

## Standard Reference Materials (SRMs) for Contaminants in Marine Tissue and Sediment

*Targeted environmental monitoring efforts, regulatory pressures, and compounds of emerging concern are expanding the list of potentially toxic contaminants that impact marine systems and are challenging the analytical community to develop new measurement technologies for organic pollutants and trace metals. NIST is responding by providing marine-matrix Standard Reference Materials (SRMs) to the marine environmental research community for method validation and quality assurance purposes, and is at the forefront of developing and disseminating new analytical technologies for measuring contaminants in marine reference materials. Brominated flame retardants have been measured in various marine tissue and sediment SRMs, and new analytical approaches have been developed to certify organometallic species in marine tissue SRMs.*

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The revision and assignment of new organic contaminant values to SRMs improves accuracy and adds new functionality to current-issue SRMs. Certified mass fraction values for seven polybrominated diphenyl ether (PBDE) congeners and reference mass fraction values for three PBDE congeners were added to SRM 1946 Lake Superior Fish Tissue. SRM 1588b Organics in Cod Liver is a reissued matrix of the same material comprising SRM 1588a, which was originally certified in 1998 for the concentrations of 14 chlorinated pesticides and 24 polychlorinated biphenyl (PCB) congeners and also had reference values for  $\alpha$ -tocopherol, 34 PCB congeners, and 3 chlorinated pesticides. SRM 1588b updates the certified values and provides certified and reference values for additional analytes, including fatty acids, PBDE congeners, and toxaphene congeners. NIST developed novel quantification strategies for determination of organometallic species in marine tissue SRMs, specifically for organomercury compounds.

Gas chromatography (GC) coupled to inductively coupled plasma mass spectrometry (ICPMS) using isotopic calibrants has become the most sensitive method for quantitative speciation of methylmercury and inorganic Hg (II). A double spike method has been implemented using a speciated  $^{202}\text{Hg}$  spike (IRMM CRM AE670) in concert with a  $^{201}\text{Hg}$  inorganic spike (Oak Ridge National Laboratory) for determination of Hg (II). A formal stability testing effort

has been initiated to monitor organometallic species stability over time. In 2005, methylmercury measurements in bivalve SRMs 1566b Oyster Tissue, 2976 Mussel Tissue (Trace Elements and Methylmercury), and 2977 Mussel Tissue (Organic Contaminants and Trace Elements) showed good agreement with certified values originally based on GC with atomic emission detection. SRMs 1947 and 1974b were certified for methylmercury content using two independent methods, solid-phase microextraction (SPME) GC/mass spectrometry (MS) using an isotopic methylmercury internal standard (IRMM CRM AE670) and isotope dilution GC-ICPMS.

In 2005 new and improved methodologies emerged, and these technologies have allowed NIST to significantly improve mass fraction accuracy and increase the utility of our marine SRMs through expanded coverage of contaminants represented by several chemical contaminant classes.

The program examples highlighted here show that CSTL's collaborative measurement capabilities lead to innovative reference materials and measurement technologies aimed at improving and assuring chemical measurement quality.

**Future Plans:** Work will be dedicated to developing analytical methods and measuring environmental compounds of emerging concern in current-issue and future marine tissue and sediment SRMs, including perfluorooctanesulfonate (PFOS), perfluorooctanoic acid (PFOA), other types of brominated flame retardants, classes of compounds like phthalate esters and their metabolites, which are prevalent in plasticizers, and representative compounds comprising the range of pharmaceutical and personal care products. We will also begin to measure organotin compounds in marine sediment and tissue SRMs.

**In 2005, critical updates that include polybrominated diphenyl ether congeners and pesticides were added to two marine tissue SRMs:**

- SRM 1946 Lake Superior Fish Tissue;
- SRM 1588b Organics in Cod Liver Oil.

**Methylmercury was certified in:**

- SRM 1566b Oyster Tissue
- SRMs 2976, 2977, 1974b Mussel Tissues
- SRM 1947 Lake Michigan Fish Tissue