



Determination of 1-chloro-4-[2,2,2-trichloro-1-(4-chlorophenyl)ethyl]benzene and related compounds in marine pore water by automated thermal desorption-gas chromatography/mass spectrometry using disposable optical fiber



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ABSTRACT

A method is described for determination of ten DDT-related compounds in marine pore water based on equilibrium solid-phase microextraction (SPME) using commercial polydimethylsiloxane-coated optical fiber with analysis by automated thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS). Thermally cleaned fiber was directly exposed to sediments and allowed to reach equilibrium under static conditions at the *in situ* field temperature. Following removal, fibers were rinsed, dried and cut into appropriate lengths for storage in leak-tight containers at -20°C . Analysis by TD-GC/MS under full scan (FS) and selected ion monitoring (SIM) modes was then performed. Pore-water method detection limits in FS and SIM modes were estimated at $0.05\text{--}2.4\text{ ng/L}$ and $0.7\text{--}16\text{ pg/L}$, respectively. Precision of the method, including contributions from fiber handling, was less than 10%. Analysis of independently prepared solutions containing eight DDT compounds yielded concentrations that were within $6.9 \pm 5.5\%$ and $0.1 \pm 14\%$ of the actual concentrations in FS and SIM modes, respectively. The use of optical fiber with automated analysis allows for studies at high temporal and/or spatial resolution as well as for monitoring programs over large spatial and/or long temporal scales with adequate sample replication. This greatly enhances the flexibility of the technique and improves the ability to meet quality control objectives at significantly lower cost.

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1. Introduction

Contaminated sediments are often a chronic source of organic pollutants to aquatic ecosystems [1]. In order to predict the bioavailability of hydrophobic organic contaminants (HOCs), such as DDT, to indigenous biota, early efforts relied upon measurement of bulk sediment concentrations and equilibrium partitioning models [2]. These methods proved unreliable due to variations in sediment composition, in particular, the relative abundance and sorptive properties of organic matter fractions such as black carbon and fresh plant material (cf., references in [3–5]). Whereas measuring the freely dissolved concentration (C_{free}) of HOCs in pore water

appears to be the best means of assessing bioavailability, conventional methods of determining C_{free} are costly, time-consuming, and often fraught with methodological difficulties [5].

Recently, passive sampling methods (PSMs) have been investigated as a means of determining C_{free} [3,6]. PSMs rely upon exposure of a polymeric sampler to the sediment matrix or pore water isolated from sediments [7] such that the HOCs of interest, which are typically at very low concentrations in pore water (ng/L to pg/L), can partition into it. PSMs can be operated in either equilibrium or kinetic modes depending on study requirements and/or constraints of the system under investigation, and exposure can be static (*in situ* or laboratory) or dynamic (*ex situ*). In any case, HOCs sorbed in the polymer are thermally desorbed or extracted (with solvents) from the sampler to facilitate instrumental analysis. Computation of C_{free} is accomplished by dividing the measured concentration in the sampler (C_p) by the compound-specific polymer-water partition coefficient (K_{pw} ; [8]).

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Among the various samplers under development are polydimethylsiloxane (PDMS) coated fused silica fibers, based on the technique of solid-phase microextraction (SPME) originally developed by Arthur and Pawliszyn [9]. Application of equilibrium SPME to HOCs under static exposure conditions is challenging because equilibration times can be quite long, on the order of weeks to months [10–12]. Moreover, it is necessary to demonstrate that the system has not been disturbed by the presence of the sampler, that is, the sampler cannot significantly deplete the contaminant content in the sediment (*aka* the ‘negligible depletion criterion’ [13]).

Mayer et al. [14,15] and Kraaij et al. [16] were the first to use commercial PDMS-coated optical fiber for measuring the C_{free} of HOCs in sediments. Because of its low cost (<\$1.50/m), optical fiber can be used as a disposable sampler. This offers distinct advantages over commercial SPME products including the possibility of greater replication, application to high-resolution spatial or temporal studies, implementation in large scale and/or long-term monitoring programs, and more overall flexibility during laboratory experimentation [14]. Larger numbers of samplers, however, place increased demands on the analytical system and this serves as the driving force for simpler handling procedures and greater automation.

Early studies in which optical fiber was exposed to contaminated sediments involved direct insertion of fibers into the inlet of a gas chromatograph [14,16] or, in one case, use of an automated thermal desorption system [17]. Subsequently, solvent extraction followed by instrumental analysis (e.g., [18–26]) appears to have predominated, and further development of automated TD-GC/MS lagged. This is somewhat surprising because thermal desorption has several advantages over solvent extraction, not least of which is the potentially increased sensitivity by release of all of the target analyte mass for analysis [3] and the reduction of time, effort and method error due to reduced sampler handling.

As part of a multi-disciplinary investigation of the factors controlling the fate of DDT in sediments of the Palos Verdes Shelf, CA [27], we began development of an automated TD-GC/MS method for determining HOCs, specifically DDT compounds, in marine sediment pore water. Because the study was expected to involve a large number of samples, our objective was to develop a robust, cost-effective, and flexible method that was both accurate and precise. This paper describes results of method development studies and presents data on method performance as well as an illustration of its application.

