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Static subcritical water extraction with simultaneous solid-phase extraction for determining polycyclic aromatic hydrocarbons on environmental solids

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Abstract

A rapid and very simple method for extracting polycyclic aromatic hydrocarbons (PAHs) from soils, sediments, and air particulate matter has been developed by coupling static subcritical water extraction with styrene-divinylbenzene (SDB-XC) extraction discs. Soil, water, and the SDB-XC disc are placed in a sealed extraction cell, heated to 250°C for 15 to 60 min, cooled, and the PAHs recovered from the disc with acetone/methylene chloride. If the cells are mixed during heating, all PAHs with molecular weights from 128 to 276 are quantitatively (>90%) extracted and collected on the sorbent disc and are then recovered by shaking with acetone/methylene chloride. After water extraction, the sorbent discs can be stored in autosampler vials without loss of the PAHs, thus providing a convenient method of shipping PAH extracts from field sites to the analytical laboratory. The method gives good quantitative agreement with standard Soxhlet extraction, and with certified reference materials for PAH concentrations on soil, sediment (SRM 1944), and air particulate matter (SRM 1649a). © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Subcritical water extraction; Solid phase extraction; Environmental analysis; Polynuclear aromatic hydrocarbons

1. Introduction

Several new extraction methods including pressurized liquid extraction (PLE), supercritical fluid extraction (SFE), and microwave assisted extraction have been developed in recent years in an effort to reduce extraction times and organic solvent requirements. Most recently, subcritical water (hot water under enough pressure to maintain the liquid state) has been used to extract a variety of polar and non-polar organics from environmental samples [1–

11] based on the fact that the solubilities of organic compounds increase dramatically with temperature in liquid water [12–14]. For example, the polycyclic aromatic hydrocarbons (PAHs) anthracene, chrysene, and perylene each have solubilities ca. 20 000-fold higher in water at 200°C, than at 25°C [13]. Similarly, solubilities of the pesticide endosulfan II increase from 0.27 µg/g at 25°C to 4500 µg/g at 200°C, and the solubility of chlorothalonil increases from 0.18 µg/g at 25°C to 23 000 µg/g at 200°C [12].

The desire to further simplify extraction methods (while reducing time and waste) has also led to coupling subcritical water extraction with solid-phase microextraction (SPME) for the determination of

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PAHs, PCBs, and natural pyrethrins [15–18], or with solid-phase extraction (SPE) for the determination of acid herbicides [19,20]. These approaches seem ideal for use in the field, since they are generally very simple to perform and require little or no organic solvent, and the apparatus required can be very inexpensive and field-rugged. In fact, earlier studies demonstrated that subcritical water extracts of PCBs from soils could be shipped from a field site to a laboratory for analysis in 2 ml autosampler vials, thus eliminating the need to transport hazardous soil samples from field sites for laboratory extractions [17].

In the present study, we have developed a method for coupling static subcritical water extraction with collection on styrene-divinylbenzene (SDB) SPE discs for quantitative extractions of PAHs from soils, sediments, and air particulate matter. The goal was to develop a very simple, inexpensive, and field-rugged approach for quantitatively extracting and collecting organic pollutants in a form that simplifies their transport to a standard laboratory for analysis.

2. Experimental

2.1. Samples

PAH-contaminated soil was collected from a former manufactured gas plant site which had been abandoned for ca. 50 years. After collection, the soil was air-dried, sieved to <6 mm, and homogenized by hand for ca. 30 min. Certified standard reference samples were obtained from the U.S. National Institute of Science and Technology (NIST) and included marine sediment from the New York/New Jersey (USA) area (SRM 1944), and urban air particulate matter (NIST “urban dust,” SRM 1649a). Both samples were used as received.

