A REFERENCE MATERIAL FOR ROUTINE PERFORMANCE MONITORING OF METHODS MEASURING DIOXIN-LIKE COMPOUNDS IN SOLID MATRICES

S. Selliah, S. Cussion, E.J. Reiner, K.A. MacPherson, T.M. Kolic, D. Toner and B. Chittim[1]

Ontario Ministry of the Environment, Laboratory Services Branch,
125 Resources Rd., Toronto, Ontario, Canada, M9P 3V6
[1]Wellington Laboratories Inc, 396 Laird Rd, Guelph, Ontario, Canada, N1G 3X7

Introduction

Matrix-matched environmental certified reference materials (CRMs) are one of the most useful tools to assess analytical laboratory performance and to assist in the resolution of data conflicts or discrepancies. Analytical laboratories supply analytical data in support of various government, environmental initiatives, such as Site Decommissioning Guidelines, Remedial Action Plans (RAPs), sediment studies for bioaccumulation in benthic organisms, and other programs. Data comparability between laboratories may become an issue, when analytical results are evaluated against specific requirements. At the present time, there are few homogeneous, solid CRMs, especially for poly chlorinated dibenzo-p-dioxins (PCDDs), poly chlorinated dibenzofuran (PCDFs) and dioxin-like (mono ortho, and coplanar) Polychlorinated Biphenyls (DLPCBs) at low levels. A Reference Material containing target compounds at levels within an order of magnitude of the laboratory Method Detection Limit (MDL) can be used to monitor a laboratory=s performance (precision and bias) at low levels and assess data quality of a specific sample set analysed along with the CRM.

A Lake Ontario sediment was identified as a potential reference material when repeat analysis of PCDDs and PCDFs in this sample in 1994 showed extraordinary reproducibility of results. This sediment has excellent homogeneity and contains a very complex mixture of analytes at low (many at 5 to 25 x MDL) levels. Analyte groups identified along with PCDDs and PCDFs include: DLPCBs, Polynuclear Aromatic Hydrocarbons (PAHs), brominated diphenylethers PCBs, trace metals, and a few organochlorine pesticide compounds. Because of these rare properties, this sediment was considered as the first Laboratory Services Branch (LSB) Candidate Certified Reference Material and assigned the identifier LSBRM9801.

Methods and Materials

CANMET, certified to ISO 9002 standards, was contracted to perform the physical processing of the sediment collected. This included air drying at room temperature, crushing, blending, bottling the material in 25 g aliquots; and labeling. A total of 1200*25g bottles were produced.

Homogeneity for metals was determined by CANMET by random sampling and analysis for trace metals by neutron activation. Results for the following elements were used by CANMET for the homogeneity assessment: antimony, arsenic, bromine, chromium, cerium, europium, gold, iron, lanthanum, lutetium, sodium, neodymium, rubidium, scandium, samarium, thorium, uranium, and ytterbium. From each of 22 bottles, two splits were analyzed. These splits are plotted in pairs.. Of the 44 results, only 6 differed by more than 5% from the mean, and all differed by less than 8% from the mean. Using ANOVA, the ratio of between-bottle to within-bottle mean squares (*F calculated*) was compared to the *F Statistic* at the 95% Confidence Level. For all elements listed

above, the *F calculated* was less than the *F Table* values, so there was no evidence of inhomogeneity.

To check for homogeneity for organic materials, 44 samples were randomly analyzed at LSB for Total Organic Carbon (TOC) by Coulometry. TOC analysis was chosen as there is evidence in the literature that in sediments, there is a strong correlation between TOC levels and organic contents, particularly PCBs. In the LSB analysis for TOC, only 0.1 g of material was used for each analysis. Using ANOVA, the ratio of between-bottle to within-bottle mean squares (*F calculated*) was compared to the *F Statistic* at the 95% Confidence Level. As for the trace metals, the *F calculated* for TOC was less than the *F Table* values, so there was no evidence of inhomogeneity, even when 0.1 g sample size was used.

