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Coupled Subcritical Water Extraction with Solid-Phase Microextraction for Determining Semivolatile Organics in Environmental Solids

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Efficient extractions of semivolatile organic pollutants from solid samples can be obtained using subcritical (hot/liquid) water by simply placing the sample in an extraction cell, filling the cell with water, and heating the system in an oven. After a 15−60-min extraction, the cell is cooled, the water is removed from the extraction cell, and the solubilized organics are analyzed using solid-phase microextraction (SPME). Quantitative determinations (recoveries typically ranging from ∼60 to 140% compared to conventional solvent extraction) of polycyclic aromatic hydrocarbons (PAHs) from soil and air particulate matter were achieved using a 250 °C extraction step and isotopically labeled PAHs as internal standards. Quantitative determinations of more volatile (e.g., alkylbenzenes) and more polar compounds (e.g., aromatic amines) from contaminated soil using external standards of pure target analytes also showed good general agreement with conventional solvent extraction. Relative standard deviations (RSDs) of replicate water extraction/SPME determinations compared favorably with those of conventional liquid solvent techniques (e.g., RSDs typically ranged from 2 to 33%). The method is simple to perform, uses very inexpensive apparatus, and utilizes no organic solvents.

The desire to reduce the time required and the quantities of organic solvents needed for the extraction of organic pollutants from water and solid samples has led to the recent development of a variety of new extraction approaches including supercritical fluid extraction (SFE)[1,2] and accelerated solvent extraction (ASE)[3] for solid samples and solid-phase microextraction (SPME) for water samples.[4,5] Each of these techniques dramatically reduces or eliminates the need for organic solvents in the sample extraction step and typically reduces the time required from several hours to <1 h.

A very recent approach for extracting organics from solids and semisolids is based on using water as the extraction solvent.[6−8] This approach employs the large reduction in polarity of liquid water that occurs at higher temperatures. In contrast to the dependence of SFE efficiencies on both pressure and temperature,[1,2,9] extraction efficiencies for polar and nonpolar organics using water depend primarily on the temperature of the extraction as long as sufficient pressure is used to maintain the extractant water in the liquid state. For example, phenols and chlorophenols have been efficiently extracted from soils and sludges at 50−100 °C, while less polar analytes such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) require 250 °C water for efficient extraction.[6−8] In these previous reports, the organic pollutants were collected by passing the extractant water through an organic solvent following flow through an extraction cell containing the sample (dynamic extraction). The concentrations were then determined using gas chromatography/mass spectrometry (GC/MS) by conventional solvent injection techniques.

SPME has recently been developed as a truly solvent-free method to extract organics from water samples. Organics partition from the water into a small volume of sorbent phase coated onto a fused silica rod mounted in a syringe device and are then determined by thermal desorption directly into a gas chromatograph.[4,5] As an equilibrium technique, SPME does not exhaustively extract the organics from the water samples. However, quantitative determinations are possible with proper calibration using either internal standards with similar partitioning behavior or external standard solutions in water or by standard additions.[4,5,10] Attempts have also been made to determine organic pollutants in soil samples using SPME by sampling the headspace above soil,[4,5] but this approach depends on vaporization of the analytes from the soil and appears to be limited to volatile components such as BTEX (benzene, toluene, ethylbenzene, and xylenes).

Due to the success of SPME as a method for quantitative determinations of organics in water, and the ability of subcritical water to quantitatively extract both polar and nonpolar organics from solids and semisolids, the present study was performed in an attempt to couple subcritical water extraction and SPME. The result is a rapid method capable of quantitatively determining organic pollutants in environmental solids which can be performed

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without organic solvents and by using very simple and inexpensive instrumentation. In essence, the subcritical water extraction is used to convert solid samples into water samples so that the pollutants can be determined by SPME. The development and quantitative abilities of the resultant approach are demonstrated with real-world samples contaminated with both nonpolar (PAHs) and polar (aromatic amines) organics.

EXPERIMENTAL SECTION

Samples. Soils from a railroad bed (contaminated with PAHs) and from an industrial site (contaminated with aromatic amines and several other compound classes) were used as received, except that both soils were sieved to remove debris which was larger than 4 mm. Both soils had been contaminated for several years. Urban air particulate matter was obtained from the National Institute of Standards and Technology (NIST, SRM 1649). Preliminary extractions demonstrated that relatively small samples yielded results with reproducibilities similar to those obtained from the extraction of larger samples, demonstrating that small samples were representative of the bulk sample. Therefore, due to limited sample quantities, the extractions of the railroad bed soil, industrial soil, and air particulate matter were performed using 500-, 100-, and 50-mg samples, respectively.