2.2. Water extractions and SPE discs

All extractions were performed using a 64 mm long×7 mm I.D. (12 mm O.D.) stainless steel pipe with national pipe thread (n.p.t.) end caps (Minnesota Valve and Fitting, Eden Prairie, MN, USA) which was rated by the supplier for a maximum pressure of 496 bar. One end of the cell was closed using an end

cap and a single layer of Teflon tape. The sample (1 g of the soil, 0.5 g of the sediment, and 0.1 g of the air particulate matter) was then weighed into the cell and spiked with the internal standard solution (if used). One sorbent disc was then placed in the cell, and 3.5 ml of HPLC-grade water (Fisher Chemical Co.), which had previously been purged with clean nitrogen for ca. 2 h to remove dissolved oxygen, was added. The cell cap was placed on, again using a single layer of Teflon tape on the pipe threads. This procedure results in a ca. 1 ml headspace of air above the water in the cell. (*Safety note: It is imperative that there is a headspace present in the cell so that the pressure in the cell upon heating is controlled by the steam/water equilibrium. If the cap of the cell is also filled with water to eliminate the headspace, the pressure in the heated cell could exceed several thousand bar. However, with the headspace the pressure at 250°C is only 40 bar.*) The assembled cell was then either placed in the same vertical direction in which the cell was filled in a Hewlett-Packard 5890 gas chromatographic oven, or mounted on a home-made rack in the GC oven which rotated at ca. 60 revolutions per min, and heated to the desired temperature. After the heating was completed, the cell was immediately removed from the oven and cooled to room temperature. Alternatively, the cell was left on the rotating rack and continued to rotate during cooling. When the cooling was complete (1 h), the cell was opened and the sorbent disc was removed with tweezers, and rinsed with pure water to remove sample particles.

Sorbent “discs” were actually cut into rectangles from the commercially available “Empore” styrene divinylbenzene (SDB-XC) discs (“Empore” SDB-XC, 3M Corporation, St. Paul, MN, USA). The discs were briefly soaked in methanol (pesticide-grade, Fisher Chemical Co.) for ca. 20 min for activation and then air dried for 5 min just prior to placing in the extraction cell. After the extraction was completed, the rinsed discs were placed in 3 ml of 1:2 acetone/methylene chloride in a 4 ml glass vial and mixed by rotation at ca. 60 revolutions per min to extract the PAHs collected on the disc.

During methods development and verification, the extractant water and soil residue were also saved, separated (by centrifugation), and extracted to determine the fractions of PAHs found in the disc

compared to PAHs left on the soil, or in the water. Water fractions were extracted three times by mixing for ca. 5 min each with ca. 1 ml aliquots of methylene chloride. The extracted soils were mixed with 1:1 sodium sulfate and extracted for 18 h in 1:2 acetone/methylene chloride (both pesticide-grade, Fisher Chemical Co.) assisted by sonication.

Soxhlet extractions of the fresh MGP soil (10 g each) were performed for 18 h with 150 ml of 1:2 acetone/methylene chloride.

2.3. Analysis

Quantitations of the PAHs from the manufactured gas plant soil were performed using a gas chromatograph (Hewlett–Packard 5890, Series II) with flame ionization detection (FID) and a 60 m DB-5 column (0.25 μm film thickness, 250 μm I.D., J&W Scientific, Rancho Cordova, CA, USA). Injections (1 μl) were performed in the splitless mode (injector temperature of 300°C) at an oven temperature of 80°C followed by a temperature program at 6°C/min to 320°C. Quantitations were based on calibration curves of authentic PAH standards (at least one PAH standard for each molecular weight of PAH in the extracts) versus *n*-undecane (C11) added to the standards and sample extracts as an internal standard. GC–MS analysis of representative extracts demonstrated that all detectable species were PAHs. Quantitations were also performed using perdeuterated PAHs as internal standards and GC–MS as described below.

