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Pressurized liquid extraction using water/isopropanol coupled with solid-phase extraction cleanup for semivolatile organic compounds, polycyclic aromatic hydrocarbons (PAH), and alkylated PAH homolog groups in sediment

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Abstract

Polycyclic aromatic hydrocarbons (PAH) are recognized as environmentally relevant for their potential adverse effects on human and ecosystem health. This paper describes a method to determine the distribution of PAH and alkylated homolog groups in sediment samples. Pressurized liquid extraction (PLE), coupled with solid-phase extraction (SPE) cleanup, was developed to decrease sample preparation time, to reduce solvent consumption, and to minimize background interferences for full-scan GC–MS analysis. Recoveries from spiked Ottawa sand, environmental stream sediment, and commercially available topsoil, fortified at 1.5–15 μg per compound, averaged 94.6 ± 7.8%, 90.7 ± 5.8% and 92.8 ± 12.8%, respectively. Initial method detection limits for single-component compounds ranged from 20 to 302 μg/kg, based on 25 g samples. Results from 28 environmental sediment samples, excluding homologs, show 35 of 41 compounds (85.4%) were detected in at least one sample with concentrations ranging from 20 to 100,000 μg/kg. The most frequently detected compound, 2,6-dimethylnaphthalene, was detected in 23 of the 28 (82%) environmental samples with a concentration ranging from 15 to 907 μg/kg. The results from the 28 environmental sediment samples for the homolog series showed that 27 of 28 (96%) samples had at least one homolog series present at concentrations ranging from 20 to 89,000 μg/kg. The most frequently detected homolog series, C_2-alkylated naphthalene, was detected in 26 of the 28 (93%) environmental samples with a concentration ranging from 25 to 3900 μg/kg. Results for a standard reference material using dichloromethane Soxhlet-based extraction also are compared.

Keywords: Polycyclic aromatic hydrocarbon; Pressurized liquid extraction; Solid-phase extraction; Sediment

1. Introduction

Methods for the analysis of polycyclic aromatic hydrocarbons (PAHs) and alkylated PAHs are important because these compounds commonly are associated with fossil fuels or combustion of fossil fuels [1,2]. They are found in air, water, and sediment and many are considered to be toxic and carcinogenic [2–4], thus indicating that long-term exposure poses a risk to aquatic and terrestrial organisms.

The natural processes and combustion of fossil fuels that form alkylated PAHs normally favor specific homolog groups according to the predominant conditions. Thus, the analysis of alkylated PAH homolog groups often can help deduce possible mechanisms or conditions required for their formation [5–7]. Alkylated PAHs can be grouped by the number of carbon atoms present, so that a particular homolog group includes all the isomers with the same number of carbon atoms in the constituents attached to the parent (or unsubstituted) PAH. The homolog constituent(s) from C_1 through

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C_5 having the same parent PAH are of particular interest in the determination of fuel source, weathering, and combustion [5–7].

Isomers within a homolog group have common physical properties, such as the same molecular weight and mass spectrometer fragmentation patterns. The fragment ions produced for each isomer within the same homolog group typically are identical, although the abundance ratios can be different. This pattern results in a complex chromatogram of partially resolved isomers [5–7]. The total response of the isomers for a particular alkyl substituted PAH group can be summed and quantified based on the calibration of a closely related PAH compound. Wang et al. [8] found that a quantitation error of 30–150% was typical for alkylated naphthalene homolog groups determined from the parent naphthalene calibration curve. For this reason, and because authentic standards are not available for every alkylated PAH isomer, the total concentration of the homolog groups is reported as generally semiquantitative.

This paper describes a method developed by the U.S. Geological Survey, coupling pressurized liquid extraction (PLE) with soild-phase extraction (SPE) for the extraction and extract cleanup of PAH and alkylated homolog groups from sediment samples. PLE has demonstrated advantages for automation, reduced extraction time, and lower solvent use than for conventional Soxhlet extraction. Recently, PLE with subcritical heated water (PLEHW) has been used for extracting polar to moderately polar organic compounds from sediment samples. At temperatures greater than 250 °C, extraction of nonpolar high molecular weight compounds, such as PAHs [9,10], PCBs [11], and brominated flame retardants [12], has been reported. The solubility of solutes in subcritical water increases dramatically [13] with increasing temperature and results from the decreasing dielectric constant (ϵ) of water.

