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Chemosphere 62 (2006) 1795–1805

CHEMOSPHERE

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Microscale analytical methods for the quantitative detection of PCBs and PAHs in small tissue masses

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Received 3 January 2005; received in revised form 12 May 2005; accepted 9 July 2005
Available online 13 October 2005

Abstract

Microscale methods (MM) were evaluated and compared to traditional methods (TM) for measuring polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in spiked and standard reference fish and mussel tissues. MMs are advantageous because they use small tissue masses (ca. 100 mg), and maintain sensitivity through reducing final extract volume (traditionally 1 ml) by an order of magnitude or more (40 μl—PCBs; 100 μl—PAHs). Procedural losses occurred in the MMs' combined cleanup/primary evaporation step (19% PAHs; 6% PCBs), and the final extract concentration (14% PAHs; 22% PCBs). The PAH MM performed comparably to the TM. Although most PCBs had recoveries >50%, the PCB MM generally yielded lower recoveries than the TM. Average method detection limits were 0.6 μg/kg (TM) and 1.0 μg/kg (MM) for PCBs and 25.7 μg/kg (TM) and 27.7 μg/kg (MM) for PAHs. MMs described for PCB and PAH tissue samples are potentially viable alternatives to TMs, and could lead to cost savings in bioaccumulation/toxicity tests.
Published by Elsevier Ltd.

Keywords: Microscale extraction; PCBs; PAHs; Tissues

1. Introduction

Organic contaminants, including polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are ubiquitous in urban river, estuarine and coastal sediments, and can pose significant risks to human health, the environment and the nation's economy (NRC, 2003). The bioavailability of PAHs and PCBs is assessed using bioaccumulation tests, which have been developed for a variety of sediment biota (EPA/USACE, 1998).

Bioaccumulation tests typically require well-replicated exposures of small invertebrates, often resulting in small tissue samples (ca. 50–500 mg). However, our laboratory typically uses traditional methods designed for significantly larger tissue masses (e.g. soxhlet extraction requires 20–25 g (EPA, 1996a), and ultrasonic techniques use 10 g of tissue (EPA, 1984)). In practice, we

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0045-6535/$ - see front matter Published by Elsevier Ltd.
doi:10.1016/j.chemosphere.2005.07.027

typically use these methods with tissue samples ranging 3–4 g wet weight, and for this paper we selected that amount to be used with traditional methods for comparisons with the microscale methods described below.

Others have reported on microscale techniques for organic pollutants including PCBs and PAHs. Peterson et al. (1976) extracted samples for pesticides as small as 0.1 g by shaking tissue ground with sodium sulfate and solvent followed by a solvent partitioning step to yield a final volume of 0.4 ml. Wirth et al. (1994) used a bead beater technique to extract PCBs from 25 μg (dry wt.) tissue yielding a 0.1 ml final extract. Klosterhaus et al. (2002) adapted Wirth's approach for analysis of PAHs. Our microscale methods (MMs) employ a relatively simple approach that compensates for small sample amounts through concentration of the final extract to 40–100 μl (Fig. 1). EPA's high-resolution dioxin Method 8290 (EPA, 1996a) uses extract concentration to 20 μl to achieve low detection limits, and while the technique has been reported for analysis of PCBs (Hess et al., 1995; Dachs and Bayona, 1997; Thomas et al., 1998) and PAHs (Dachs and Bayona, 1997), it has not been developed as a technique to reduce tissue mass requirements for analytical methods supporting bioaccumulation tests used in sediment evaluation. In this report, microscale methods (MMs) were (a) quantified for stepwise procedural losses, (b) tested for capability to remove sample lipids, and (c) compared to traditional methods (TMs). MMs and TMs were compared relative to accuracy, precision, and detection capability for selected PAHs and PCB congeners in spiked and standard reference fish and mussel tissue.

2. Materials and methods

2.1. Chemicals

Pesticide grade hexane, acetone, toluene, sodium sulfate, and sulfuric acid were purchased from JT Baker (Phillipsburg, NJ) and high purity dichloromethane was purchased from Burdick & Jackson (Muskegon, MI). Silica gel, grade 923, was purchased from Fisher Scientific (Pittsburgh, PA) and Hydromatrix, a diatomaceous earth product, was purchased from Varian (Palo Alto, CA). Unless otherwise noted, all standards were purchased for PCB congeners from Ultra Scientific (North Kingstown, RI) and for PAHs from Supelco (Bellafonte, PA).

2.2. Standard reference materials and tissue homogenates

Standard reference materials (SRM) were purchased from the National Institute of Standards and Technology (NIST, Gaithersburg, MD), and cod tissue for spiking studies was purchased locally. Cod tissue was prepared by processing fillets through a meat grinder five times with thorough mixing between each grinding. Cod tissue had a moisture content of 80% and a lipid content of 1.4%, and was stored at −20 °C. For PAH analyses, spiked cod tissue was used to compare methods and calculate method detection limits (MDLs) for 17 PAHs, and SRM 2978 (freeze-dried mussel homogenate with moisture content 7.1%, lipid content 1.8%; NIST, 2000) was used to compare PAH methods for 3 PAHs with certified values greater than MDLs. For

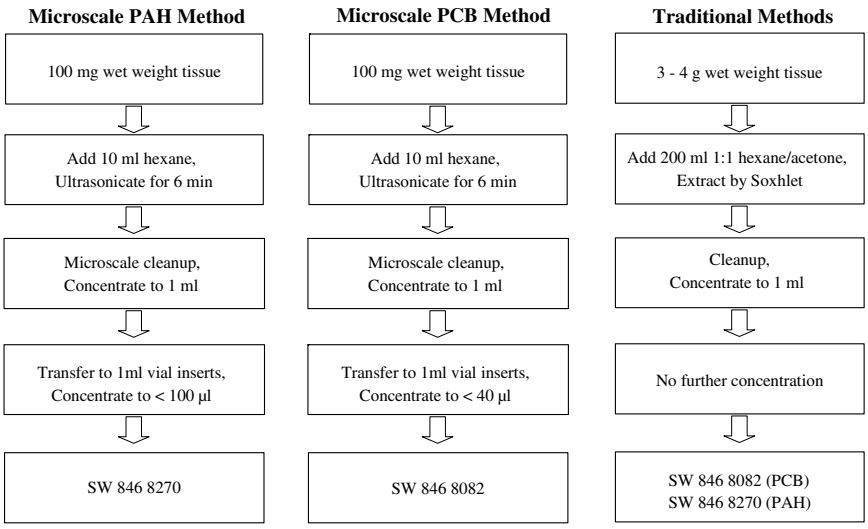

Fig. 1. Schematic comparison of key methodological differences between microscale PAH and PCB methods, and traditional methods used in this study. Refer to text for full details of methods.