NIST Approach to the Certification of Selected Chlorinated Organic Components in Recently Issued Natural-matrix Certified Reference Materials

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1. Introduction

Certified values for organic constituents in NIST environmental certified reference materials (CRMs) are generally based on agreement of results obtained from two or more independent and reliable analytical procedures. For the certification of concentrations of organic components in complex natural matrix reference materials, the extraction and cleanup/isolation steps as well as the final analytical measurements are based on different separation characteristics to minimize the possibility of similar biases in both measurements[1]. Advances in technology have enabled the implementation of additional, more independent, analytical procedures, that utilize differences in gas chromatographic (GC) separation and detection, for the determination of polychlorinated biphenyl (PCB) congeners and chlorinated pesticides in a number of recently-issued NIST natural-matrix Standard Reference Materials (SRMs): SRM 1945, Organics in Whale Blubber; SRM 1941a, Organics in Marine Sediment; and SRM 1974a, Organics in Mussel Tissue. In the validation of these procedures, five existing natural-matrix CRMs (a marine sediment, a marine tissue, and three fish [cod and mackerel] oils) were analyzed for selected PCB congeners and chlorinated pesticides[2].

2. Description and validation of procedures

Procedures evaluated at NIST for the analytical determination of chlorinated hydrocarbons included the use of three GC capillary columns with different selectivity (a 5% phenyl-substituted methylpolysiloxane stationary phase [DB-5], a dimethylpolysiloxane phase containing 50% methyl C-18 [CP Sil 5 C18 CB], and a 14% cyanopropylphenyl-substituted methylpolysiloxane phase [DB-1701]) and two different GC detectors, electron capture (ECD) and mass spectrometric (MSD) detection as well as different extraction and isolation steps. Schantz *et al.*[2], have reported and compared the results of using these procedures for the analysis of three NIST SRMs and two Community Bureau of Reference (BCR) CRMs, for approximately 40 PCB congeners and chlorinated pesticides. The materials analyzed were: SRM 1588, Organics in Cod Liver Oil; SRM 1941, Organics in Marine Sediment; SRM 1974, Organics in Mussel Tissue; CRM 349, Chlorobiphenyls in Cod Liver Oil; and CRM 350, Chlorobiphenyls in Mackerel Oil. The results obtained using the four procedures for the five reference materials were in good agreement, and discrepancies in the results can be attributed to the separation of co-eluting congeners due to differences in the selectivity of the columns or to the selectivity of the mass spectrometric detection.

3. Certification of SRM 1945, Organics in Whale Blubber

An example of the use of this approach is shown in the certification of the recently issued NIST SRM 1945, Organics in Whale Blubber, for PCB congener and chlorinated pesticide concentrations that is described in detail in Reference 3. Two groups of this frozen blubber tissue homogenate samples, were selected from the SRM sample pool according to a stratified random scheme. Analytical techniques used for these two groups of samples utilized two different detectors, ECD and MSD. The ECD measurements included using two GC capillary columns with different selectivity (a 5% phenyl-substituted methylpolysiloxane stationary phase and a dimethylpolysiloxane phase containing 50% methyl C-18). For the ECD analyses, samples were Soxhlet-extracted with dichloromethane, the majority of the lipid and biogenic material was removed using size exclusion chromatography, and normal-phase liquid chromatography was used to isolate two fractions containing (1) the PCB congeners and lower polarity chlorinated pesticides and (2) the more polar chlorinated pesticides for the analytical GC analyses. For the GC/MS analyses, the second group of samples were Soxhlet-extracted with 1:1 hexane/acetone (v/v), sulfuric acid was used to remove lipid interferences, and a silica solid-phase extraction column was then used to remove the polar interferences in the extracts. Aliquots of a solution of five internal standards were added to the blubber prior to extraction for quantification purposes. Calibration response factors for the analytes relative to the internal standards were determined by analyzing aliquots of the following: SRM 2261 (Concentrated Chlorinated Pesticides in Hexane), SRM 2262 (Concentrated PCB Congeners in Iso-octane), gravimetrically prepared solutions of additional analytes not contained in SRMs 2261 and 2262, and the internal standards. (The purities of the components in the solution of "additional analytes" were assessed and the concentrations verified chromatographically.) Samples of SRM 1588, Organics in Cod Liver Oil, were analyzed similarly and concurrently with the whale blubber samples. Experiments for each technique were designed so that sources of possible random error in the measurements would be replicated to reduce the bias they could cause. The results from these three analytical procedures were in good agreement and were combined to provide certified concentrations for 27 PCB congeners and 15 chlorinated pesticides[4]. A summary of the analytical results by method and the resulting certified concentration for 36 of the 42 certified constituents is shown in Table 1.