Water Extraction. All water extractions were performed using a 64-mm-long, 7-mm-i.d. (12-mm-o.d.) stainless steel pipe with national pipe thread (npt) end caps (Minnesota Valve and Fitting, Eden Prairie, MN) 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 was then weighed into the cell, and the cell was filled with HPLC-grade water (~3.5 mL) which had previously been purged with clean nitrogen for ~2 h to remove dissolved oxygen. After being capped (again using a single layer of Teflon tape on the pipe threads), the cell was placed vertically in a Hewlett-Packard 5890 gas chromatographic oven which had been preheated to the desired temperature. No attempt was made to mix the sample and extractant water during the heating step. After the heating was completed, the cell was immediately removed from the oven and cooled under tap water. The top cap was then removed, and 1.8 mL of the supernatant water was pipetted into a 2-mL autosampler vial containing a clean, Teflon-coated stir bar. The vial was immediately sealed with a Teflon-lined cap to avoid the loss of more volatile components. Internal standards were added in a small volume of acetone (6−20 μL) either prior to the heating step (for the PAH determinations) or after the heating step (for the determination of the target analytes in the industrial soil). Note that the highest pressure expected during the heating step is the steam/water equilibrium pressure of 86 bar, which would occur at the highest temperature tested (300 °C), a pressure much lower than the vessel rating of 496 bar. However, care must be taken to avoid the extraction of samples which may react with water to yield higher pressures.

SPME and GC/MS Determinations. The concentrations of the organics in the extractant water were determined using SPME sorption and gas chromatography/mass spectrometry (GC/MS) with a Hewlett-Packard Model 5972 GC/MS (Palo Alto, CA) equipped with a split/splitless injection port. Details for optimizing the use of a split/splitless injection port for the desorption from a SPME sorbent are discussed in detail elsewhere.[10,11] Briefly, the procedure for the SPME determinations was as follows: (1) the sorbent fiber was inserted into and exposed to the water extract for 15 min, with stirring; (2) the fiber was then withdrawn from the water sample, and the analytes were recovered by inserting the fiber into the heated split/splitless injection port.

All determinations were performed using a 100-μm-film-thickness poly(dimethylsiloxane)-coated fiber mounted in a manual syringe holder (Supelco, Bellefonte, PA). Each sample was stirred vigorously during the sorption step using a 1.5-mm-diameter × 8-mm-long stir bar and a stirring plate. Thermal desorption of the analytes was achieved by inserting the sorbent fiber into the injection port (held at 300 °C) for 3 min. All desorptions were performed in the splitless mode. Earlier reports demonstrated that the use of the 300 °C desorption temperature did not result in degradation of the sorbent fiber or affect its performance, yet this temperature was sufficient to quantitatively recover even fairly nonvolatile organics.[10,11] To further ensure that the desorption procedure was sufficient to completely recover the analytes in the present study, sorbent fibers were periodically subjected to a second desorption and GC/MS analysis. The lack of detectable analytes demonstrated that the 3-min desorption at 300 °C was sufficient to recover all of the analytes discussed in this study.

GC separations were performed with a 30-m HP5-MS capillary column (0.25-mm i.d., 0.25-μm film-thickness) supplied by Hewlett Packard. For the PAH determinations, the GC oven temperature was held at 80 °C during the 3-min desorption of the SPME fiber and then ramped at 15 °C/min to 320 °C and held for 5 min. For extracts from the industrial soil contaminated with aromatic amines, the GC oven was held at 45 °C during the 3-min desorption step, ramped at 8 °C to 320 °C and held for 5 min. GC/MS determinations of the PAHs were performed using selected ion monitoring (SIM) at the nominal molecular weight of the PAHs and deuterated PAHs. GC/MS of the industrial soil extracts was performed in the full-scan mode (45−400 m/z), and the integrated areas of an intense ion characteristic of the target species (normally the molecular ion) were determined. Unless otherwise noted, all GC/MS identifications were based on a comparison of the mass spectra and GC retention time of the test compound with those of authentic standards.

Internal standards for the PAH determinations included the perdeuterated forms of each PAH quantitated in this study. Benzo[*a*]pyrene and perylene were synthesized by a deuterium/hydrogen exchange method previously described.[12] All other perdeuterated standards were purchased from Cambridge Isotopes (Woburn, MA). All PAH internal standards were >99% in both chemical and isotopic purity. The concentrations of the individual perdeuterated PAHs ranged from 12 to 438 μg/mL for the analysis of the railroad bed soil (i.e., relative concentrations were typical of PAH distributions found in creosote-treated wood). Concentrations of all perdeuterated PAHs were ~20 μg/mL in the internal standard solution used with the urban dust. Aliquots of 20 μL for the railroad bed soil and 10 μL for the urban dust internal standard solution (prepared in acetone) were injected into the water in the extraction cell prior to the heating step. Quantitation of the sample PAHs was based on the GC/MS peak areas found for the sample PAHs compared to the peak area (and

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Table 1. Effect of Water Temperature and Extraction Time on the PAH Concentrations Determined from Railroad Bed Soil

