An Interlaboratory Study for the Development of Reference Dioxin Values

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Introduction

More analytical laboratories are recognizing that the use of certified reference materials (CRMs) is vital to ensure accuracy for routine and non-routine analysis, method development and method validation. Unfortunately, the availability of natural matrix environmental reference materials certified for dioxins worldwide is very limited. For this reason, the Analytical Chemistry Division of the National Institute of Standards and Technology (NIST) and the Analysis and Air Quality Division of the Environmental Technology Centre (ETC), Environment Canada, have collaborated to develop dioxin reference values for two reference materials. One of the materials is the currently available Urban Dust/Organics, SRM 1649a, and the other one is a proposed new marine sediment - New York/New Jersey Waterway Sediment, SRM 1944. An interlaboratory study involving 13 established environmental laboratories in Canada, USA, Germany and Sweden was initiated in mid-1997, to analyze these two reference materials.

Study Design

Each participating laboratory received sufficient sample materials in two sealed sample vials and a unknown standard solution in a sealed ampoule. Information regarding concentration range and suggested sample size was also provided. Laboratories were required to analyze each of the two solid samples in triplicate for all 17 2,3,7,8-substituted congeners and the tetra through hepta homologues of PCDD and PCDF using their routine analytical procedures and the gas chromatograph - high-resolution mass spectrometry (GC-HRMS) technique.

Preliminary Results and Discussion

Preliminary results of PCDD/PCDF in urban dust, marine sediment and standard solution are summarized in Table 1. Potential outliers have not yet been determined statistically. The relative

standard deviations (RSD) of congeners in the toluene solution are between 8.1 and 13.8% with an average of 9.8%. This low variability suggests that the accuracy of the calibration standards among laboratories is comparable. However, RSDs for congeners in both solid samples are at least twice the values for the standard solution. The 158% RSD for 1,2.3,7.8,9-H6CDF in the urban dust is due to two extremely large values. This congener also shows high variability in the sediment at a concentration near the detection limit. About half of the laboratories analyzed 2,3,7,8-TCDF using a confirmative GC column such as DB-225 or equivalent to separate the target compound from neighboring isomers. As a result, these laboratories reported lower 2,3,7,8-TCDF values than those using only a DB-5 column. The toxic equivalents (TEQ) were calculated for comparison by using the International Toxicity Equivalency Factors (I-TEF). It is interesting to note that the variability of TEQ seems to be much smaller than the individual congeners. The RSD of TEQ is 11 and 8% for urban dust and marine sediment, respectively. Median and mean values are almost identical for most of the analytes indicating that overall the data are homogeneous. Further assessment of these data will be undertaken, to eventually provide reference values for these CRMs.

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Table 1 Comparison of Laboratory Results - Dioxins in Reference Materials

	Urban Dust/Organics SRM 1649a				Sediment SRM 1944				Standard Solution			
	Median ng/g	Mean ng/g	RSD %	n	Median ng/g	Mean ng/g	RSD %	n	Median ng/ml	Mean ng/ml	RSD %	n
2378-TCDD	0.011	0.012	42.6	10	0.132	0.131	10.2	13	5.20	5.16	10.8	13
12378-P5CDD	0.090	0.089	22.1	12	0.018	0.019	21.9	13	9.50	9.83	12.7	13
123478-H6CDD	0.257	0.255	12.4	12	0.026	0.025	17.4	13	10.0	10.3	9.5	13
123678-H6CDD	0.673	0.670	10.7	12	0.053	0.054	14.9	13	5.20	5.03	8.1	13
123789-H6CDD	0.726	0.648	27.4	12	0.052	0.052	23.1	13	10.2	10.2	8.9	13
1234678-H7CDD	18.9	18.6	13.9	12	0.830	0.780	15.0	13	10.0	10.1	8.1	13
OCDD	202	198	16.1	12	5.91	5.64	18.8	13	20.7	20.4	8.6	13
2378-TCDF[a]	0.147	0.130	28.6	7	0.138	0.134	29.5	7	5.00	5.07	7.6	13
2378-TCDF[b]	0.060	0.068	29.2	7	0.038	0.039	47.9	7				
12378-P5CDF	0.091	0.089	18.9	12	0.040	0.045	26.5	13	13.0	13.3	10.1	13
23478-P5CDF	0.290	0.281	15.8	12	0.045	0.044	14.5	13	9.09	9.00	9.3	13
123478-H6CDF	0.975	0.890	48.7	12	0.213	0.223	25.9	13	9.97	10.2	9.4	13
123678-H6CDF	0.405	0.426	22.7	12	0.084	0.091	20.7	13	10.0	10.1	9.7	13
234678-H6CDF	0.683	0.642	24.2	11	0.052	0.053	19.4	12	10.2	10.0	6.5	13
123789-H6CDF	0.053	0.161	158	12	0.008	0.023	115	10	9.70	10.0	9.4	13
1234678-H7CDF	3.83	3.75	9.22	12	0.970	0.970	14.4	13	10.0	10.3	10.9	13
1234789-H7CDF	0.456	0.452	26.0	12	0.040	0.039	24.6	12	10.0	10.2	13.2	13
OCDF	6.73	6.54	15.8	12	0.980	0.950	14.5	13	20.0	20.3	13.8	13
TEQ[c]	1.00	0.999	11.2	12	0.253	0.248	8.05	13	22.3	22.7	8.6	13
TOTAL TCDD	0.111	0.327	189	12	0.259	0.249	30.0	13				
TOTAL P5CDD	0.816	0.849	30.0	12	0.183	0.175	47.9	13				
TOTAL H6CDD	5.86	5.83	12.5	12	0.590	0.610	22.8	13				
TOTAL H7CDD	36.1	36.0	15.7	12	1.90	1.76	15.7	13				
TOTAL TCDF	0.399	0.497	39.5	12	0.620	0.719	50.0	13				
TOTAL P5CDF	1.68	1.62	23.9	12	0.744	0.771	27.4	13				
TOTAL H6CDF	4.67	4.91	21.1	12	0.950	1.02	22.6	13				
TOTAL H7CDF	9.63	9.69	13.8	12	1.37	1.42	14.1	13				
TOTAL DIOXINS	248	241	15.1	12	8.67	8.43	16.8	13				
TOTAL FURANS	23.5	23.2	12.3	12	4.70	4.89	18.8	13				

[a] results of a DB-5 column; [b] confirmative results of DB-225, DB-dioxin, BPX5 or Rtx-2330 column; [c] as 2378-TCDD toxicity equivalents; n - number of data points