4. SRM 1941a, Organics in Marine Sediment and SRM 1974a, Organics in Mussel Tissue

Similarly, the certified concentrations of 21 PCB congeners and 6 chlorinated pesticides in SRM 1941a, a marine sediment, are based on results obtained using different extraction/sample preparation procedures and analytical techniques based on GC-ECD on two stationary phases of different selectivity and GC-MS[5]. The certified values for 23 polycyclic aromatic hydrocarbons (PAHs) are based on the results obtained from the analyses of the sediment using different extraction/sample preparation procedures and analytical techniques based on GC-MS on two stationary phases of different selectivity (a 5% phenyl-substituted methylpolysiloxane phase and a smectic liquid crystalline phase) and reversed-phase liquid chromatography with fluorescence detection. Concentrations of selected PCBs, chlorinated pesticides, and PAHs in the recently issued SRM 1974a, Organics in Mussel Tissue, (a replacement for the now depleted SRM 1974) were certified using these procedures as well.

Table 1. Certified Concentrations and Summary of Analytical Results for 36 of the 27 PCB Congeners[a] and 15 Chlorinated Pesticides Certified in SRM 1945[4)]

	Concentration (µg/kg wet weight)			
Constituent	Certified[b] Concentration	GC-ECD[c] (CP Sil 5 C18 CB)[d]	GC-ECD[c] (DB-5)[d]	GC-MSD[c] (DB-5)[d]
PCB 18	4.48 ± 0.88	4.91 (0.32)	3.78 (0.30)	4.76 (0.33)
PCB 44	12.2 ± 1.4	12.25 (0.64)	13.17 (0.74)	11.25 (0.94)
PCB 49	20.8 ± 2.8	18.54 (0.84)	22.64 (0.74)	21.28 (0.95)
PCB 52	43.6 ± 2.5	45.1 (2.5)	42.8 (2.9)	42.4 (2.1)
PCB 66	23.6 ± 1.6	23.2 (1.8)		23.7 (1.9)
PCB 95	33.8 ± 1.7	34.1 (1.7)		33.6 (1.6)
PCB66/95			[59.7][e] (2.8)	
PCB 87	16.7 ± 1.4	16.25 (0.68)	17.71 (0.91)	16.66 (0.47)
PCB 99	45.4 ± 5.4	41.5 (2.9)	47.3 (2.8)	47.3 (2.3)
PCB 101	[65.2 ± 5.6]	61.6 (3.3)	[66.3] (4.3)	[68.3] (2.3)
90				
PCB 105	30.1 ± 2.3	31.6 (2.4)	30.0 (2.4)	29.8 (1.3)
PCB 118	74.6 ± 5.1	74.9 (4.7)	75.6 (4.8)	71.7 (3.7)
PCB 128	23.7 ± 1.7	23.2 (2.2)	24.6 (2.1)	22.9 (1.5)
PCB 138	131.5 ± 7.4	131.7 (8.0)	127.7 (9.0)	134.2 (5.7)
163				
164				
PCB 149	106.6 ± 8.4	101.6 (6.6)	106.6 (7.5)	110.6 (4.7)
PCB 156	10.3 ± 1.1	9.76 (0.69)	10.93 (0.66)	10.07 (0.72)
PCB 170	[40.6] ± 2.6	39.3 (2.6)[h]	[40.2] (2.6)	[42.4] (1.9)
190				
PCB 180	106.7 ± 5.3	105.5 (6.2)	108.8 (6.7)	109.5 (4.9)
PCB 183	36.6 ± 4.1	39.5 (2.9)	36.0 (2.8)	34.4 (1.8)
PCB 187	105.1 ± 9.1	111.7 (7.0)	103.1 (6.7)	100.9 (5.1)
PCB 194	39.6 ± 2.5	39.2 (2.4)	41.3 (2.6)	39.4 (1.8)
PCB 206	31.1 ± 2.7	32.9 (1.9)	30.7 (1.9)	29.7 (1.6)
PCB 209	10.6 ± 1.1	10.75 (0.87)	11.16 (0.94)	9.95 (0.85)
2,4'-DDE	12.28 ± 0.87	12.46 (0.57)	11.69 (0.70)	12.27 (0.54)
4,4'-DDE	445 ± 37	421 (31)	453 (25)	440 (34)
2,4'-DDD	18.1 ± 2.8	20.0 (1.3)	16.2 (1.4)	17.96 (0.93)
4,4'-DDD	133 ± 10	128 (10)	132.4 (9.1)	138.3 (6.2)
2,4'-DDT	106 ± 14	113.0 (7.0)	98 (10)	101.6 (6.3)
4,4'-DDT	245 ± 15	238 (46)		246 (12)
HCB	32.9 ± 1.7	32.2 (2.1)	33.1 (2.2)	33.8 (1.8)
γ-HCH	3.30 ± 0.81	3.90 (0.37)	2.63 (0.37)	3.37 (0.24)
α-HCH	16.2 ± 3.4	18.6 (1.2)	14.4 (1.3)	15.3 (1.0)
heptachlor epoxide	10.8 ± 1.3	10.74 (0.87)	10.1 (1.2)	11.2 (1.0)
oxychlordane	19.8 ± 1.9	20.6 (1.5)	20.7 (1.0)	18.61 (0.83)
cis-chlordane	46.9 ± 2.8	47.2 (3.2)	46.0 (3.4)	47.2 (2.5)
trans-nonachlor	231 ± 11	229 (16)	233 (16)	232 (10)
Mirex	28.9 ± 2.8	30.1 (2.3)	29.6 (2.3)	26.8 (2.2)

