PROGRESS UPDATE ON CERTIFYING HBCD IN NIST STANDARD REFERENCE MATERIALS (SRMS)

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Introduction

Standard Reference Materials (SRMs) are homogeneous, well-characterized materials that are used to validate measurements and improve the quality of analytical data. SRMs of different matrices, such as marine sediment, air particulate material, and numerous biological materials, are produced by the National Institute of Standards and Technology (NIST). NIST provides certified concentrations in SRMs for numerous environmental contaminants including PBDEs, PAHs, PCBs, pesticides and trace elements [1]. Recently, HBCDs have been characterized in existing and newly developed SRMs with the ultimate goal of certifying the concentrations of these contaminants of emerging concern.

Materials and methods

SRMs of diverse matrices were selected for analysis. These included biotic materials of whale blubber (SRM 1945), fish tissue (SRMs 1946 and 1947), mussel tissue (SRMs 1974b, 2977, 2974a), human serum (SRMs 1957 and 1958), and human milk (SRMs 1953 and 1954). Abiotic materials were also selected: sediment (SRMs 1941b and 1944), sludge (SRM 2781), house dust (SRM 2585), and urban dust/air particulate material (SRMs 1648a, 1649b, 2786, and 2787). A known quantity of the SRMs were spiked with ^{13}C-HBCD internal standards, extracted with pressurized fluid extraction (microwave extraction for serum and milk), cleaned up with two to three methods (typically alumina solid-phase extraction (SPE), acidified silica SPE, and size exclusion chromatography), and analyzed on a liquid chromatograph tandem mass spectrometer (LC/MS/MS; Agilent 1100 HPLC [Santa Clara, CA] with an API 4000 MS/MS [Applied Biosystems, Foster City, CA] or Agilent 1200 HPLC with a 4000 QTrap [Applied Biosystems]). Deuterated HBCDs were added to final extracts to quantify recovery of the internal standards. Extracts of SRMs 1953, 1954, 1957, 1958 were analyzed with a single method using a C18 analytical column (Agilent Eclipse Plus C18 3.0 mm x 150 mm x 3.5 μm) and negative electrospray ionization (ESI). Extracts of remaining SRMs were analyzed with two methods, either by differing the analytical columns or by using different ionization sources. Extracts of SRMs 2977, 2974a, 2781, 2585, 1648a, 1649b, 2786, and 2787 were analyzed with two different sources (ESI vs. atmospheric pressure photospray ionization [APPI]) with a single analytical column (C18). Extracts of SRMs 1945, 1946, 1947, 1974b, 1941b, 1944, and 2585 were analyzed with two different analytical columns (C18 vs a Waters YMC Carotenoid S5 C30 column 4.6 mm x 250 mm x 5 μm column) using only ESI. Calibration standards (Cambridge Isotope Laboratories, Andover, MA or Wellington Laboratories, Guelph, Ontario) were processed alongside SRM samples from extraction to analysis and ranged from 0.2 ng to 100 ng of each isomer.

Results and discussion

HBCD isomers were below detection limits in the non-fortified human serum and milk SRMs (1957 and 1953), but α–HBCD was measurable in the human serum (≈ 0.3 ng/g) and milk (≈ 0.5 ng/g) SRMs (1958 and 1954) that were fortified with this compound plus 171 other compounds. Values from the two MS/MS sources agreed within 23% for all isomers in all SRMs analyzed (2977, 2974a, 2781, 2585, 1648a, 1649b, 2786, and 2787), except β–HBCD in SRM 2974b differed by 63% (concentration was near the limit of detection). Likewise, values from the two columns agreed within 17% for two isomers (α–HBCD and γ–HBCD) in all SRMs analyzed (1945, 1946, 1947,

1974b, 1941b, 1944, and 2585), but β−HBCD was consistently at least twice as high in concentrations using the C30 column compared to the C18 column. This difference for β−HBCD can be attributed to only the column choice and differences in mobile phases, suggesting an interference might be affecting either the native or the mass-labeled compounds on one column. Examples of these comparisons are provided in Figures 1 and 2. Future research will refine methods to reduce discrepancies between methods and verify the purity of the HBCD standards used to make these measurements, so that the values can be used for certification of HBCDs in these SRMs.