2. Materials and methods

2.1. Chemicals

High purity solvents (dichloromethane – DCM, methanol – MeOH, hexane) were used without further purification. Ten DDT-related compounds (hereafter referred to as DDX; [28]) were targeted for analysis: 4,4'-DDNS, 4,4'-DDNU, 4,4'-DDMU, 2,4'-DDE, 4,4'-DDMS, 4,4'-DDE, 2,4'-DDD, 4,4'-DDD, 2,4'-DDT, and 4,4'-DDT (for IUPAC names, see Table S-1, Supplementary Data). For quantitation, one or more of three internal standards (ISs) were used: TCMX (1,2,3,5-tetrachloro-4,6-dimethylbenzene), PCB 11, and/or PCB 207. Seven compounds (RSs) were included in the multipoint calibration standard solutions for use in method development studies: PCB 30, PCB 103, PCB 121, 4,4'-DDE-D8, 4,4'-DDD-D8, 4,4'-DDT-D8, and PCB 198. With four exceptions (i.e., PCB 11, 4,4'-DDNU, 4,4'-DDMS, and 2,4'-DDD), all standards had certified purities greater than 99% and were used as neat material without further purification. Prior to preparing IS, RS, multipoint (MP) calibration, spike (SS), and single-point calibration standard (CS) solutions, each compound was dissolved in hexane, and its purity

was confirmed by liquid injection-gas chromatography/full scan mass spectrometry (LI-GC/MS_{FS}). Sources and certified purities of the standards can be found in the Table S-1 (Supplementary Data).

A flow chart of the standard solution preparation scheme is provided in Fig. S-1 (Supplementary Data). Solutions were made at concentrations suitable for thermal desorption-gas chromatography/mass spectrometry in both full scan (TD-GC/MS_{FS}) and selected ion monitoring (TD-GC/MS_{SIM}) modes. MP, IS, SS and RS standard solutions were prepared by weighing neat materials on a microbalance with dissolution in hexane followed by serial dilution. Eight-level MP solutions with targeted DDX analytes were used for instrument calibration. Single-point continuing calibration verification (CCV) standard solutions (*aka* CS), which contained all of the targeted DDX analytes and RS compounds at concentrations mid-level within the MP solution concentration ranges and IS compounds at the same concentrations as the MP solutions, were used to monitor instrument calibration during sample analyses. SS solutions, containing the targeted DDX and RS compounds but lacking IS compounds, were used to establish method detection limits (MDLs) and to perform simulated ‘matrix spike’ analyses. Immediately following preparation, all MP solutions were analyzed by LI-GC/MS to verify purity and relative response, after which the solutions were sealed in glass ampoules. When not in use, neat standards and standard solutions were stored in a freezer at –20 °C.

Finally, two sets of standard solutions were prepared by the U.S. Environmental Protection Agency (USEPA) Quality Assurance Technical Support Program in Las Vegas, NV for purposes of initial calibration verification (ICV). These solutions contained eight of the ten targeted DDX (*viz.*, 4,4'-DDNU, -DDMU, -DDE, -DDD, and -DDT + 2,4'-DDE, -DDD, and -DDT) at concentrations within the MP solution ranges: 5, 10 and 50 ng/μL/component for TD-GC/MS_{FS}, and 20, 40 and 200 pg/μL/component for TD-GC/MS_{SIM}.

2.2. SPME fibers and field sediments

2.2.1. Fibers

For a given analyte and environmental conditions, the rate at which a SPME fiber approaches equilibrium is inversely related to fiber coating thickness (or surface area/volume ratio [SA_f/V_f]; [3,4,10]). Because the targeted DDX are hydrophobic, equilibration times can be long [10,11]. It was, therefore, deemed essential that a fiber with a relatively thin PDMS coating (≤ 5 – $10 \mu\text{m}$) be used for method development in order that equilibrium be established within a reasonable period of time (weeks to months) while providing adequate method sensitivity. [Note: It was reasoned that because rates of degradation for the major DDX compounds of concern (i.e., 4,4'-DDMU, -DDNU, -DDE) were ~ 0.05 – 0.16 year^{-1} [27], analyte transformation within the exposure period would be insignificant [3].] Moreover, we wanted to develop a method that was cost-effective, relatively easy to implement, and amenable to automation and sample replication. This led us to consider use of commercial PDMS-coated optical fiber.

While not available in a large selection of coating thicknesses, optical fiber is made of relatively uniform, high-quality materials and can be purchased in large quantities at very low cost. Prior investigations in which optical fiber from FiberguideSM Industries, Inc. (Stirling, NJ; [14,16]) and Polymicro TechnologiesTM (Phoenix, AZ; [15]) had been used for exposure to sediments, motivated us to acquire samples of two products from FiberguideSM: APC210/230R (210 ± 4.2 -μm fused silica core, 10 ± 0.2 -μm PDMS coating) and SPC210/2130R (210 ± 4.2 -μm fused silica core, 10 ± 0.2 -μm PDMS coating). Dr. M.T.O. Jonker (Utrecht University, The Netherlands) generously provided a third sample from Polymicro TechnologiesTM (100-μm fused silica core, 34-μm PDMS coating). As discussed below, these fibers were evaluated prior to final selection.

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