[a] PCB congeners are numbered according to the scheme proposed by Ballschmiter and Zell[6]. When two or more congeners are known to coelute, the PCB congener listed first is the major component and the additional congeners may be present as minor components. Quantitative results are based on the response of the congener listed first.
[b] The certified values are weighted means of results from three analytical techniques. The uncertainty is based on a 95% confidence interval for the true concentration and includes an allowance for differences between the analytical methods used.
[c] Numbers in parentheses are one standard deviation of a single measurement.
[d] Capillary column stationary phase
[e] Numbers in [ ] indicate known coelution of two or more congeners. PCB 66 and 95 coelute under the GC-ECD (DB-5 column) conditions used; PCB 164 is separated from PCB 138 and PCB 163 when using the CP Sil 5 C18 column; PCB 190 is separated from PCB 170 when using the CP Sil 5 C18 column.

5. Certification in progress: SRM 1944

A similar approach is currently being used for the determination of selected PCB congeners and chlorinated pesticides in a new NIST reference material, SRM 1944, a highly contaminated sediment. Likewise, independent and validated procedures are being used to certify other constituents of this sediment such as PAHs and trace elements. In addition, the candidate SRM 1944 sediment is being analyzed by a large number of national and international laboratories in intercomparison exercises for both selected organic and elemental analytes. These data, from laboratories using a number of different extraction, cleanup and analytical techniques, will be evaluated for use in the certification.

6. Conclusion

Through the use of validated procedures designed to differentiate among potential sources of measurement bias by exploiting differences in separation and selectivity characteristics in the extraction, isolation, and measurement steps, the possibility of having similar biases in these SRM measurements is minimized. Even though these analytical procedures have some similarities (i.e., nonpolar solvent extraction and GC separations) and are therefore not totally independent, this approach is appropriate for SRM certification given the current state of the art for the measurement of PCB congeners and pesticides.

7. References

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