PAH quantitations for the urban air particulate matter (SRM 1649a) and the marine sediment (SRM 1944) were performed using a Hewlett–Packard model 5972 GC–MS equipped with a 30 m HP-5MS column (0.25 μm film thickness, 250 μm I.D., Hewlett–Packard). Injections (1 μl) were performed in the splitless mode at an oven temperature of 70°C, followed by a temperature program of 12°C/min to 320°C. The MS transfer line was held at 300°C. Quantitations were based on calibration with standard PAHs (at least one for each molecular weight of PAH in the sample extracts) compared to either 1-chloroanthracene as an internal standard, or compared to perdeuterated internal standards for each molecular weight of PAH (discussed later in the text). Perdeuterated PAH internal standards included

naphthalene, acenaphthene, phenanthrene, pyrene, chrysene, benzo[*a*]pyrene, perylene, and benzo[*ghi*]perylene. Peak identifications were based on the retention times and full scan mass spectra of the standard and sample PAHs. Quantitations were based on selected ion monitoring (SIM) for the molecular ion of each PAH and *d*-PAH.

3. Results and Discussion

3.1. Development of the method

Initial experiments were performed to determine the stability of the Empore SDB-XC discs under subcritical water conditions since loss of sorptive ability and/or physical breakdown of the disc material would make the method unusable. To test the disc's stability, ca. 1×2 cm rectangles of the disc material were exposed to subcritical water at temperatures up to 300°C using the same experimental cells as described above for the sample extractions. After cooling, the disc was extracted with 1:2 acetone/methylene chloride, and the water was extracted with methylene chloride. These extracts were analyzed by GC–FID and GC–MS. Fortunately, the disc material appeared physically stable, and no large artifact peaks were detected by GC–FID or GC–MS.

Additional tests were performed to determine the recovery of PAHs (which had been extracted from the manufactured gas plant soil at 250°C and collected on the disc material as described below) as well as the disc's stability during the recovery step. Initially, the PAHs were extracted from the discs using sonication for 1 to 18 h. Either time gave good recoveries of the PAHs from the discs, but the disc extracts were cloudy, and multiple injections of the extracts quickly deteriorated the GC peak shapes and overall chromatographic performance. Apparently, when the disc material is sonicated, the SDB bead material is removed from the Teflon supporting web, and is subsequently injected into the GC. Accumulation of this bead material in the injection port (and perhaps, in the head of the column) provides a very active surface for retention of the PAHs during injection, and results in severely tailing peaks. Fortunately, sonication of the discs was not

necessary, and simply mixing the disc material for 1 h with 3 ml of 1:2 acetone/methylene chloride by rotation at ca. 60 revolutions per min yielded quantitative recovery of the PAHs from the disc, and was used for all subsequent experiments.

The subsequent methods development was performed using the manufactured gas plant soil. First, the effects of disc size and the presence or absence of mixing on the extraction efficiencies (defined for methods development purposes as the fraction of each PAH found on the disc after extraction compared to the fractions found in the soil residue plus the extractant water) was determined. Initial tests were performed using 1 g samples of the soil, 3.5 ml of water, and either a 0.5×2 cm (1 cm²) disc, or a 2×3 cm (6 cm²) disc. Samples were extracted either by simply placing the cells in the GC oven (no mixing), or by attaching the cells to a rotating rack which was connected by a rod through the GC oven door to an external motor rotating at ca. 60 revolutions per min. All extractions were conducted 250°C for 1 h, since earlier reports have shown that these

conditions give quantitative extraction of PAHs from soil and related samples [1,15].

The fractions of several PAHs collected on the SDB-XC discs by each method are shown in Table 1. If the extraction cell contents are not mixed during extraction, the recovery of the PAHs from the soil is only ca. 45%. However, with mixing the 1 cm² disc achieves ca. 85% recovery of the PAHs. Performing a second identical extraction on the soil residue with a fresh 1 cm² disc gives a total PAH recovery (first and second disc versus the soil residue plus water) of nearly 100%, demonstrating that the overall efficiency of the method is controlled by the partitioning of the PAHs between the soil and disc material while the cell is cooling. When the disc size is increased to 6 cm², ca. 95% of the PAHs are collected on the disc (Table 1).