PAH	Soxhlet concn, μg/g (%RSD)	% recovery water/SPME concn, vs Soxhlet concn (%RSD)[a]					
		200 °C		250 °C, 15 min		250 °C, 60 min	
		15 min	60 min	operator 1	operator 2	operator 1	operator 2
naphthalene	0.05 (14)	64 (11)	138 (23)	197 (13)	194 (13)	278 (7)	272 (32)
acenaphthene	0.20 (12)	60 (3)	67 (25)	105 (14)	122 (33)	210 (6)	240 (22)
phenanthrene	8.0 (5)	45 (6)	70 (13)	82 (16)	90 (9)	99 (12)	98 (11)
anthracene	3.7 (11)	22 (9)	58 (13)	121 (20)	150 (13)	324 (14)	294 (13)
fluoranthene	28 (9)	38 (5)	52 (2)	73 (20)	89 (15)	91 (10)	84 (13)
pyrene	20 (9)	36 (5)	53 (4)	79 (20)	91 (17)	104 (10)	95 (13)
benz[*a*]anthracene	3.6 (10)	36 (9)	46 (12)	107 (26)	108 (21)	153 (13)	142 (15)
chrysene	15 (8)	25 (7)	33 (4)	73 (27)	67 (15)	100 (9)	91 (11)
benzo[*a*]pyrene	5.7 (1)	15 (14)	23 (7)	55 (23)	55 (18)	98 (22)	63 (5)
perylene	1.2 (13)	19 (16)	21 (18)	46 (22)	65 (19)	161 (11)	96 (16)
benzo[*ghi*]perylene	1.8 (3)	26 (68)	20 (2)	59 (25)	45 (7)	80 (16)	61 (8)

[a] The values listed are the concentrations determined using triplicate water/SPME determinations compared to those based on triplicate 24-h Soxhlet extractions. Since the SPME is an equilibrium rather than an exhaustive extraction method, "% recovery" refers to the PAH concentrations determined rather than the actual percent of PAHs extracted by the SPME analysis.

spike quantity) of the same deuterated PAH internal standards (e.g., phenanthrene concentrations were based on the response of the phenanthrene-d_{10} spikes).

For the determination of the aromatic amines and other contaminants from the industrial soil, the internal standard, 2,4-diethylamine, was added directly to the extraction cell (in 6 μL of acetone) after the heating step but before the water was removed from the extraction cell. After the cell contents were mixed, a water aliquot was removed for SPME analysis. In contrast to the PAH quantitations, quantitations of the organics from the industrial soil were based on external standard solutions of the target organics spiked into water and analyzed using SPME in a manner identical to that used for the sample water extracts.

Conventional Extractions. Concentrations of the individual organics in the railroad bed soil (PAHs) and in the industrial soil (aromatic amines and other miscellaneous organics) were determined using Soxhlet extraction for 24 h with a cycle time of ~15 min. The railroad bed soil (triplicate 1-g samples) was extracted with 150 mL of methylene chloride. The industrial soil (triplicate 1-g samples) was extracted in an identical manner, except that 150 mL of a 50:50 volume mix of methylene chloride and acetone was used, and the soil was mixed with an equal amount of sodium sulfate prior to extraction. Due to the loss of the more volatile analytes in the industrial soil which occurred during the Soxhlet extraction, additional extractions were performed on triplicate 0.1-g samples using 18 h of sonication (4 mL of 50:50 acetone/methylene chloride) in 15-mL centrifuge vials sealed with plastic snap caps. The same internal standards were used for the quantitation of the organics in the sonication and Soxhlet extracts as were used for the SPME determinations. After extractions were completed, the solvent volume was concentrated under a gentle stream of nitrogen to ~2 mL for the railroad bed soil and ~200 μL for the industrial soil. The extracts were analyzed using GC/MS with the same chromatographic and MS conditions described above for the SPME determinations.

RESULTS AND DISCUSSION

Effect of Time and Temperature on the Water Extraction of PAHs from Soil. Initial development was performed using the PAH-contaminated railroad bed soil. Replicate samples were subjected to a 15-min heating step at 50 °C intervals from 50 to 300 °C. None of the PAHs showed significant extraction at 50 °C, but the extraction of all of the PAHs was enhanced by higher temperature, with the lower molecular weight PAHs showing significant extraction at the lower temperatures. However, increasing the extraction temperature from 250 to 300 °C had little effect on the extraction of any of the PAHs. These results agree with previous reports for the dynamic (flowing water) extraction of PAHs from soil and waste sludges; i.e., 250 °C was necessary to achieve good recoveries of the higher molecular weight PAHs, while somewhat lower temperatures were sufficient to extract lower molecular weight PAHs.[6−8] It should be noted that timing for the extractions began when the cell was placed in the preheated GC oven. Thus, the cell contents were not at full temperature during the entire extraction time. For example, during the 250 °C extractions (based on a thermocouple placed in the extractant water), the cell contents required ~4 min to reach 240 °C and 7 min to reach 250 °C.

