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DETERMINATION OF POLYCHLORINATED DIBENZO-*p*-DIOXIN AND DIBENZOFURAN CONGENERS IN AIR PARTICULATE AND MARINE SEDIMENT STANDARD REFERENCE MATERIALS (SRMs)

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Introduction

Since the early 1980's the National Institute of Standards and Technology (NIST) has developed a number of natural matrix Standard Reference Materials (SRMs) for the determination of organic contaminants in environmental matrices (1). The first particle-based, environmental natural matrix SRM developed by NIST for organic contaminants was SRM 1649, Urban Dust/Organics, which was issued in 1982 with certified concentration values for five polycyclic aromatic hydrocarbons. In the late 1980's and early 1990's the first natural matrix SRMs certified for individual polychlorinated biphenyl (PCB) congeners and chlorinated pesticides were issued including cod liver oil, marine and river sediments, mussel tissue, and whale blubber (2-4). To date, however, no NIST natural matrix SRMs have been issued with values assigned for PCDDs and PCDFs. Since the mid-1990's a limited number of environmental matrix certified reference materials (CRMs) with natural levels (i.e., not fortified) for PCDDs and PCDFs have been issued by several other reference material producing organizations: fish tissue (CARP-1, National Research Council of Canada) (5), two Great Lakes sediments (Environment Canada, National Water Research Institute) (6), and milk powder (CRM 607) (7) and fly ash (CRM 490) (8) (Standards, Measurements and Testing Programme of the European Commission). Because of the lack of natural matrix CRMs with concentration values assigned for PCDD and PCDF prior to 1995, Nestruck et al. (9,10) proposed in 1983 the use of two existing NIST air particulate matter SRMs, SRMs 1648 and 1649, as reference materials for these measurements. SRM 1648 Urban Particulate Matter, which has certified concentrations for selected inorganic constituents, was collected in the mid-1970's in St. Louis, MO. SRM 1649, Urban Dust/Organics, which as mentioned above was originally issued in 1982 with certified concentrations for several polycyclic aromatic hydrocarbons, was collected in 1976-77 in Washington, DC. This same material was recently reanalyzed and reissued as SRM 1649a, Urban Dust, with certified and reference concentrations reported for 45 PAHs, 35 PCB congeners, and 8 chlorinated pesticides. Nestruck et al. (9,10) reported values for 22 tetrachloro-, 10 hexachloro-, 2 heptachloro-, and octachloro-substituted dibenzo-*p*-dioxin congeners, and 2,3,7,8-tetrachlorodibenzofuran (TCDF) in both of these SRMs. To increase the number of CRMs for PCDD and PCDF measurements, an interlaboratory study was undertaken by NIST and the Analysis and Air Quality Division, Environmental Technology Centre, Environment Canada to establish reference concentration values for selected PCDDs and PCDFs in two existing NIST SRMs: SRM 1649a Urban Dust and SRM 1944 New York/New Jersey Waterway Sediment.

Study Design and Analytical Methods

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Each participating laboratory received a 50 g bottle of SRM 1944, a 5 g bottle of SRM 1649a, and a sealed ampoule of an unknown standard solution. The standard solution contained the seventeen 2,3,7,8-substituted congeners in a range of 5 to 20 ng/mL in toluene. Laboratories were requested to analyze the unknown standard solution and the two SRM samples in triplicate for the determination of all seventeen 2,3,7,8-substituted congeners and the tetra- through hepta-homologues of PCDDs and PCDFs using their routine analytical procedures for extraction and cleanup and gas chromatography/high resolution mass spectrometry (GC/HRMS). The analytical procedures used by all of the laboratories included spiking the samples with ¹³C-labeled surrogates (internal standards); Soxhlet extraction with toluene for 16 h; sample extract cleanup using columns packed with materials such as multi-bed silica coated with acid/base silica, alumina, and carbon; and finally analysis of the cleaned up extract using GC/HRMS with a resolution of 10,000 or higher. All of the laboratories used a 60 m 5% phenyl-substituted methylpolysiloxane phase capillary column, except for one laboratory that used a 60 m 90% biscyanopropyl 10% phenyl cyanopropyl column; about half of the laboratories confirmed 2,3,7,8-TCDF using a 50% cyanopropylphenyl-substituted methylpolysiloxane phase capillary column.

Results and Discussion

A total of 14 laboratories participated in the interlaboratory study (see acknowledgments for participating laboratories). The analysis of the unknown standard solution was incorporated into the interlaboratory study design to assess the comparability of the calibration solutions used by the various laboratories. Both the median and the mean results from the 13 laboratories for the seventeen 2,3,7,8-substituted congeners were within 10% of the design values with most of the means within 5% of the design value. The relative standard deviations for the interlaboratory results for all 2,3,7,8-substituted congeners ranged between 7% and 14%. The low variability of the measurements for the PCDD and PCDF congeners in the standard solution suggests that the calibration processes among the laboratories were comparable. The results from the interlaboratory study were used to determine the reference concentration values for the seventeen 2,3,7,8-substituted PCDD and PCDF congeners, the total tetra- through hepta-substituted PCDD and PCDF homologues, and the total PCDD and PCDFs as summarized in Table 1. The reference value is the mean of the laboratory means (determined from the triplicate measurements) and the associated uncertainty is a 95% confidence level (see footnote "a" in Table 1 for detailed description of the uncertainty). Only the results from the laboratories using a confirmative column were used to establish the reference value for 2,3,7,8-TCDF due to coelution with other congeners on the DB-5 column. The relative uncertainties for the individual congeners in SRM 1649a ranged from 5% to 30% with the exception of the two congeners that had concentrations near the detection limit. For SRM 1944 the relative uncertainties were only 6% to 15% with the exception of one congener. A total Toxic Equivalents (TEQ) value was also determined for each of the SRMs. The TEQ value is the sum of the products of each of the 2,3,7,8-substituted congeners multiplied by their individual toxic equivalency factors (TEFs) recommended by the North Atlantic Treaty Organization (NATO) (12). With the addition of the PCDD and PCDF values, SRM 1649a and SRM 1944 are the most characterized natural matrix SRMs with certified and reference values for over 160 organic and inorganic constituents.

