

DETERMINATION OF POLYBROMINATED DIPHENYL ETHERS IN MUSSEL TISSUE AND SEDIMENT STANDARD REFERENCE MATERIALS

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Introduction

The National Institute of Standards and Technology (NIST) provides a wide range of natural matrix environmental Standard Reference Materials (SRMs) that are characterized for a number of compounds in various contaminant classes, including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), chlorinated pesticides, and inorganic compounds such as mercury, cadmium, and lead. Up until recently, only limited information has been available for polybrominated diphenyl ethers (PBDEs) in environmental matrices though this is rapidly increasing as the measurements of these compounds in the environment are increasing as these are now considered ubiquitous contaminants in not only the environment but also in people.¹ Concentrations of PBDEs have been determined in a number of NIST natural-matrix SRMs including marine mammal blubber, fish tissue, house dust², and human serum. Selected environmental SRMs have been examined for PBDEs by Zhu and Hites.³ Certified and reference concentration values are available for selected congeners in selected materials. Two additional matrices have been examined for PBDEs: mussel tissue and marine sediment. The specific SRM materials are the following SRMs: SRM 1974b Organics in Mussel Tissue (*Mytilus edulis*), SRM 2977 Mussel Tissue (Organic Contaminants and Trace Elements), SRM 1941b Organics in Marine Sediment, and SRM 1944 New York/New Jersey Waterway Sediment.

SRM 1974b is the third and current material in a series of cryogenically homogenized mussel tissue SRMs prepared from mussels collected near Boston Harbor, Massachusetts. SRM 2977 is a freeze-dried tissue homogenate prepared from mussels collected in Guanabara Bay, Brazil. SRM 1941b is the third and current material in a series of freeze-dried sediment SRMs prepared from sediment collected at the mouth of the Baltimore Harbour, Maryland. SRM 1944 is a mixture of marine sediment collected near urban areas in New York and New Jersey. The determination of the concentrations of PBDEs in the mussel tissue and marine sediment SRMs with an emphasis on the approach and methods used for the chemical characterization of these natural-matrix SRMs are described below.

Materials and Methods

The SRM materials analyzed for the determination of the concentrations of PBDEs were original, "as-received" materials and were not altered physically (i.e., sieved, filtered, or dried) or chemically (i.e., fortified with contaminants) prior to analysis. About 0.5 to 10.0 g of each SRM was extracted by pressurized fluid extraction or Soxhlet extraction using dichloromethane. Following extraction of mussel tissue SRMs, aliquots were taken for lipid measurements followed by gel permeation chromatography to remove lipids. Following gel permeation chromatography for the mussel tissue samples and solvent extraction for the sediment samples, samples were further cleaned-up using solid phase extraction. Samples were quantified for PBDEs using gas chromatography equipped with a mass spectrometer operated in negative chemical ionization (GC/NCI-MS) and selected samples were analyzed using electron impact ionization (EI). PBDE congeners were separated using a 15 m x 0.25 mm 5% phenyl-methyl polysiloxane capillary column (0.25 µm film thickness). Internal standards consisted of selected ¹³C labeled PBDE congeners and in some cases a ¹³C labeled chlorinated diphenyl ether or fluorinated PBDE congeners.

Fluorinated PAHs have recently been used for the determination of PAHs in selected environmental SRMs.⁴ Calibration solutions consisting of mixtures of PBDE congeners and blank samples were processed alongside the SRM samples.

Results and Discussion

Mussel Tissue SRMs. Concentrations of PBDEs in SRM 1974b Organics in Mussel Tissue (*Mytilus edulis*) range from < 0.1 ng/g wet mass to approximately 3.5 ng/g wet mass. Concentrations for selected congeners are presented in Figure 1. Results from the two ionization methods deployed in the mass spectrometer are compared (NCI and EI) and in general are in good agreement (Figure 1). A representative chromatogram (NCI) is provided in Figure 2 for SRM 1974b. Concentrations of PBDEs in SRM 2977 Mussel Tissue (Organic Contaminants and Trace Elements) are currently underway.