To determine the effect of extraction time, additional extractions were performed using 200 and 250 °C for both 15 and 60 min. As shown in Table 1, increasing the extraction time from 15 to 60 min did increase the recoveries achieved at 200 °C, but the increases were not large. The concentrations determined using the water/SPME approach at 200 °C were still generally lower than those resulting from the 24-h Soxhlet extractions. Therefore, extractions were performed for both 15 and 60 min at 250 °C. In addition, the water/SPME determinations at 250 °C were independently performed by two different operators in an effort to eliminate any possible bias in the results. As shown in Table 1, the extractions performed with 250 °C water generally showed reasonable agreement with the Soxhlet values, although the recoveries were somewhat higher when the extraction time was extended from 15 to 60 min. Also note that the concentrations obtained by the two operators agreed well for both the 15- and 60-min extractions.

While the majority of PAHs showed good agreement between the water/SPME and Soxhlet determinations, the concentrations of three of the PAHs determined with the 60-min extractions at 250 °C are considerably higher than the Soxhlet values. Since naphthalene and acenaphthene are fairly volatile, the higher recoveries found using the water/SPME procedure are likely a

Table 2. Water/SPME Determination at 250 °C of PAHs in Urban Dust (SRM 1649)

PAH	NIST concn, μg/g (±SD)		water/SPME concn, μg/g (±SD)[c]	
	original[a]	revised[b]	15 min	60 min
phenanthrene	4.5	4.1 ± 0.4	4.6 ± 0.3	5.3 ± 0.4
fluoranthene	7.1 ± 0.5	6.5 ± 0.2	9.7 ± 1	8.4 ± 0.3
pyrene	6.6	5.3 ± 0.3	5.1 ± 0.5	7.2 ± 0.3
benz[*a*]anthracene	2.6 ± 0.3	2.2 ± 0.1	1.8 ± 0.2	3.1 ± 0.1
chrysene + triphenylene[d]	5.3	4.4	2.3 ± 0.2	3.2 ± 0.2
benzo[*b*+*k*]fluoranthene[e]	8.1	8.3	3.6 ± 0.3	5.1 ± 0.5
benzo[*a*]pyrene	2.9 ± 0.5	2.5 ± 0.9	1.6 ± 0.2	3.0 ± 0.4
benzo[*ghi*]perylene	4.5 ± 1.1	4.0 ± 0.9	1.3 ± 0.1	2.3 ± 0.1

[a] Original values provided with the NIST certificate. The concentrations of fluoranthene, benz[*a*]anthracene, benzo[*a*]pyrene, and benzo[*ghi*]-perylene are certified by NIST. The remaining concentrations are information values provided by NIST. [b] Revised values as per ref 14. All values certified by NIST. [c] Concentrations were determined by extraction at 250 °C for 15 or 60 min and a 15-min SPME sorption step. Standard deviations are based on triplicate determinations. [d] Chrysene + triphenylene concentration is based on chrysene-d_{12} response. [e] Benzo[*b*+*k*]fluoranthene concentration is based on benzo[*b*]fluoranthene-d_{12} response.

result of losses which occur during the Soxhlet extraction (note that the water extraction cell is sealed during the heating step; therefore, volatilization losses during the water extraction are not possible). However, volatilization losses are not a reasonable explanation for the high concentrations determined for anthracene (~300% versus Soxhlet), particularly since the concentrations of phenanthrene (which has the same boiling point as anthracene) were virtually identical from the water/SPME and Soxhlet procedures. Further study of the GC/MS peak areas for the individual deuterated internal standards revealed that the area for anthracene-d_{10} was unexpectedly low compared to the area determined when water spiked with the same internal standard solution was analyzed by SPME without prior heating. This result indicates that degradation of the anthracene-d_{10} could be occurring during the hot water extraction. Since the concentration of anthracene on the soil was determined by ratioing the sample anthracene peak area to that of the anthracene-d_{10} internal standard, degradation of anthracene-d_{10} would lead to artificially high concentrations of the sample anthracene. Also note the significant increase in percent recovery of anthracene when the extraction time is extended to 1 h (Table 1), which also supports a degradation explanation, because it is reasonable to expect that anthracene-d_{10} degradation would increase with time at high temperatures.

To further investigate the possibility of degradation, water solutions containing all of the standard PAHs listed in Table 1 and all of their deuterated analogs were prepared and subjected to heating for 60 min at 250 °C in the extraction cell (i.e., the solution was handled in a manner identical to a sample extraction, except that no soil was present). Only deuterated anthracene showed a lower concentration in the water after heating. Surprisingly, *no* degradation of nondeuterated anthracene was detected. This was further confirmed by heating an additional water sample spiked with only anthracene and anthracene-d_{10} using the same conditions. Again, no degradation of the nondeuterated anthracene was detected, while the majority of the anthracene-d_{10} was converted to anthraquinone-d_8 (based on its full-scan mass spectra). Thus, the unreasonably high concentrations determined for anthracene using the 60-min water extraction at 250 °C is a result of the degradation of the anthracene-d_{10} internal standard rather than actual higher extraction efficiencies. The degradation of anthracene-d_{10} during the extraction step was somewhat surprising since hot/liquid water is relatively unreactive (and much less corrosive) than either supercritical water or steam,[13] and since all water used in this study was purged to remove oxygen. However, the results do demonstrate that the analyst must be aware of potential degradation in using the water extractions at higher temperatures.