Based on the results of the recovery studies performed above, the final conditions selected for verification of the method were 250°C extractions for 1 h, a 6 cm² disc, 3.5 ml of water, a maximum sample size of 1 g, and mechanical rotation at ca. 60

Table 1
Effect of mixing and disc size on PAH collection efficiencies from contaminated soil using coupled subcritical water/SPE disc extraction

| PAH | Mol. wt. | % Recovery ^a | | | |
|--|----------|-------------------------|--------------------|--------------------------------------|--------------------------------------|
| | | No mixing | Mixed ^b | | |
| | | | 1 cm ² | 1 cm ² (1st) ^c | 1 cm ² (2nd) ^c |
| Naphthalene | 128 | 47 | 86 | 95 | 96 |
| 2-Methyl naphthalene | 142 | 44 | 87 | 99 | 99 |
| 1-Methyl naphthalene | 142 | 43 | 88 | 99 | 99 |
| Acenaphthene | 154 | 41 | 86 | 100 | 93 |
| Phenanthrene | 178 | 45 | 87 | 100 | 94 |
| Anthracene | 178 | 46 | 90 | 100 | 93 |
| Fluoranthene | 202 | 49 | 84 | 97 | 99 |
| Pyrene | 202 | 49 | 83 | 96 | 91 |
| Benz[<i>a</i>]anthracene | 228 | 44 | 89 | 99 | 94 |
| Chrysene | 228 | 43 | 85 | 99 | 99 |
| Benzo[<i>b+j+k</i>]fluoranthene ^d | 252 | 41 | 88 | 99 | 93 |
| Benzo[<i>a</i>]pyrene | 252 | 44 | 86 | 99 | 93 |
| Perylene | 252 | 45 | 87 | 99 | 93 |
| Indeno[1,2,3- <i>cd</i>]pyrene | 276 | 41 | 89 | 100 | 92 |
| Benzo[<i>ghi</i>]perylene | 276 | 42 | 87 | 100 | 92 |

^a % Recovery based on the fraction of each PAH found on the disc versus on the soil residue plus in the extractant water. Recoveries are the mean of triplicate experiments. RSDs were typically <10%. All extractions were at 250°C for 1 h, as described in the text.

^b Extraction cells were rotated in the oven at ca. 60 revolutions per min.

^c Recovery using a 1 cm² disc on fresh soil (1st), followed by a second extraction of the same soil residue with a fresh disc (2nd). Recoveries for the second disc are totals found in the 1st and 2nd discs.

^d The *b*, *j*, and *k* isomers of benzofluoranthene were not resolved at the chromatographic conditions used, so are reported as the total of all three isomers.

revolutions per min during the 1 h heating and 1 h cooling steps. The addition of internal standards to the soil before extraction, and to the solvent used to recover the PAHs from the disc after extraction was investigated. Since the results from both approaches were essentially identical (within analytical error as reported in Table 2), internal standards were routinely added to the soil prior to the extraction.

3.2. Method verification for PAHs

3.2.1. Manufactured gas plant soil

Comparisons of 18 h Soxhlet extractions (triplicate 10 g samples) with the static subcritical water extraction/SPE disc method (triplicate 1 g samples) for the manufactured gas plant soil are shown in Table 2. The reproducibility of the method was somewhat poorer with GC-FID using *n*-undecane as the internal standard (RSDs typically 10–20%), than

with GC-MS (RSDs typically <10%) using the perdeuterated PAHs as internal standards. However, all results using the subcritical water/SPE disc method agreed with the Soxhlet extractions within the analytical error of the method regardless of whether the extracts were analyzed by GC-FID or by GC-MS (Table 2).

