ELSEVIER

Chemosphere 66 (2007) 326–331

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

Enantiomer fractions of polychlorinated biphenyls in three selected Standard Reference Materials

Joshua A. Morrissey, Derek S. Bleackley, Nicholas A. Warner, Charles S. Wong *

Department of Chemistry, 11227 Saskatchewan Drive, University of Alberta, Edmonton, Alta., Canada T6G 2G2

Received 30 October 2005; received in revised form 26 April 2006; accepted 29 April 2006
Available online 14 June 2006

Abstract

The enantiomer composition of six chiral polychlorinated biphenyls (PCBs) were measured in three different certified Standard Reference Materials (SRMs) from the US National Institute of Standards and Technology (NIST): SRM 1946 (Lake Superior fish tissue), SRM 1939a (PCB Congeners in Hudson River Sediment), and SRM 2978 (organic contaminants in mussel tissue—Raritan Bay, New Jersey) to aid in quality assurance/quality control methodologies in the study of chiral pollutants in sediments and biota. Enantiomer fractions (EFs) of PCBs 91, 95, 136, 149, 174, and 183 were measured using a suite of chiral columns by gas chromatography/mass spectrometry.

Concentrations of target analytes were in agreement with certified values. Target analyte EFs in reference materials were measured precisely (<2% relative standard deviation), indicating the utility of SRM in quality assurance/control methodologies for analyses of chiral compounds in environmental samples. Measured EFs were also in agreement with previously published analyses of similar samples, indicating that similar enantioselective processes were taking place in these environmental matrices.

Keywords: Chiral polychlorinated biphenyls; Standard Reference Materials; Enantiomeric fractions

1. Introduction

The analysis of chiral compounds in the environment is an area of emerging significance, because many biological processes can be enantioselective (Hühnerfuss et al., 1993). Many persistent chiral organochlorine compounds (OCs) are released into the environment as racemic mixtures. Enantiomers of chiral compounds exhibit identical chemical and physical properties, with the exception of the direction of rotation of a plane of polarized light, and their reaction rates with other chiral or prochiral substrates. Enzymes may interact in a preferential manner with one enantiomer over the other (Williams, 1996). Because of the kinetic differences between enantiomers, changes in the enantiomeric fractions (EFs) of chiral OCs may be indicative of the occurrence of biological processes such as microbial reductive dechlorination (Pakdeesusuk et al., 2003) and biotransformation within living organisms (Hoekstra et al., 2002; Wong et al., 2002b; Borga and Bidleman, 2005; Warner et al., 2005).

Enantiomers of chiral OCs exhibit varying biological responses, such as activity (Miyazaki et al., 1978), metabolic rates (Vetter et al., 2001; Fisk et al., 2002), and toxicities (Hoekstra et al., 2001). Because of these differences, analyses of chiral OCs in various environmental matrices have become relevant issues in analytical chemistry and risk assessment. As a part of these studies, reference materials are an integral component of quality assurance/quality control protocol (Robson and Harrad, 2004; Kurt-Karakus et al., 2005). Current methods for chiral OC analysis employ a number of extraction and cleanup procedures and analytical techniques, such as gas chromatography (GC) (Jaus and Oehme, 1999; Wong and Garrison, 2000; Schurig, 2002), comprehensive two-dimensional gas chromatography (GC × GC) (Harju et al., 2003; Bordajandi

* Corresponding author. Tel.: +1 780 492 5778; fax: +1 780 492 8231.
E-mail address: charles.wong@ualberta.ca (C.S. Wong).

0045-6535/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2006.04.085

et al., 2005), and liquid chromatography (LC) (Haglund, 1996; Champion et al., 2004). While the pollutant composition of many reference materials have been extensively quantified, there is little data on the enantiomer composition of such materials, with a few exceptions (Wong et al., 2002a). Here we report the enantiomer composition of additional Standard Reference Materials (SRMs) often used for OC analytical method development and quality assurance/quality control. Although our findings are not certified values, we hope that they will nonetheless be useful for these purposes.

2. Experimental

The chiral PCB congeners 91, 95, 136, 149, 174, and 183 were selected for analysis based on their presence in the environment, as well as their ability to be separated by chiral GC (Wong and Garrison, 2000). Standard Reference Materials analyzed were obtained from the US National Institute of Standards and Technology (NIST): SRM 1939a (PCBs in Hudson River Sediment, $n = 4$) (Rebbert et al., 1992; National Institute of Standards and Technology, 1998), SRM 1946 (Lake Superior fish tissue, $n = 6$) (Poster et al., 2003; National Institute of Standards and Technology, 2004), and SRM 2978 (Mussel Tissue, Raritan Bay, NJ, $n = 6$) (National Institute of Standards and Technology, 2000; Poster et al., 2004). These reference materials were selected based on their relevance for environmental studies to be representative of varying matrices as a part of quality analysis and quality control practices. Reference materials CRM EC-5 (Lake Ontario Sediment from Environment Canada) and NIST SRM 1945 (Organics in Whale Blubber) were run concurrently with selected SRMs to serve as additional quality assurance/quality control (Wong et al., 2002a). It must be noted that SRM 1945 is a restricted material by the Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES), and requires import permits for entry into Canada.