Water/SPME Determinations of PAH Concentrations on Urban Dust. Based on the results discussed above for the determination of PAHs on soil, the water/SPME approach was applied to the determination of PAHs from a completely different matrix, urban air particulate matter (NIST urban dust, SRM 1649). Quantitation of the individual PAHs was based on the extraction of 50-mg samples of the urban dust and deuterated PAHs (~0.2 μg of each of the deuterated PAHs corresponding to the PAHs listed in Table 2), which were added to the extractant water prior to the heating step. Preliminary extractions demonstrated that water extraction at 200 °C was not sufficient to efficiently extract the PAHs, similar to the results shown in Table 1 for the railroad bed soil. Therefore, subsequent extractions were performed at 250 °C. As shown in Table 2, the determination of the PAH concentrations using the water/SPME approach yielded reasonable agreement with the concentrations reported by NIST (based on 48-h Soxhlet extractions). Lower molecular weight PAHs showed good agreement with 15- or 60-min extractions. However, 60-min extractions gave the best agreement for the higher molecular weight PAHs.

In contrast to the railroad bed soil, which contained PAHs as the major organic contaminants, urban dust has very high concentrations of extractable alkanes (branched and straight-chained) in the range of ~C_{20}−C_{36}. The presence of these high concentrations of alkanes can make the determination of the PAHs difficult, since they elute in the same chromatographic time range as the target PAHs. Figure 1 (top) shows that extractions by sonication with methylene chloride (18 h) and by hot water result in very similar selected ion current chromatograms for PAHs. In contrast, very high concentrations of alkanes are extracted by methylene chloride sonication, while essentially no alkanes are extracted by the hot water, as shown in Figure 1 (bottom). Yang et al. previously reported that liquid water at 250 °C effectively extracted PAHs but not alkanes larger than ~C_{18};[6,8] thus, the

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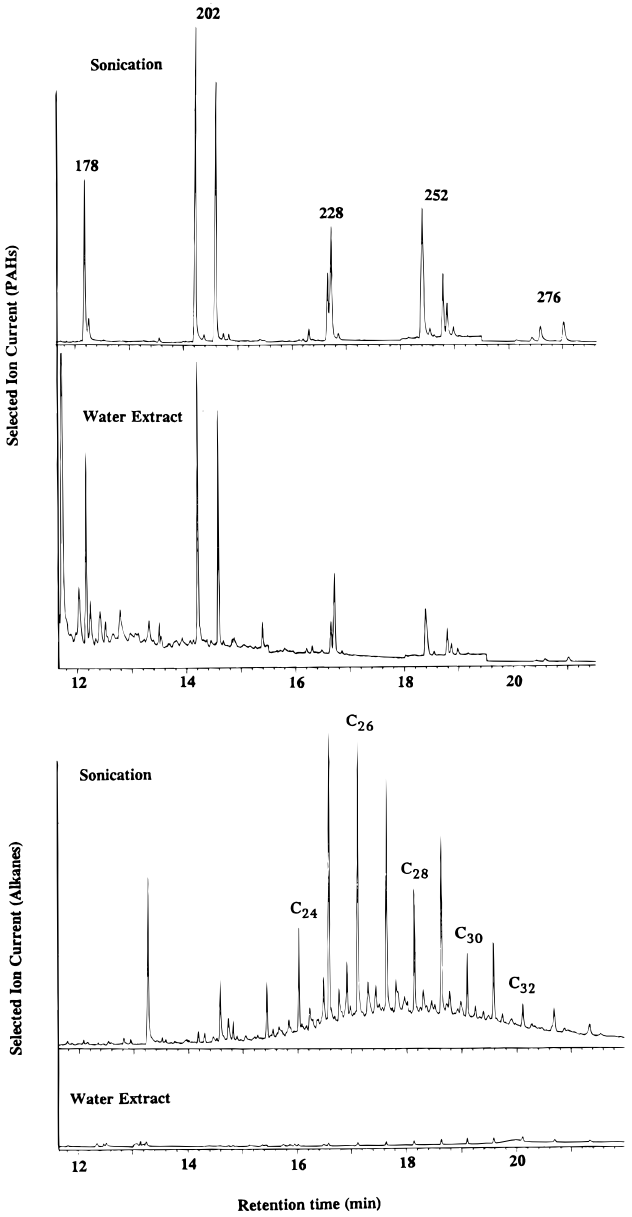

Figure 1. GC/MS selected ion current chromatograms of PAHs (top) and alkanes (bottom) extracted from urban air particulate matter using methylene chloride sonication for 24 h and water extraction at 250 °C for 15 min. The masses of the individual selected ions for the PAHs are listed above the chromatographic peaks. The alkanes were monitored using $m/z = 85$. Note the lack of alkane peaks in the water extract.

selectivity of the water/SPME method appears to be a result of the selectivity of the water extraction step rather than the SPME sorption. This is further supported by the fact that the SPME phase [poly(dimethylsiloxane)] is an extremely effective sorbent for alkanes; thus, any alkanes present in the water extract should be present in the chromatogram using SPME analysis. In addition, significant concentrations of alkanes were not detected in a methylene chloride extract of the extractant water (i.e., the same static water extraction method used for water/SPME, but using methylene chloride extraction rather than SPME to collect the organics from the extractant water for GC analysis), therefore confirming that the water extraction step is responsible for the selectivity shown for PAHs over *n*-alkanes in Figure 1.