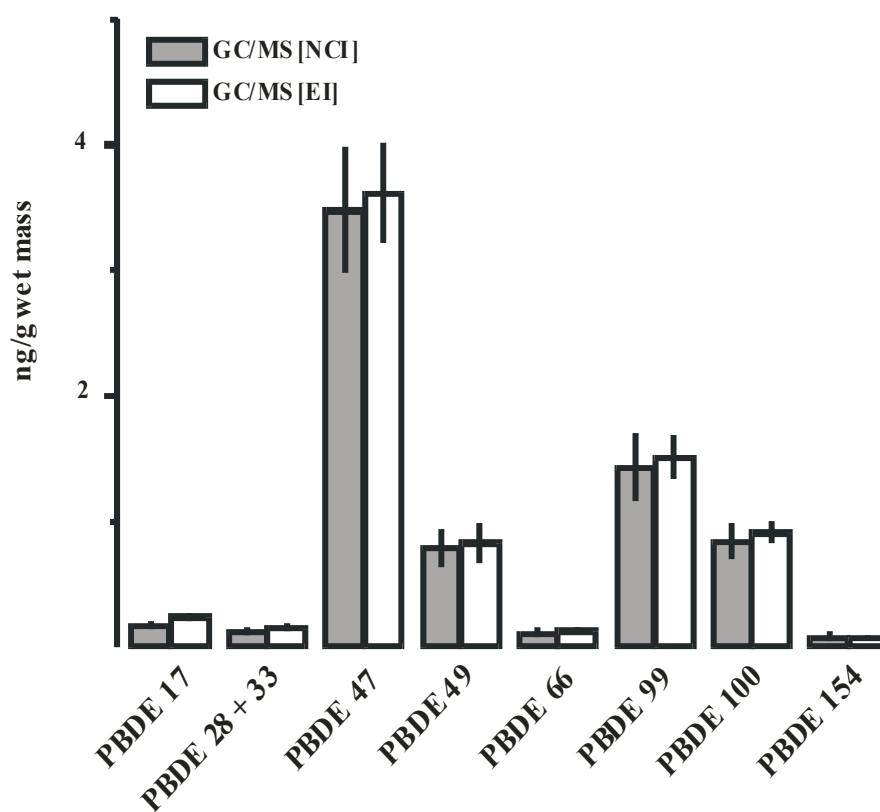


Figure 1. Concentrations of selected PBDE congeners in SRM 1974b Organics in Mussel Tissue (*Mytilus edulis*) determined using gas chromatography equipped with a mass spectrometer operated using negative chemical ionization (GC/NCI-MS) and electron impact ionization (EI). Each error bar is the standard deviation of the mean (n=5).

Sediment SRMs. Many studies have measured PBDE levels in marine and aquatic sediments and observed levels ranging from less than detection limits up to 7,000 ng/g dry mass.¹ Decabromodiphenyl ether (PBDE 209) typically accounts for the largest proportion of total PBDEs measured in sediment samples and this is the case for SRM 1941b Organics in Marine Sediment. Concentrations of PBDEs in SRM 1941b range from < 0.1 ng/g dry mass to about 26

ng/g dry mass for PBDE 209. Concentrations for selected congeners are presented in Figure 3. Results from the two ionization methods deployed in the mass spectrometer are compared (NCI and EI) and in general are in good agreement (Figure 3). A representative chromatogram (NCI) is provided in Figure 4 for SRM 1941b. Concentrations of PBDEs in SRM 1944 New York/New Jersey Waterway Sediment range from < 0.1 ng/g as received to about 90 ng/g as received (PBDE 209).