Results and Discussion

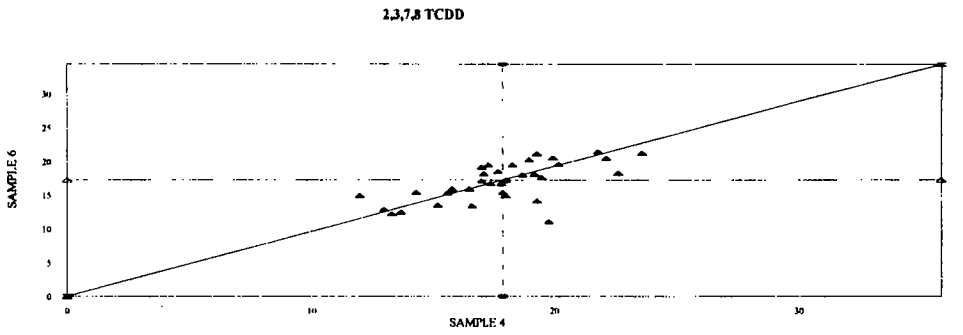
The material (LSBRM9801) was subjected to an intercalibration study for PAH in the fall of 1998[1]. Results indicated that the material was very homogeneous and contained low (10 to 300ppb) levels of the 16 priority PAH compounds. In the fall of 1999, LSB offered an interlaboratory study, to a number of international laboratories in order to obtain certified values for PCDDs, PCDFs and DLPCBs in LSBRM9801. The study design consisted of an injection ready standard (provided by Wellington Laboratories) to assess instrument performance, two samples of the candidate reference material (LSBRM9801) and 3 additional reference materials from NIST and Environment Canada. Thirty-seven laboratories from 17 countries participated. Raw data (outliers not removed) for the replicate LSBRM9801 samples and the injection ready standard are summarized in Table 1. Data in Table 1 shows that the percent coefficient of variation (%CV) for both samples is lower than the %CV for a number of components in the injection standard. These data confirm the excellent homogeneity of LSBRM9801.

The greatest variability in data is exhibited for 1,2,3,7,8-PeCDF, 1,2,3,7,8,9-HxCDF, PCB - 81, 123, 126, 167, 169 with the variability for many of the PCBs being considerably greater than for the PCDDs and PCDFs. In most instances, these are the congeners that co-elute with other isomers or congeners of higher degree of chlorination or are present at relatively lower levels, therefore resulting in greater variability of results. The number of experienced labs analysing for PCDDs and PCDFs is considerably greater than those that analyse for DLPCBs. In addition, for the DLPCBs there is much greater variation in the analytical methodology, sample preparation and standards used. This is seen in the data in Table 1 and in the the Youden plots[2] - Figure 1 (2,3,7,8-TCDD) and (PCB 126). Data for 2378-TCDD (Figure 1) exhibits considerably less variability and bias than data for PCB 126. Homogeneous CRMS at 5 to 25 times MDL values (typical calibration range) will greatly help increase precision and accuracy of analytical tests especially for methods like PCBs.

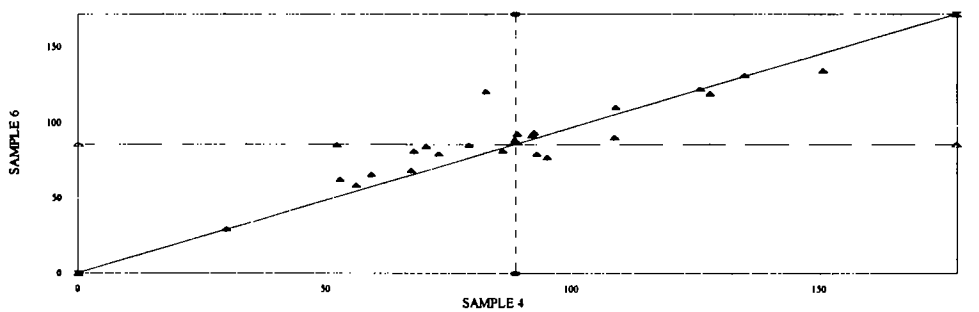
Table 1: Raw Data MOE Intercalibration Study 99-2