Soil/Water and Water/SPME Partitioning. The water/SPME method for PAHs includes two processes: the extraction of the PAHs from the soil and the SPME sorption of the PAHs from the water, neither of which is necessarily exhaustive. SPME sorption is an equilibrium process for which every PAH has a different distribution coefficient (K_D), which is defined as the equilibrium concentration of a species in the fiber sorbent phase, divided by its concentration in the water.[4,5,10] For example, low molecular weight PAHs have lower K_D values (are more soluble in water, so partition less into the fiber) than higher molecular weight PAHs.[10] Fortunately, in order to perform quantitative determinations, it is not necessary to know the partitioning constants, since quantitative calibration standards can be prepared from solutions of the PAHs in water. To perform quantitative calibration, the standard and the sample water solutions are simply analyzed using SPME sorption and GC analysis under identical conditions (note that it is not even necessary for the SPME sorption to be long enough to achieve equilibrium, as long as the sorption time is the same for the standard and sample water solutions).

However, quantitative calibrations for the coupled water extraction/SPME method described in the present study cannot be performed using only water solutions of the standard PAHs, since the PAHs which are extracted during the water extraction step may not quantitatively remain in water solution when the water extract is cooled (i.e., prior to the SPME sorption step). Since the solubility of the PAHs in water will decrease as the water is cooled, some of the individual PAHs may repartition from the water back to the solid sample. Therefore, quantitative determination of the PAHs requires that the extractant water contain internal standards (i.e., the deuterated PAHs used in this study) that show the same partitioning behavior between the extractant water and the solid sample during the cooling step following the hot water extraction. In addition, they must show the same SPME absorption behavior. Therefore, in order to obtain quantitative determinations of the sample PAHs, the relative distribution of the individual PAHs and their deuterated analogs must be the same after heating and cooling the water and during the SPME step. As shown by the reasonable quantitative results for the soil and urban dust samples (Tables 1 and 2), this assumption is generally true; i.e., the quantitative results can show good agreement with the Soxhlet extraction results only if the individual PAHs from the samples and their deuterated analogs show the same distribution between the extractant water, the solid sample, and the SPME sorbent phase.

Based on the previous reports, demonstrating that 250 °C water extractions are sufficient to quantitatively remove the PAHs from solids into water,[6,8] it is reasonable to expect that the conditions used in this study were sufficient to solvate all of the PAHs into the water when it was heated to 250 °C, as long as sufficient extraction times were used. However, it is also possible that the sample and deuterated PAHs (especially the higher molecular weight compounds) show some readsorption to the solid sample when the water is cooled. To determine the fraction of the individual PAHs which remained in the water after the cooling step, the cooled extractant water and the soil residue from the railroad bed soil were both extracted with methylene chloride (18 h of sonication for the soil, by shaking for several minutes for the water) and analyzed by GC/MS. As would be expected, the lower molecular weight PAHs remained mostly in the extractant water after cooling, since they have the highest water solubilities at ambient temperature, while the higher molecular weight PAHs

showed somewhat more partitioning back to the soil. For example, naphthalene (MW = 128), phenanthrene (MW = 178), fluoranthene (MW = 202), chrysene (MW = 228), and benzo[*ghi*]perylene (MW = 276) showed 76, 62, 55, 39, and 24%, respectively, of the PAHs remaining in the cooled water phase. Interestingly, the concentrations of high molecular weight PAHs found in the water phase were substantially higher than would be expected on the basis of reported water solubilities of pure compounds.[15] For example, pyrene, chrysene, perylene, and benzo[*ghi*]perylene had concentrations in the extractant water of 613, 272, 12, and 15 μg/L, respectively, which are ~5-, 136-, 30-, and 50-fold higher than their reported water solubilities of 135, 2, 0.4, and 0.3 μg/L, respectively.[15] Even if the water/soil mixture was left in contact overnight, the fraction of the individual PAHs found in the water versus the soil residues did not change significantly, indicating that coextracted material (e.g., humic and fulvic acids) may be responsible for holding higher concentrations of the PAHs in solution than might be expected only on the basis of their pure compound solubility. In any case, the good agreement between the conventional Soxhlet extraction concentrations and the water extraction/SPME approach shown in Tables 1 and 2 clearly demonstrates that the deuterated PAHs and the sample PAHs partition in a similar manner both during the water extraction (and cooling) step and during the SPME sorption step, thus allowing quantitative determinations to be made.