Disclaimer

Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

References

1. Wise SA, Poster DL, Kucklick JR, Keller JM, Vanderpol SS, Sander LC, Schantz MM. (2006); *Anal Bioanal Chem*. 386: 1153-90

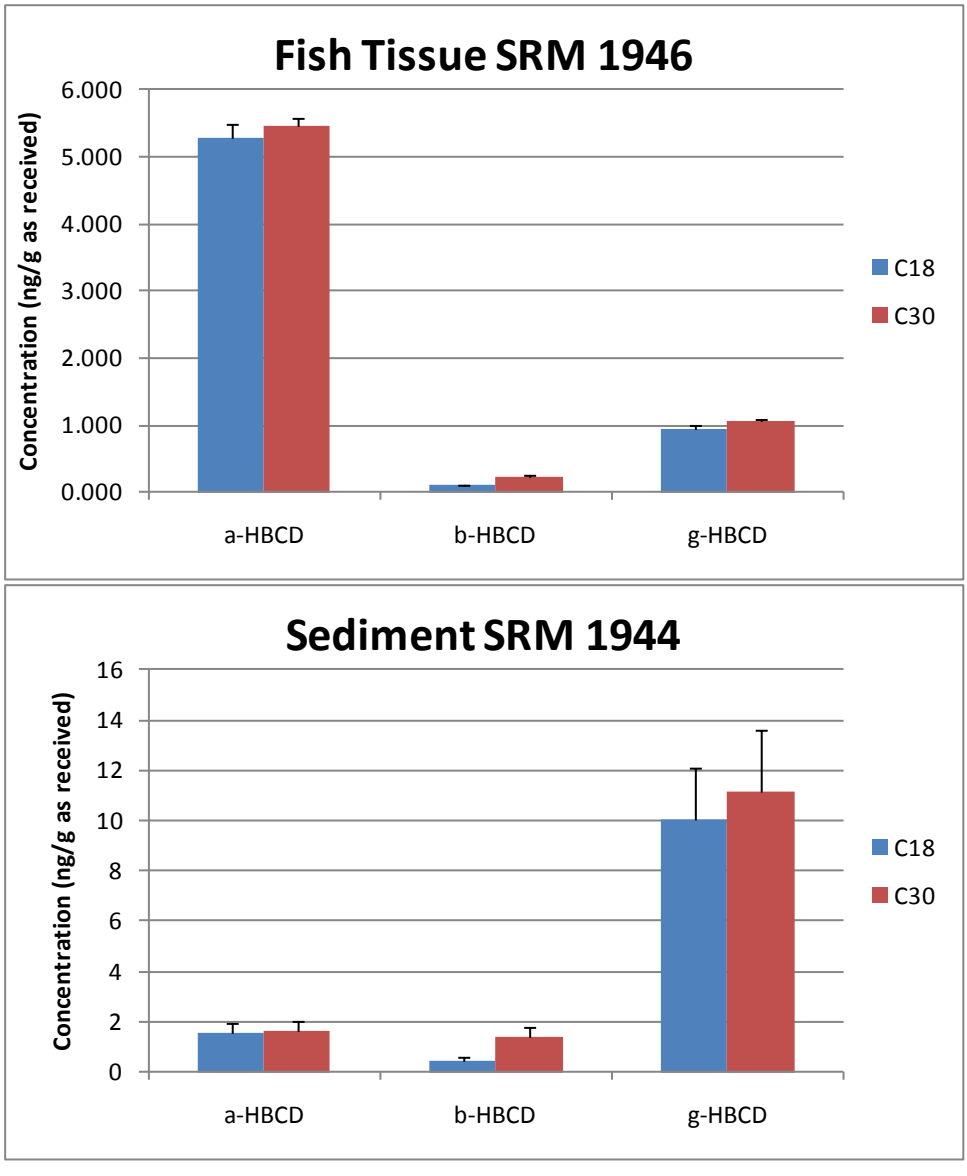

Figure 1. Comparison of HBCD data generated from a C18 vs. C30 column for two SRMs.