Discs from a second triplicate set of extractions were also stored in 2 ml autosampler vials for 48 h (to simulate shipping from the field to the analytical laboratory), both in the 1:2 acetone/methylene chloride solvent used to extract the PAHs from the disc (“wet” in Table 2), and in an empty vial (“dry” in Table 2). Good agreement for these replicate extracts with the fresh extract was obtained by both methods, demonstrating that storage on the SPE disc after subcritical water extraction is quantitatively conservative, at least for sufficient time to transfer the extracts from the field to the lab. The results of

Table 2

Comparison of Soxhlet extraction with coupled subcritical water/SPE disc extraction of PAHs from a manufactured gas plant soil

| PAH | Concentrations by GC-FID \pm SD ^a (mg/kg) | | | | Concentrations by GC-MS \pm SD ^b (mg/kg) | |
|--|--|--------------------|-------------------------|-------------------------|---|----------------|
| | Soxhlet | Water/SPE Disc | | | Soxhlet | Water/SPE Disc |
| | | Fresh ^c | Stored dry ^c | Stored wet ^c | | |
| Naphthalene | 48 \pm 2 | 50 \pm 11 | 50 \pm 10 | 61 \pm 7 | 41 \pm 2 | 53 \pm 1 |
| 2 Methyl naphthalene | 118 \pm 4 | 100 \pm 20 | 100 \pm 17 | 110 \pm 10 | – ^d | – |
| 1 Methyl naphthalene | 112 \pm 4 | 100 \pm 20 | 100 \pm 19 | 120 \pm 8 | – | – |
| Acenaphthene | 78 \pm 3 | 50 \pm 11 | 51 \pm 9 | 61 \pm 10 | 39 \pm 1 | 58 \pm 2 |
| Phenanthrene | 430 \pm 19 | 360 \pm 76 | 380 \pm 64 | 450 \pm 18 | 380 \pm 7 | 419 \pm 6 |
| Anthracene | 110 \pm 7 | 70 \pm 16 | 80 \pm 16 | 90 \pm 17 | 82 \pm 4 | 71 \pm 6 |
| Fluoranthene | 130 \pm 6 | 120 \pm 25 | 120 \pm 22 | 140 \pm 19 | 150 \pm 5 | 158 \pm 3 |
| Pyrene | 196 \pm 8 | 180 \pm 42 | 190 \pm 34 | 220 \pm 26 | 217 \pm 1 | 238 \pm 5 |
| Benz[<i>a</i>]anthracene | 74 \pm 2 | 72 \pm 14 | 73 \pm 13 | 78 \pm 22 | 86 \pm 3 | 84 \pm 8 |
| Chrysene | 77 \pm 3 | 70 \pm 14 | 70 \pm 12 | 80 \pm 16 | 83 \pm 2 | 86 \pm 7 |
| Benzo[<i>b+j+k</i>]fluoranthene ^e | 88 \pm 12 | 70 \pm 12 | 67 \pm 11 | 70 \pm 17 | 74 \pm 4 | 91 \pm 13 |
| Benzo[<i>e</i>]pyrene | 39 \pm 5 | 36 \pm 6 | 37 \pm 5 | 41 \pm 7 | 34 \pm 2 | 43 \pm 6 |
| Benzo[<i>a</i>]pyrene | 50 \pm 6 | 40 \pm 14 | 49 \pm 8 | 50 \pm 13 | 50 \pm 3 | 58 \pm 9 |
| Perylene | 11 \pm 3 | 12 \pm 1 | 13 \pm 9 | 13 \pm 2 | 7.4 \pm 0.3 | 8.5 \pm 1.4 |
| Indeno[1,2,3- <i>cd</i>]pyrene | 19 \pm 2 | 31 \pm 4 | 29 \pm 6 | 29 \pm 6 | 23 \pm 1 | 22 \pm 5 |
| Benzo[<i>ghi</i> -]perylene | 27 \pm 3 | 28 \pm 4 | 33 \pm 6 | 33 \pm 5 | 27 \pm 1 | 25 \pm 5 |

^a Based on triplicate extractions with *n*-undecane as the internal standard.

^b Based on triplicate extractions with perdeuterated PAHs as internal standards.