Water Extraction/SPME of Polar Analytes. As described above, a disadvantage of the coupled water extraction/SPME approach to determining complex mixtures of nonpolar (e.g., PAHs) analytes is that an internal standard that shows the same water/sample partitioning is needed for each target compound. Thus, the deuterated analogs of each PAH were required for obtaining the quantitative results presented above. However, if the analytes extracted during the water step remain in the extractant water after cooling (i.e., do not repartition to the sample matrix), the need for an individual internal standard for each target analyte would be eliminated. For such samples, SPME determinations of the concentrations of the target analytes on the solid sample would be performed using conventional SPME analysis of the extractant water, i.e., with the quantitative calibrations being performed on the basis of external standard solutions made in pure water.[10] An internal standard can be added to both the sample extractant water and the water calibration solution. However, the purpose of such an internal standard is more conventional, i.e., it normalizes the chromatographic system's performance rather than adjusting for the equilibria between the water and soil (as was the case for the deuterated PAHs above).

The use of coupled water extraction/SPME for more polar organics was investigated with the industrial soil. As shown in Figure 2 and Table 3, water extraction/SPME analysis of the soil demonstrated a very complex mixture of contaminant organics, including aromatic amines, alkylbenzenes, and chlorinated hydrocarbons. Replicate water extraction/SPME determinations showed reasonable reproducibility for raw peak areas for all of the major species shown in Figure 2, indicating that the method could be used to determine concentrations of all of these components. However, since water/SPME distribution coefficients vary for each different analyte, quantitative determination of individual species using SPME requires the availability of

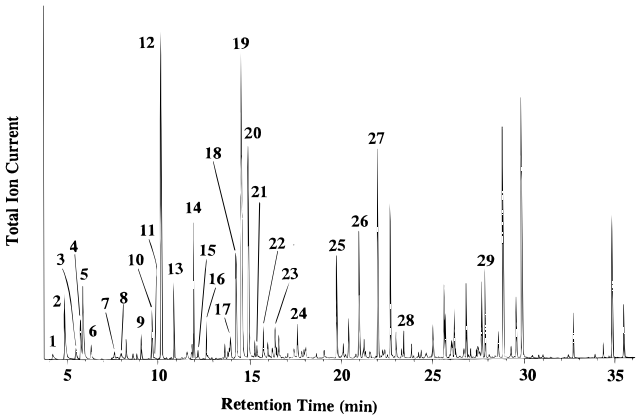

Figure 2. GC/MS separation of the organic pollutants extracted from industrial soil using the water/SPME technique. Numbered peaks are identified in Table 3.

standard compounds so that proper calibration standards in water can be made. Thus, due to the lack of many suitable standards, quantitation of only the compounds listed in Table 4 was possible.

As described above, the quantitative determination of these organics also requires that they remain in solution when the extractant water is cooled. Only then can quantitative calibrations of the SPME step be performed using standards prepared in water (i.e., in contrast to the PAH determinations described above, no isotopically labeled internal standards were available to account for any repartitioning of the analytes to the soil upon cooling the extractant water). Fortunately, when the cooled extractant water (from a 250 °C, 15-min water extraction) and the resultant soil residue were extracted with methylene chloride and methylene chloride/acetone, respectively, more than 88% of each species listed in Table 4 (except naphthalene) was found in the cooled extractant water. Approximately 75% of naphthalene was found in the extractant water, which would be expected due to its lower water solubility. These results clearly demonstrate that, in contrast to the PAHs, the organic contaminants in this sample remain in the extractant water after cooling and, therefore, can be quantitated on the basis of external calibration water standards, as is normally done for SPME determinations of organics in water.

Initial water extractions of the industrial soil were performed at 150 and 250 °C. As was the case for PAHs, 250 °C yielded the most concentrated extract; therefore, subsequent extractions were performed at 250 °C.

A comparison of the concentrations obtained using the water extraction/SPME approach (15-min water extraction, 15-min SPME sorption) with both conventional Soxhlet extraction (24 h) and sonication with 1:1 methylene chloride/acetone (18 h) is shown in Table 4. In general, the three procedures yielded reasonably similar concentrations for the less volatile organics, including aniline and the chlorinated anilines. A notable exception is the significantly higher value for *N*-methylaniline obtained from the water/SPME procedure than from either the Soxhlet or sonication extractions. The reason for the high water/SPME value for *N*-methylaniline is not known. Blank extractions show no detectable quantities, indicating that contamination from the water/SPME procedure is not responsible. Because of the 250 °C extraction temperature, it is possible that higher molecular weight amines degrade during the extraction process to form the *N*-methylaniline. For example, the water extract contains significant quantities of a species tentatively identified as *N*,*N*′-dimethyl-

(15) Lee, M. L.; Novotny, M. V.; Bartle, K. D. *Analytical Chemistry of Polycyclic Aromatic Hydrocarbons*; Academic Press: New York, 1991; p 10.