2.1. Sample extraction procedure

All samples were homogenized with anhydrous sodium sulfate (Tracepur ACS-grade, EMD Chemicals, Gibbstown, NJ). Sodium sulfate was ashed at 550 °C for 3 h to remove trace organic contaminants prior to use. Surrogate standards of PCB 30 and 204 (AccuStandard Inc. New Haven, CT) were added to all samples prior to extraction. Approximately 2 g of each SRM sample was extracted with pesticide-grade dichloromethane (DCM) in a Soxhlet apparatus for 16 h, filtered through a bed of anhydrous sodium sulfate, and concentrated using a rotary evaporator. Lipid percentage was determined gravimetrically using a small aliquot of the concentrated extract (~10%). Gel permeation chromatography using 200–400 mesh SX-3 Biobeads (Bio-Rad Laboratories, Hercules CA), with 1:1 DCM: hexane as a mobile phase was used to remove lipids and large biological materials from the extracts of biological samples (SRMs 1945, 1946 and 2978). This step was not necessary for sediments (EC-5 and SRM 1939a). Extracts were solvent exchanged into hexane and concentrated to 1 ml. Column chromatography using 3% by weight deactivated silica gel (70–270 mesh, Aldrich Chemicals, Fair Lawn, NJ) and 8.5% by weight deactivated aluminum oxide (150 mesh, Aldrich Chemicals, Fair Lawn, NJ) was used to separate the extract into two fractions. Fraction 1 (F1) containing PCBs was collected using 30 ml of hexane, and fraction 2 (F2) containing the remainder of chlorinated pesticides was collected using 35 ml of 5% acetone in hexane (Foreman et al., 1995). Sulfur was removed from sediment samples using activated copper (Sigma-Aldrich Inc. St. Louis, MO). Extract fractions were concentrated to approximately 200 µl using a nitrogen evaporator and fortified with PCB 166 (AccuStandard Inc., New Haven, CT) as an internal standard.

2.2. Chiral analysis

Chiral PCB enantiomers were quantified using a HP 5890/5971 gas chromatograph/mass selective detector using electron impact ionization (70 eV) in selective ion monitoring mode. The three most abundant ions of the molecular ion cluster (e.g., m/z 358, 360, and 362 for hexachlorobiphenyls) were used for detection. A collection of chiral columns was used to obtain data for target chiral PCB enantiomers. PCBs 91, 95 and 136 were quantified using a Cyclosil-B column (30 m × 0.25 mm internal diameter (i.d.) × 0.25 µm film thickness (df), J&W Scientific, Folsom, CA), while PCBs 91, 95, 136, 149, and 174 were quantified on a Chirasil-Dex column (30 m × 0.25 mm i.d. × 0.25 µm df, Varian, Walnut Creek, CA), and PCB 183 on a BGB-172 column (30 m × 0.25 mm i.d. × 0.18 µm df, BGB Analytik, Adiswil, Switzerland) as previously described (Wong et al., 2002a).

Enantiomeric fractions (EFs) (Harner et al., 2000) were calculated as follows.

$$\mathrm{EF} = \frac{(+)}{(+)+(-)} \qquad \mathrm{EF} = \frac{\mathrm{E1}}{\mathrm{E1}+\mathrm{E2}} \tag{1}$$

Peak areas of (+) and (−) enantiomers were used where enantiomer elution order is known (PCBs 136, 149, 174) (Haglund and Wiberg, 1996; Wong et al., 2002a). Where the enantiomer elution order is unknown, peak areas of first-eluting enantiomer (E1) and second-eluting enantiomer (E2) were used. Racemic enantiomer distributions have an EF of 0.5, whereas EFs of 0 or 1 indicate pure single enantiomers of (−) or (+), respectively. Elution orders of enantiomers on the columns used are described elsewhere (Haglund and Wiberg, 1996; Wong and Garrison, 2000). A 95% confidence interval of ±0.032 from measured racemic (EF = 0.500) standards was used for statistical comparisons of sample EFs compared to racemic standards (Wong et al., 2004). Extraction blanks were run with every extraction set and processed identically to SRMs analyzed; no target analytes were detected in blanks. Analyte concentrations were corrected for surrogate standard recovery.