For example, the solubilities of triazine herbicides increase about three-fold with every 25 °C increase in temperature [14]. The addition of a cosolvent has a similar effect on solubility as increasing the temperature and made it possible quantitatively to extract atrazine from beef kidney at a moderately low temperature of 100 °C with an ethanol concentration of 30% [14]. The pressure required for PLEHW must be high enough to maintain water in the liquid state, but otherwise it has little effect on ϵ or solubility [15]. The PLEHW of sediments provides more selectivity for compounds than conventional Soxhlet extraction using organic solvents, as evidenced by a reduction in the extraction of the bulk organic nonpolar matrix [10]. Although it is possible to gain some degree of selectivity using PLEHW by varying the cosolvent concentration, the use of organic cosolvents produces dirtier extracts, which often require cleanup prior to analysis. In a production laboratory, where stable reproducible instrument response with minimum maintenance is desirable, extract quality (low matrix background, greater than 60% analyte recovery) is important. PLEHW on-site extraction of petroleum-contaminated sediment samples with simultaneous absorption onto SPE disks has been reported to produce clean extracts [9]. However, in a laboratory setting, more options are possible for washing, adjusting the pH, and eluting SPE cartridges if SPE is used after PLE.

The ASE $^{\text{TM}}$ 200 is a commercially available PLE instrument produced by Dionex (Sunnyvale, CA, USA), and the extraction process, which also has been termed “accelerated solvent extraction” (ASE), generally uses conventional organic solvents at a temperature of about 100 °C. The upper operating temperature limit of 200 °C for the ASE$^{\text{TM}}$ 200 is too low to effectively extract nonpolar high molecular weight organic compounds, such as PAHs (about molecular weight 202 or higher) using subcritical water, without the addition of a cosolvent [16]. Thus, a cosolvent is necessary to increase the solvating power of PLEHW to effectively extract hydrophobic high molecular weight compounds.

Environmental sediment samples generally require extensive extract cleanup procedures to provide the low matrix background extract that can be analyzed routinely in a production laboratory and yet retain the compounds of interest [17,18]. Because most existing environmental sediment methods generally use labor-intensive Soxhlet extraction and require extensive extract cleanup steps, it has become imperative to implement more efficient, environmental-friendly methods. Analytical methods that use SPE have been implemented for the determination of pesticides and wastewater compounds in water [19–25] because they are rapid, efficient, use much less solvent than liquid–liquid extraction, and, consequently, are more affordable and produce less toxic waste. Coupling SPE and PLE allows for complex matrices to be extracted, matrix interferences to be minimized, and full-scan gas chromatography–mass spectrometry (GC–MS) analysis to be performed.

The scope of the study described in this paper includes determination of method performance in Ottawa reagent-sand, in stream-sediment samples collected from Cherry Creek near Garland Park, Denver, CO, USA, and in topsoil from a commercially available mixture. Table 1 lists the compounds of interest. Method performance was determined at two concentrations for each compound (1.5 and 15 μg spikes for most compounds) in each sediment type. Initial method detection limits (MDL) were determined according to an accepted statistical procedure outlined by the U.S. Environmental Protection Agency (USEPA) [26]. The method also was tested on a National Institute of Standards and Technology (NIST) standard reference material and a set of 28 environmental soil and sediment samples collected throughout the United States.

In the method described herein, 25 groups of alkylated PAH homologs can be identified qualitatively and semiquantitated using the response factor and calibration curve from a closely related reference compound within its homolog series or the appropriate parent PAH. Reference mass spectral agreement and isotopic patterns are used qualitatively to identify the alkylated PAH homolog groups, which then