, 2, 3, 6, 7, 8 - HxCDD

1, 2, 3, 4, 6, 7, 8 - HpCDD	13C - 1, 2, 3, 4, 6, 7, 8 - HpCDD
OCDD	13C - OCDD
2, 3, 7, 8 - TCDF	13C - 2, 3, 7, 8 - TCDF
1, 2, 3, 7, 8 - PeCDF	13C - 1, 2, 3, 7, 8 - PeCDF
2, 3, 4, 7, 8 - PeCDF	13C - 1, 2, 3, 7, 8 - PeCDF
1, 2, 3, 4, 7, 8 - HxCDF	13C - 1, 2, 3, 4, 7, 8 - HxCDF
1, 2, 3, 6, 7, 8 - HxCDF	13C - 1, 2, 3, 4, 7, 8 - HxCDF
1, 2, 3, 7, 8, 9 - HxCDF	13C - 1, 2, 3, 4, 7, 8 - HxCDF
2, 3, 4, 6, 7, 8 - HxCDF	13C - 1, 2, 3, 4, 7, 8 - HxCDF
1, 2, 3, 4, 6, 7, 8 - HpCDF	13C - 1, 2, 3, 4, 6, 7, 8 - HpCDF
1, 2, 3, 4, 7, 8, 9 - HpCDF	13C - 1, 2, 3, 4, 6, 7, 8 - HpCDF
OCDF	13C - OCDF

Result and Discussion

Chromatograms of TCDD and TCDF are shown in Fig. 1. As shown in Fig. 1, the material contains high concentrations of 1,3,6,8 - TCDD and 1,3,7,9 - TCDD, but contains very small amount of 2,3,7,8 - TCDD. Resolution of 2,3,7,8 - TCDF from 2,3,4,8 - TCDF isomer was not complete, but quantitation was possible by dividing the peaks into two isomers. By using high resolution mass spectrometry (R : 10,000), direct injection of reference material gave a typical gaschromatographic pattern of PCDDs and PCDFs of incinerator source. Clean - up procedures seemed not important for these samples.

Fig. 1 Chromatogram of fly - ash extract reference material for TCDF and TCDD.



Analytical result for toxic PCDDs and PCDFs (2,3,7,8 - related isomers) is summarized in Table 2. All these isomers are analyzed by isotope - dilution method using C^{13} - rabelled isomers, and the analytical values may be more reliable than other isomers. Among these, however, some of the PCDF isomers (1,2,3,7,8 - PeCDF and 1,2,3,4,7,8 - HxCDF) were not well determined because of the poor resolution on SP2331 column. 2,3,7,8 - TCDD, 2,3,7,8 - TCDF, OCDD and OCDF were analyzed in different years, and the 12analytical data were collected.

Table 2 Concentration of toxic PCDDs and PCDFs in fly - ash - extract reference material

	A	B	C	D	E	Average (ng / ml)	σ
2,3,7,8-TCDD	3.4	3.0	5.5	6.9	3.8	4.52	1.64
1,2,3,7,8-PeCDD	75.1	65.8	74.5	69.1	65.4	69.98	4.63
1,2,3,4,7,8-HxCDD	91.9	85.3	96.1	70.6	108.5	90.48	13.97
1,2,3,6,7,8-HxCDD	191.6	172.5	188.0	138	182.3	174.48	21.63
1,2,3,7,8,9-HxCDD	159.2	141.5	150	103	150.3	140.80	22.04
1,2,3,4,6,7,8-HpCDD	879	919	907	604	876	837.00	131.53
OCDD	593	633	562	410	584	556.40	85.78
2,3,7,8-TCDF	16.9	15.7	19.6	17.1	13.8	16.62	2.12
1,2,3,4,8/							
1,2,3,7,8-PeCDF	47.6	49.3	43.5	30.1	37.6	41.62	7.86
2,3,4,7,8-PeCDF	66.8	59.4	65.7	48.4	45.0	57.06	9.94
1,2,3,4,7,8-HxCDF	41.2	58.9	66.7	62.2	58.2	57.44	9.68
1,2,3,4,7,9/							
1,2,3,6,7,8-HxCDF	40.3	46.0	61.8	52.9	51.1	50.42	8.03
1,2,3,7,8,9-HxCDF	6.5	13.77	9.6	23.0	11.0	12.77	6.29
2,3,4,6,7,8-HxCDF	55.8	82.0	83.9	90.1	81.9	78.74	13.25
1,2,3,4,6,7,8-HpCDF	166.2	152.9	154.0	217	176.3	173.28	26.26
1,2,3,4,7,8,9-HpCDF	33.6	31.9	33.0	34.3	30.4	32.64	1.53
OCDF	107.6	120.8	108	115	116	113.48	5.63

Extended determination (N=12) of 2,3,7,8-TCDD, 2,3,7,8-TCDF, OCDD and OCDF gave a similar result : 4.1 ± 1.2 (2,3,7,8-TCDD), 16.9 ± 3.1 (2,3,7,8-TCDF), 563 ± 47 (OCDD), and 113.5 ± 6.5 (OCDF). No significant change was observed 5-years storage at - 20°C.

Table 3 gives the result of PCDDs and PCDFs congeners. Because of the difficulty of using all PCDD and PCDF isomers, quantitation was made based on the assumption that the PCDD and PCDF isomers have the same response factor as 2,3,7,8 - isomers. Thus, those valves contains a systematic error arising from different ionization efficacy among isomers, and hence they are tentative values.

Relative standard deviation of these data was 5 - 15 % indicating fairly good agreement if we consider that these analysis is ultra - trace level. The material described here seems to contain all PCDDs and PCDFs that can occur through incineration process. A quantitative determination of individual isomers is achieved on retention times by using this material as the gaschromatographic elution of these isomers are given on different capillary columns (Ref. 1). Those mean that the fly -ash-extract material proposed here may be used as a reference material both for qualitative and quantitative determination of PCDDs and PCDFs from incinerator source. It is also noted that the material may be used for characterization of organic matters in fly-ash as it contains a different type of compounds including organo-halogen compounds.

Table 3 Dioxin and Dibenzofuran Congeners in Fly - ash Extract Reference material

	A	B	C	D	E	Average (μg /ml)	σ
TCDDs	1.24	1.19	1.35	1.40	1.37	1.31	0.09
PeCDDs	3.42	2.70	2.73	3.03	2.64	2.90	0.33
HxCDDs	2.62	2.48	2.59	2.20	2.74	2.53	0.20
HpCDDs	1.43	1.65	1.57	1.13	1.60	1.48	0.21
O_8CDDs	0.59	0.63	0.56	0.51	0.58	0.57	0.04
Total CDDs	9.30	8.65	8.80	8.28	8.93	8.79	0.37
TCDFs	0.56	0.56	0.64	0.63	0.59	0.60	0.04
P_5CDF	0.84	0.82	0.80	0.55	0.66	0.73	0.12
H_6CDF	0.45	0.62	0.69	0.68	0.57	0.60	0.10
H_7CDF	0.36	0.33	0.34	0.43	0.44	0.38	0.05
O_8CDF	0.11	0.12	0.11	0.12	0.12	0.12	0.01
Total PCDFs	2.32	2.45	2.58	2.41	2.38	2.43	0.10

Ref. 1) Ryan J.J., Conacher H.B.S., Panopio L.G., Lau B.P.-Y., Hardy J.A. and Masuda Y. J. Chromatogr. 541, 131-183 (1991)