^c “Fresh” discs were extracted and analyzed immediately after subcritical water extraction. “Dry” discs were stored for 48 h in empty 2 ml autosampler vials prior to adding 2 ml of 1:2 acetone/methylene chloride to extract the PAHs. “Wet” discs were stored in 2 ml autosampler vials with 2 ml of 1:2 acetone/methylene chloride for 48 h prior to analysis.

^d Not determined.

^e The *b*, *j*, and *k* isomers of benzofluoranthene were not resolved at the chromatographic conditions used, so are reported as the total of all three isomers.

storing the “dry” disc are of special interest, since the quantitative recoveries show that extractions in the field can be conducted without the need to transport any solvents (other than the extractant water and a few mls of methanol to wet the discs prior to extraction).

3.2.2. Marine sediment (SRM 1944)

Comparisons of the PAH concentrations found by subcritical water extraction/SPE disc extraction of the PAHs from the marine sediment are shown in Table 3. Quantitative agreement with the certified values was reasonably good, regardless of whether 1-chloroanthracene or the perdeuterated PAHs were used as internal standards. Similar to the results for the manufactured gas plant soil (Table 2), the reproducibility of the method was reasonably good, with RSDs typically less than 10%. Note also that, since the deuterated PAHs added as internal standards also act as calibration standards for the PAH quantitations, their use helps to reduce the total analysis time by eliminating the need for separate calibration runs. Since several extraction cells can be placed in the oven at one time, sample throughput is

relatively high, especially with the use of the deuterated PAHs.

3.2.3. Urban air particulate matter (SRM 1649a)

Table 4 shows a comparison of the subcritical water/SPE disc results with the certified values (based on 48 h Soxhlet extractions) for urban air particulate matter. As for the marine sediment, quantitative agreement with the certified values is generally good. It should also be noted that the subcritical water/SPE extracts could be analyzed without any post-extraction clean-up to remove the bulk diesel exhaust alkanes associated with urban air particulates, while the Soxhlet extract used for the certified values required class-fractionation to reduce the bulk alkane constituents prior to analysis.

Although the subcritical water/SPE method worked well with the urban air particulate matter, initial attempts to use the same method for diesel exhaust particulate matter were not successful (recoveries were only a few percent). It appears that highly hydrophobic matrices (diesel exhaust particulates are mostly organic carbon soot) do not “wet” well during the static subcritical water ex-

Table 3
Subcritical water/SPE disc extraction of PAHs from urban marine sediment (SRM 1944)

| PAH | Cert. Conc. \pm SD (mg/kg) ^a | Conc. \pm SD (mg/kg) by Subcritical Water/SPE | |
|--|--|--|-------------------------|
| | | Cl-anthracene I.S. ^b | d-PAH I.S. ^b |
| Phenanthrene | 5.3 \pm 0.2 | 6.0 \pm 1.4 | 6.6 \pm 0.2 |
| Anthracene | 1.8 \pm 0.3 | 3.5 \pm 0.2 | 1.6 \pm 0.0 |
| Fluoranthene | 8.9 \pm 0.3 | 8.7 \pm 0.6 | 10.5 \pm 0.8 |
| Pyrene | 9.7 \pm 0.4 | 9.4 \pm 0.7 | 10.7 \pm 0.9 |
| Benz[<i>a</i>]anthracene | 4.7 \pm 0.1 | 3.7 \pm 0.5 | 4.5 \pm 0.4 |
| Chrysene | 4.9 \pm 0.1 | 5.8 \pm 0.3 | 6.4 \pm 0.4 |
| Benzo[<i>b+j+k</i>]fluoranthene ^c | 8.3 | 6.4 \pm 0.7 | 12.7 \pm 1.0 |
| Benzo[<i>e</i>]pyrene | 3.3 \pm 0.1 | 3.4 \pm 0.5 | 5.2 \pm 0.5 |
| Benzo[<i>a</i>]pyrene | 4.3 \pm 0.1 | 3.4 \pm 0.2 | 4.7 \pm 0.3 |
| Indeno[1,2,3- <i>cd</i>]pyrene | 2.8 \pm 0.1 | 3.0 \pm 0.1 | 2.1 \pm 0.2 |
| Benzo[<i>ghi</i>]perylene | 2.8 \pm 0.1 | 3.1 \pm 0.1 | 2.4 \pm 0.3 |

^a Concentrations certified by NIST, based on Soxhlet and pressurized organic liquid extraction.