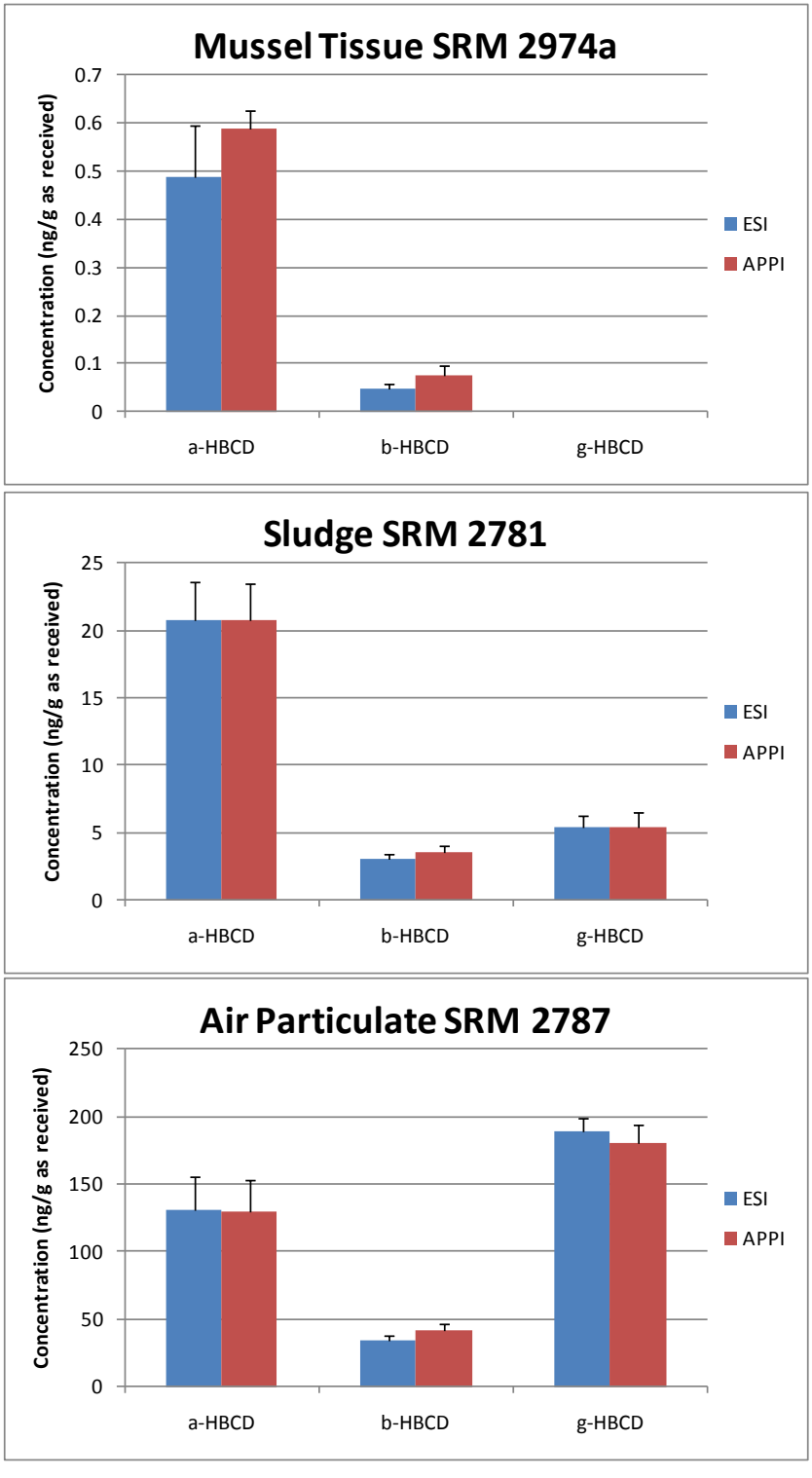

Figure 2. Comparison of HBCD data generated from ESI vs. APPI for three SRMs.