NIST SRM 1945, WHALE BLUBBER, NIST SRM 1974, ORGANICS IN MUSSEL TISSUE, AND NIST SRM 1941a, ORGANICS IN MARINE SEDIMENT AS CERTIFIED REFERENCE MATERIALS FOR POLYCHLORINATED DIOXINS AND FURANS IN MARINE ECOSYSTEMS

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Abstract

No natural matrix Standard Reference Materials are available for the validation of analytical methods measuring polychlorinated dioxins and furans (PCDDs and PCDFs) in marine ecosystems. The concentrations of PCDDs and PCDFs in SRM 1945, SRM 1974, and SRM 1941a are of interest because the analysis of marine mammal, mussel tissues and sediments have become important tools in the determination of organochlorine contamination in the environment. Because these SRMs have been demonstrated to be homogenous for other organic contaminants, they would be expected to be reliable standards for validation of polychlorinated dioxins and furans in marine mammals, mussels and sediments as well.

Introduction

Ideally, standard reference materials (SRMs) should be used by laboratories to validate their analytical methods and assess accuracy. Even after validation, these methods must be monitored to verify that they continue to produce acceptable data and are in a state of statistical control[1]. The SRM matrix and analyte concentrations used should be a reasonable match to that of the samples to be analyzed[2]. It is virtually impossible to find an SRM that meets all of the matrix and concentration requirements and, therefore, some compromises are inevitable. Even though the availability of SRMs has increased in the past few years, and their use is the best available approach to determination of the precision and accuracy of measured data, no natural matrix SRMs are available for the validation of analytical methods measuring polychlorinated dioxins and furans (PCDDs and PCDFs) in marine ecosystems.

The National Institute of Standards and Technology (NIST) has developed several SRMs to assist in the validation of analytical measurements of environmental contaminants in natural matrices. SRM 1945, Whale Blubber, is a frozen blubber homogenate that has been certified for 26 polychlorinated biphenyl (PCB) congeners and for 15 chlorinated pesticides[3]. SRM 1974, Organics is Mussel Tissue, is a frozen mussel tissue homogenate with certified values for nine PAHs, and non-certified values

for PCBs, chlorinated pesticides, PAHs, and inorganic constituents[4]. SRM 1941a is homogenized marine sediment with certified and non-certified values for PCBs, chlorinated pesticides, PAHs, and inorganics[5].

Presently, NIST does not have available a natural matrix SRM with certified concentrations of PCDDs and PCDFs. The concentrations of polychlorinated dioxins and furans in SRM 1945, SRM 1974, and SRM 1941a are of interest because of their high toxicity factors[6], and because the analysis of marine mammal, mussel tissues and sediments have become important tools in the determination of organochlorine contamination in the environment[7]. Because these SRMs have been demonstrated to be homogenous for other organic contaminants, they would be expected to be reliable standards for validation of polychlorinated dioxins and furans in marine mammals, mussels and sediments as well. The objective of this study was to determine the concentration of PCDDs and PCDFs in three readily available NIST SRMs to see if they would be useful as reference materials for environmental contaminant studies focusing on these analytes.

Experimental

Three to five grams of the NIST SRMs (tissues and sediments) were spiked with the appropriate internal standards. Tissues were mixed with sodium sulfate and extracted with three aliquots of methylene chloride with a Tekmar tissuemizer for 5 minutes each. Sediment samples were extracted for 18 hours with toluene in a soxhlet extractor fitted with a Dean Stark trap. A 44% mixture of concentrated sulfuric acid/silica gel was used to remove lipid interferences from the tissue samples. Further purification of all sample extracts was achieved by mixed-bed silica, basic alumina, and AX-21 Super Activated Carbon column chromatography. The extracts were reduced to a final volume of 20μL and the appropriate recovery standards added[9].

Two μL of the concentrated extract are injected into an HRGC/HRMS system capable of performing selected ion monitoring at resolving powers of at least 10,000. The identification of the sixteen 2,3,7,8-substituted isomers for which a ^{13}C-labeled standard is available is based on their elution from a DB-5MS analytical column at their exact retention time and the simultaneous detection of the two most abundant ions in the molecular ion region. The identification of OCDF is based on its retention time relative to ^{13}C-OCDD. Confirmation is based on a comparison of the ratios of the integrated ion abundance of the molecular ion species to their theoretical abundance ratios. Quantitation of the individual congeners is achieved in conjunction with the establishment of a multipoint calibration curve for each homologue, during which each calibration solution is analyzed once[10]. Concentrations of 2,3,7,8-TCDF were confirmed on a DB-225 analytical column.

Results and Discussion

Results from replicate analyses of NIST SRM 1945, SRM 1974, and SRM 1941a are given in Table 1. Included are measured concentrations of the seventeen 2,3,7,8-substituted PCDD/PCDF isomers, average concentration, relative standard deviation, and percent recovery of the isotopically labeled internal standards.

SRM 1941a, Organics in Marine Sediment contained measurable concentrations of sixteen out of seventeen 2,3,7,8-substituted PCDD/PCDF isomers within the calibration range of the instrument. In general, concentrations increase with increasing degree of chlorination, with the OCDF and OCDD analytes present at approximately

5,000 ppt and 13,000 ppt, respectively. One analyte, 1,2,3,7,8,9-HxCDF, was not found to be present in the sediment. (Results for the sediment are given on a dry weight basis.)