^b Concentrations determined by a 1 h extraction at 250°C using either 1-chloroanthracene (triplicate 0.5 g samples) or perdeuterated PAHs (separate triplicate 0.5 g samples) as the internal standards.

^c The *b*, *j*, and *k* isomers of benzofluoranthene were not resolved at the chromatographic conditions used, so are reported as the total of all three isomers.

Table 4
Subcritical water/SPE disc extraction of PAHs from urban air particulate matter (SRM 1649a)

| PAH | Cert. conc. \pm SD (mg/kg) ^a | Conc. \pm SD (mg/kg) by Subcritical Water/SPE | |
|--|--|--|-------------------------|
| | | Cl-anthracene I.S. ^b | d-PAH I.S. ^b |
| Phenanthrene | 4.1 \pm 0.4 | 4.4 \pm 0.3 | 5.2 \pm 0.3 |
| Anthracene | 0.43 \pm 0.08 | 0.70 \pm 0.04 | 0.63 \pm 0.05 |
| Fluoranthene | 6.5 \pm 0.2 | 7.0 \pm 0.2 | 7.4 \pm 0.6 |
| Pyrene | 5.3 \pm 0.3 | 5.8 \pm 0.6 | 6.1 \pm 0.4 |
| Benz[<i>a</i>]anthracene | 2.21 \pm 0.07 | 3.1 \pm 0.2 | 2.4 \pm 0.4 |
| Chrysene | 3.05 \pm 0.06 | 5.9 \pm 0.4 | 5.6 \pm 0.8 |
| Benzo[<i>b+j+k</i>]fluoranthene ^c | 8.4 | 9.1 \pm 0.5 | 13.3 \pm 2.3 |
| Benzo[<i>e</i>]pyrene | 3.1 \pm 0.2 | 3.4 \pm 0.7 | 5.0 \pm 0.8 |
| Benzo[<i>a</i>]pyrene | 2.5 \pm 0.1 | 2.7 \pm 0.5 | 2.7 \pm 0.4 |
| Perylene | 0.65 \pm 0.08 | 1.9 \pm 0.2 | 1.0 \pm 0.3 |
| Indeno[1,2,3- <i>cd</i>]pyrene | 3.2 \pm 0.7 | 3.6 \pm 0.1 | 2.2 \pm 0.6 |
| Benzo[<i>ghi</i>]perylene | 4.0 \pm 0.9 | 4.4 \pm 0.1 | 4.4 \pm 1.2 |

^a Concentrations certified by NIST based on Soxhlet extraction.

^b Concentrations determined by a 1 h extraction at 250°C using triplicate 100 mg samples with either 1-chloroanthracene as the internal standard, or triplicate 100 mg samples with perdeuterated PAHs as the internal standards.

^c The *b*, *j*, and *k* isomers of benzo[*b+j+k*]fluoranthene were not resolved at the chromatographic conditions used, so are reported as the total of all three isomers.

traction, and thus solvation of the PAHs during subcritical water extraction was not efficient.

4. Conclusions

Coupling static subcritical water extraction with SPE sorbent disc collection provides a very simple and rapid approach to the quantitative extraction and recovery of PAHs from contaminated soils and sediments. The ability to store the SPE discs in autosampler vials for shipment, the elimination of organic solvents needed in the field (except for a small amount of methanol to wet the disc prior to extraction), and the simplicity of the apparatus should make this approach particularly attractive for the extraction of contaminated samples under field conditions.

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