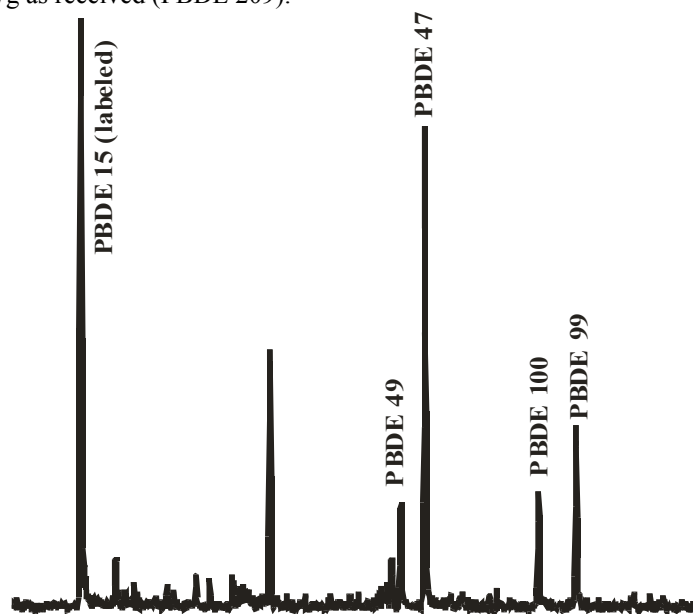


Figure 2. GC/MS chromatogram (NCI) of selected PBDEs in SRM 1974b Organics in Mussel Tissue (*Mytilus edulis*).

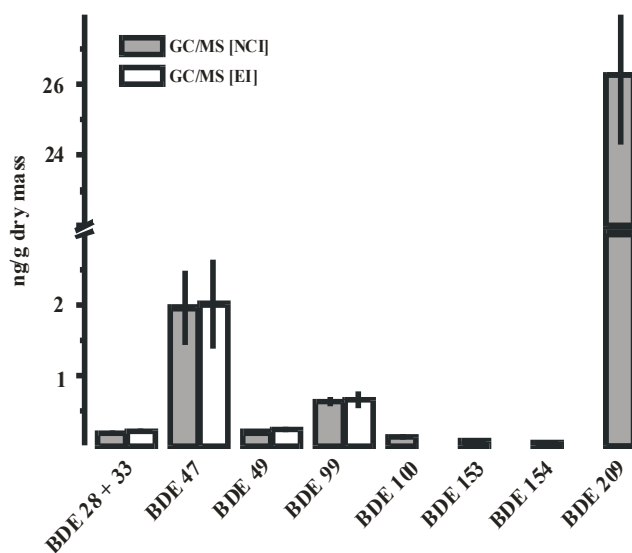


Figure 3. Concentrations of selected PBDE congeners in SRM 1941b Organics in Marine Sediment determined using gas chromatography equipped with a mass spectrometer operated using negative chemical ionization (GC/NCI-MS) and electron impact ionization (EI). Each error bar is the standard deviation of the mean (n=5).

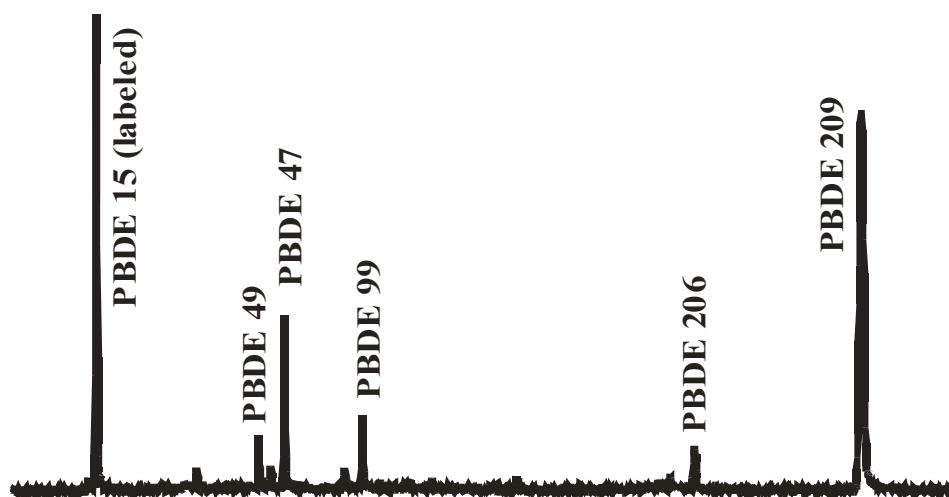


Figure 4. GC/MS chromatogram (NCI) of selected PBDEs in SRM 1941b Organics in Marine Sediment.

References

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