SRM 1974, Organics is Mussel Tissue, was found to contain the 2,3,7,8-TCDD isomer at 1.31 ppt, a concentration near the lowest instrument calibration point for the sample size extracted. It also contained four additional 2,3,7,8-substituted isomers at concentrations that were consistently reproduced within the calibration range. SRM 1945, Whale Blubber, was found to contain 2,3,7,8-TCDF and 1,2,3,4,6,7,8-HpCDD at concentrations similar to those found in the Mussel Tissue. It also had measurable concentrations of OCDD at approximately one-fifth the level found in the Mussel Tissue, as well as several other isomers at levels below the lowest instrument calibration point. Internal Standard recoveries were acceptable for all samples analyzed.

Conclusions

The results demonstrate that PCDD/PCDF isomers are present in NIST SRM 1941a, Organics in Marine Sediment, at concentrations which would make it useful as a Certified Reference Material for marine ecosystem studies. SRM 1945 and SRM 1974 contain low concentrations of selected isomers, making them potential candidates for use as Standard Reference Materials used in low-level contaminant studies involving marine mammals or mussel tissue. These three Standard Reference Materials are homogenous natural matrices and are readily available for interlaboratory comparison of results.

References

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Table 1 Concentrations of the seventeen 2,3,7,8-substituted PCDD/PCDF isomers in three NIST Standard Reference Materials.

NIST SRM ID	1945	1945	1945	Average Conc.	Relative St.Dev.	1974	1974	Average Conc.	Relative St.Dev.	1941
Compound Name	Conc (pg/g)	Conc (pg/g)	Conc (pg/g)	(pg/g)	%	Conc (pg/g)	Conc (pg/g)	(pg/g)	%	Conc (pg/g)
2,3,7,8-TCDF	5.57	5.89	5.01	5.49	8	6.66	7.27	6.97	6	62.4
1,2,3,7,8-PeCDF	*	0.86	2.47	1.11	113	12.8	15.4	14.1	13	68.5
2,3,4,7,8-PeCDF	1.80	2.53	5.84	3.39	64	*	0.79	NA	NA	69.3
1,2,3,4,7,8-HxCDF	1.29	0.81	2.58	1.56	59	*	1.40	NA	NA	205
1,2,3,6,7,8-HxCDF	0.89	0.96	2.20	1.35	55	*	1.98	NA	NA	48.7
2,3,4,6,7,8-HxCDF	1.67	2.18	3.63	2.49	41	*	1.10	NA	NA	42.7
1,2,3,7,8,9-HxCDF	*	1.29	3.86	1.72	114	*	1.86	NA	NA	*
1,2,3,4,6,7,8-HpCDF	*	0.96	*	NA	NA	*	1.35	NA	NA	457
1,2,3,4,7,8,9-HpCDF	*	*	*	NA	NA	*	*	NA	NA	193
OCDF	*	0.82	*	NA	NA	*	3.41	NA	NA	5108
2,3,7,8-TCDD	*	0.81	*	NA	NA	*	1.31	NA	NA	5.40
1,2,3,7,8-PeCDD	*	*	*	NA	NA	*	*	NA	NA	14.1
1,2,3,4,7,8-HxCDD	*	0.69	*	NA	NA	*	*	NA	NA	17.7
1,2,3,6,7,8-HxCDD	*	1.18	*	NA	NA	*	*	NA	NA	67.9
1,2,3,7,8,9-HxCDD	*	0.90	*	NA	NA	*	*	NA	NA	46.3
1,2,3,4,6,7,8-HpCDD	*	1.34	3.53	1.62	110	3.37	4.55	3.96	21	1182
OCDD	3.55	3.86	5.19	4.20	21	19.5	19.8	19.6	1	13412
Internal Standard % Recoveries	% Recov	% Recov	% Recov	Average % Recov		% Recov	% Recov	Average % Recov		% Recov
13C-2,3,7,8-TCDF	79	68	79	75		79	43	61		68
13C-1,2,3,7,8-PeCDF	80	87	58	75		76	50	63		72
13C-2,3,4,7,8-PeCDF	79	89	59	76		79	50	64		53
13C-1,2,3,4,7,8-HxCDF	89	73	90	84		68	43	56		25
13C-1,2,3,6,7,8-HxCDF	95	64	102	87		51	36	44		25
13C-2,3,4,6,7,8-HxCDF	92	81	102	92		57	38	48		65
13C-1,2,3,7,8,9-HxCDF	96	95	95	95		55	41	48		80
3C-1,2,3,4,6,7,8-HpCDF	78	77	92	82		69	43	56		22
3C-1,2,3,4,7,8,9-HpCDF	94	114	93	100		79	47	63		49
13C-2,3,7,8-TCDD	80	85	95	87		89	37	63		102
13C-1,2,3,7,8-PeCDD	84	97	76	86		106	51	78		78
13C-1,2,3,4,7,8-HxCDD	84	92	91	89		109	46	77		54
13C-1,2,3,6,7,8-HxCDD	89	75	102	89		47	38	42		44
3C-1,2,3,4,6,7,8-HpCDD	86	93	94	91		78	38	58		55
13C-OCDD	78	110	137	108		43	22	33		57