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Table 1. Reference Concentrations for Selected PCDD and PCDF Congeners in SRM 1649a Urban Dust and SRM 1944 New York/New Jersey Waterway Sediment.

	mass fraction in µg/kg (dry-mass basis) ^a			
	SRM 1649a		SRM 1944	
2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin	0.011	± 0.004	0.133	± 0.009
1,2,3,7,8-Pentachlorodibenzo- <i>p</i> -dioxin	0.091	± 0.012	0.019	± 0.002
1,2,3,4,7,8-Hexachlorodibenzo- <i>p</i> -dioxin	0.26	± 0.02	0.026	± 0.003
1,2,3,6,7,8-Hexachlorodibenzo- <i>p</i> -dioxin	0.68	± 0.05	0.056	± 0.006
1,2,3,7,8,9-Hexachlorodibenzo- <i>p</i> -dioxin	0.64	± 0.11	0.053	± 0.007
1,2,3,4,6,7,8-Heptachlorodibenzo- <i>p</i> -dioxin	18.8	± 1.5	0.80	± 0.07
Octachlorodibenzo- <i>p</i> -dioxin	201	± 20	5.8	± 0.7
2,3,7,8-Tetrachlorodibenzofuran	0.068	± 0.015	0.039	± 0.015
1,2,3,7,8-Pentachlorodibenzofuran	0.090	± 0.010	0.045	± 0.007
2,3,4,7,8-Pentachlorodibenzofuran	0.28	± 0.03	0.045	± 0.004
1,2,3,4,7,8-Hexachlorodibenzofuran	0.87	± 0.26	0.22	± 0.03
1,2,3,6,7,8-Hexachlorodibenzofuran	0.43	± 0.06	0.09	± 0.01
2,3,4,6,7,8-Hexachlorodibenzofuran	0.69	± 0.03	0.054	± 0.006
1,2,3,7,8,9-Hexachlorodibenzofuran	0.066	± 0.029	0.019	± 0.018
1,2,3,4,6,7,8-Heptachlorodibenzofuran	3.8	± 0.2	1.0	± 0.1
1,2,3,4,7,8,9-Heptachlorodibenzofuran	0.46	± 0.07	0.040	± 0.006
Octachlorodibenzofuran	6.8	± 0.8	1.0	± 0.1
Total Toxic Equivalents (TEQ) ^b	1.00	± 0.07	0.25	± 0.01
Total Tetrachlorodibenzo- <i>p</i> -dioxins	0.16	± 0.08	0.25	± 0.05
Total Pentachlorodibenzo- <i>p</i> -dioxins	0.88	± 0.16	0.19	± 0.06
Total Hexachlorodibenzo- <i>p</i> -dioxins	6.0	± 0.5	0.63	± 0.09
Total Heptachlorodibenzo- <i>p</i> -dioxins	36.4	± 3.4	1.8	± 0.2
Total Tetrachlorodibenzofurans	0.52	± 0.13	0.7	± 0.2
Total Pentachlorodibenzofurans	1.6	± 0.2	0.74	± 0.07
Total Hexachlorodibenzofurans	5.0	± 0.6	1.0	± 0.1
Total Heptachlorodibenzofurans	9.8	± 0.8	1.5	± 0.1
Total Dibenzo- <i>p</i> -dioxins ^c	244	± 22	8.7	± 0.9
Total Dibenzofurans ^c	23.9	± 1.9	5.0	± 0.5

^a Each reference value is the mean of the results from up to 14 laboratories participating in an interlaboratory exercise. The expanded uncertainty in the reference value is equal to $U = ku_c$ where u_c is the combined standard uncertainty calculated according to the ISO Guide (11) and k is the coverage factor. The value of u_c is intended to represent at the level of one standard deviation the combined effect of all the uncertainties in the reference value. Here u_c is the uncertainty in the mean arising from the variation among the laboratory results. The degrees of freedom is equal to the number of available results minus one (typically 12 for SRM 1649a and 13 for SRM 1944). The coverage factor, k , is the value from a student's t -distribution for a 95 % confidence interval. Concentrations reported on dry-mass basis; as received both SRM 1649a and SRM 1944 contain approximately 1.3 % moisture.

^b TEQ is the sum of the products of each of the 2,3,7,8-substituted congeners multiplied by their individual toxic equivalency factors (TEFs) recommended by the North Atlantic Treaty Organization (NATO) (12).

^c Total of tetra- through octachlorinated congeners.