PARAMETER	Sample 4			Sample 6			Injection Standard			
	Mean (pg/g)	CV	N	Mean (pg/g)	CV	N	Design Value	Mean (pg)	CV	N
2,3,7,8-TCDD	17.79	15%	35	17.08	16%	35	25.0	24.07	19.0%	34
1,2,3,7,8-PeCDD	7.875	19%	33	7.57	25%	34	62.5	61.31	19.2%	34
1,2,3,4,7,8-HxCDD	8.891	22%	33	8.26	22%	34	62.5	61.06	25.8%	34
1,2,3,6,7,8-HxCDD	20.52	20%	34	19.93	16%	35	62.5	62.32	23.8%	34
1,2,3,7,8,9-HxCDD	16.62	28%	34	16.16	33%	35	62.5	59.90	21.9%	34
1,2,3,4,6,7,8-HpCDD	294.0	17%	35	287.5	15%	35	62.5	63.66	20.5%	34
OCDD	1901	16%	35	1862	14%	35	125.0	124.3	23.8%	34
2,3,7,8-TCDF	57.82	17%	35	54.76	21%	35	25.0	26.65	24.4%	34
1,2,3,7,8-PeCDF	12.75	41%	35	12.46	30%	35	62.5	64.00	23.8%	34
2,3,4,7,8-PeCDF	19.24	29%	35	18.56	29%	35	62.5	63.67	23.5%	34
1,2,3,4,7,8-HxCDF	73.13	45%	35	69.66	29%	35	62.5	62.16	23.8%	34
1,2,3,6,7,8-HxCDF	22.24	60%	35	20.95	25%	34	62.5	63.15	26.8%	34
1,2,3,7,8,9-HxCDF	8.69	210%	28	5.14	116%	29	62.5	61.15	26.4%	34
2,3,4,6,7,8-HxCDF	14.13	38%	33	14.51	38%	35	62.5	61.53	28.0%	34
1,2,3,4,6,7,8-HpCDF	290.7	25%	35	305.5	24%	35	62.5	63.40	27.1%	34
1,2,3,4,7,8,9-HpCDF	14.94	24%	34	14.29	23%	33	62.5	62.89	25.2%	33
OCDF	506.2	34%	34	515.9	21%	34	125.0	123.4	25.3%	33
TCDD - Total	54.88	37%	33	51.54	33%	33	25	24.62	20.0%	27
PeCDD - Total	69.77	37%	33	67.56	38%	33	62	62.70	33.6%	28
HxCDD - Total	240.7	24%	33	231.3	18%	33	188	177.9	30.4%	28
HpCDD - Total	585.6	22%	33	591.8	19%	33	62	65.81	22.0%	27
TCDF - Total	367.3	35%	33	335.1	38%	33	25	25.82	30.7%	28
PeCDF - Total	227.0	33%	33	210.9	32%	33	125	123.6	28.9%	28
HxCDF - Total	266.1	22%	33	263.7	22%	33	250	243.1	31.3%	28
HpCDF - Total	391.9	30%	33	394.2	29%	33	125	124.0	23.9%	27
PCB 77	1779	27%	27	1852	35%	27	500	488.6	28.4%	27
PCB 81	90.53	65%	23	82.03	59%	23	100	153.3	211.7%	27
PCB 105	4075	23%	27	4153	28%	27	1,000	1083	22.3%	28
PCB 114	232.4	45%	26	242.5	51%	25	100	104.8	24.7%	27
PCB 118	8227	25%	27	8497	30%	27	1,000	1057	25.8%	28
PCB 123	333.0	100%	23	317.5	96%	24	100	113.4	34.2%	27
PCB 126	108.4	90%	26	87.59	31%	26	100	106.7	19.6%	27
PCB 156	670.8	28%	28	715.8	24%	27	500	537.7	17.5%	28
PCB 157	174.6	33%	27	188.3	30%	26	100	106.2	18.2%	27
PCB 167	529.6	91%	27	524.9	81%	26	100	112.3	24.3%	27
PCB 169	36.23	294%	28	21.64	303%	24	100	110.6	20.2%	28
PCB 189	74.23	37%	25	89.64	34%	24	100	105.8	9.2%	27

Figure 1: Youden Plot of 2,3,7,8-TCDD and PCB 126



PCB 126



Conclusion

Results for MOE Interlaboratory study 99-2 show that LSBRM9801is very homogeneous and contains low levels of PCDDs, PCDFs, DLPCBs (including other non-DLPCBs), as well as brominated diphenyl ethers, metals and PAHs[1,2]. Matrix matched CRMs with analytes at 5 to 20 times MDL allow laboratories to monitor and assess performance on real samples in their normal working range. This will improve the comparison of data between laboratories and provide additional confidence in data when used for regulatory purposes.

References

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2.W.J.Youden, *Graphical Diagnosis of Interlaboratory Test Results*, Industrial Quality Control, Vol XV, No11, May 1959