Table 3. Identities of Compounds Shown in Figure 2

peak no.[a]	species	peak no.[a]	species
1	toluene	16	C_4-alkylaniline
2	tetrachloroethylene	17	methylnaphthalene
3	chlorobenzene	18	C_4-alkylaniline
4	ethylbenzene[b]	19	2,5-dichloroaniline[b]
5	(*m*+*p*)-xylene[b]	20	2,3-dichloroaniline[b]
6	*o*-xylene[b]	21	biphenyl
7	benzaldehyde[b] + C_3-alkylbenzene	22	diphenyl ether
8	aniline[b] + C_3-alkylbenzene	23	trichloroaniline
9	dichlorobenzene	24	C_3-alkylquinoline
10	*N*-methylaniline[b]	25	C_2-alkylaminonaphthalene
11	2-methylaniline[b]	26	*N*-benzyl-*N*-ethylaniline
12	*N*,*N*-dimethylaniline[b]	27	*N*,*N*′-dimethyl-*N*,*N*′-diphenylurea
13	2-chloroaniline[b]	28	dibutyl phthalate
14	naphthalene[b]	29	4,4′-methylenebis[*N*,*N*-dimethylaniline]
15	4-chloroaniline[b]		

[a] Peak numbers refer to the chromatogram in Figure 2. [b] Identities were confirmed by comparing the retention times and EI fragmentation patterns with those of standard compounds. The remaining compounds were identified on the basis of comparison of their EI spectra with published spectra.

Table 4. Water/SPME Determination at 250 °C of Volatile and Polar Analytes in an Industrial Soil

	concentration, μg/g (%RSD)[a]		
compound	hot water/ SPME, 15 min	sonication, 18 h	Soxhlet, 24 h
ethylbenzene	0.21 (9)	0.32 (7)	nd[b]
(*m*+*p*)-xylene	0.18 (9)	0.26 (4)	nd
o-xylene	0.097 (8)	0.16 (4)	nd
benzaldehyde	1.6 (3)	2.1 (13)	nd
aniline	0.56 (12)	0.91 (18)	0.84 (17)
N-methylaniline	5.7 (3)	0.082 (6)	0.17 (7)
2-chloroaniline	3.3 (6)	2.5 (7)	4.1 (8)
naphthalene	0.25 (7)	0.23 (3)	0.30 (15)
4-chloroaniline	1.0 (16)	1.5 (18)	1.7 (9)
2,5-dichloroaniline	6.0 (6)	5.8 (11)	8.8 (12)
2,3-dichloroaniline	2.6 (7)	2.3 (11)	2.9 (13)

[a] Relative standard deviations are based on triplicate determinations for each method. [b] Not detected in the extract.

N,*N*′-diphenylurea, which might hydrolyze during the 250 °C water extraction to form *N*-methylaniline as one product. Although *N*,*N*′-dimethyl-*N*,*N*′-diphenylurea could not be obtained to test this hypothesis, *N*,*N*′-diethyl-*N*,*N*′-diphenylurea was obtained and subjected to the same 250 °C water/SPME procedure. While only a trace amount of *N*-ethylaniline was formed (corresponding to <1% of the *N*,*N*′-diethyl-*N*,*N*′-diphenylurea), the results do suggest that the formation of *N*-methylaniline did occur during the soil extraction and may account for the high water/SPME value. Therefore, as was the case for anthracene-d_{10} discussed above, the analyst using the water/SPME procedure must be aware of possible analyte degradation.

In contrast to the general good agreement between water/SPME and the Soxhlet and sonication extractions for the less volatile analytes, some notable differences do occur for the volatile components. For example, the alkylbenzenes and benzaldehyde were not detected with the 24-h Soxhlet extraction, which would be expected since losses of volatile components are normal during the Soxhlet process. However, the water/SPME determinations show reasonable agreement with sonication extraction. For all of the species in Table 4, the reproducibility of the water/SPME technique compares favorably with those of the conventional extraction methods.

CONCLUSIONS

Subcritical (hot/liquid) water extraction can be performed in a simple sealed vessel to generate a water sample suitable for SPME determinations of organic pollutant concentrations on solid samples. Upon cooling the extractant water after the heated extraction step, very nonpolar organics such as PAHs show significant partitioning back to the solid sample. However, quantitative determinations of nonpolars can be performed by adding internal standards that have the same water/sample and the same SPME/water partitioning behavior prior to the water extraction/SPME procedure. More soluble analytes (e.g., alkylbenzenes, aromatic amines) remain in the water solution after cooling of the extractant water. Therefore, isotopically labeled internal standards are not required, and quantitation of analyte concentrations on the solid samples can be based on conventional SPME analysis of the extractant water and calibration procedures using water solutions of the target organics. The water extraction/SPME method is a rapid method that requires no organic solvents and utilizes simple and inexpensive equipment.

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