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Efficient Extraction of Fuel Oil Hydrocarbons from Wood

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Abstract: Sequential cold (room temperature) extraction from aged contaminated wood samples (southern yellow pine) with acetone followed by *n*-pentane (upon a 3–4 days of sample incubation with each solvent) yielded more than 90% analyte recovery for both ambient (natural moisture content) and water-submerged wood, significantly exceeding the recoveries obtained with one-step extraction using single solvents and/or their mixtures. By contrast, a much faster ultrasound/Soxhlet extraction led to a virtually complete analyte recovery while using a 1:1 mixture of these two solvents. Evidence obtained indicates that a possible role for the first solvent, acetone (in addition to collection of loose analyte), is the removal of an aqueous barrier surrounding the strongly adsorbed hydrocarbon, thus enabling its extraction by the second (non-polar) solvent. For larger analyte concentrations (>60 mg *n*-hexadecane/g wood), the high-affinity binding sites became saturated (yielding 5–10 mg unrecovered analyte/g wood), and then a single solvent was sufficient for a near-quantitative extraction.

Keywords: Fuel oil, hydrocarbons, solvent extraction, wood

INTRODUCTION

Building structural elements, e.g., wood, can be contaminated as a result of storage, production, and spillage of organic compounds (1) or by design (wood impregnation with preservatives or adhesives) (2). During

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catastrophic floods (as that in Grand Forks, ND, USA, April 1997), fuel oil tanks located in residential basements ruptured, forcing the spilled oil, mixed with flood water, to become entrapped in the pores of wooden framing structures (as well as other building materials). Fuel oil is a mixture of petroleum hydrocarbons, e.g., aliphatic (alkanes, cycloalkanes, and olefins from approximately C_{10} to C_{23}), aromatic (alkylbenzenes, toluene, naphthalenes), and polycyclic (3).

Once trapped in the microscopic pores of the matrix (wood), organic compounds become less mobile and thus are more difficult to remove. Over the course of time, these chemicals slowly evaporate, possibly posing health risks for humans (4, 5). Under flood conditions, the problem is further aggravated because water can seal off the trapped pollutants. As a result, the pollutant's mobility is significantly hindered which may lead to prolonged human exposure time (6, 7). It has been observed that the removal of organic compounds from wood structures, regardless of the applied treatment technology, is a mass transfer limited phenomenon (1, 4). Therefore, conventional cleaning techniques such as pump-and-treat technologies or heating were shown to be ineffective for the removal of organic pollutants entrapped in wood pores (1).

To develop a cost-effective and safe route to decontaminate and reuse the affected wood, the nature of interactions between these "foreign" chemicals and wood matrix as well as their transport through wood need to be understood. The first step in such an evaluation is to develop effective techniques for analyte extraction from wood. These methods would not only provide an analytical tool for monitoring the removal of the contaminants but also render insight into transport and sorption mechanisms which are essential for the development of efficient remediation protocols. However, one major setback is that solvent extractions often turned out to be incomplete, particularly when contaminated wood samples were "aged," i.e., incubated for prolonged time (8). For instance, the pollutants considered in the present study could be completely extracted with a single solvent, 2-propanol, within the first few hours following the wood contamination. However, for more aged samples their extraction recovery was reduced to less than 70% (1, 9).

Common techniques used for extraction of organic pollutants from environmental matrices include Soxhlet extraction, ultrasound-assisted extraction, pressurized liquid extraction (PLE), microwave-assisted extraction (MAE), supercritical fluid extraction (SFE), surfactant-enhanced extraction, and acid/base pretreatments (10–19). PLE, MAE, and SFE methods are generally faster although expensive and require the use of specific instrumentation. By contrast, ultrasound-assisted and Soxhlet extraction, along with simple cold solvent extraction, are simple and economical. Though time- and solvent-consuming, their benefits may outweigh these disadvantages in field studies. The most commonly used extraction solvents for organic analytes are acetone, hexane, 2-propanol, benzene, methanol, toluene, and dichloromethane (20–24). Solvent selection within current EPA methods is

based either on the analyte/matrix polarities or on the method used for the subsequent analyte determination. For example, dichloromethane is a common solvent for GC analysis whereas methanol is often used for LC analysis (23).

Wood is a complicated matrix known to entrain pollutants in wood cells, which can be viewed as anisotropic capillaries aligned with polar polymers, cellulose and hemicellulose (9, 25, 26). So-called wood-swelling chemicals remain trapped in cells, due to either low polarity or large size. By contrast, wood-swelling polar chemicals can be absorbed into hemicellulose and other wood components thus becoming less accessible to extraction solvents. Less polar wood constituents, such as lignin (polymerized methoxyphenols), are mostly disconnected from wood cells and are not readily accessible to the bulk of contaminants (26). Given these specific features, the extraction of chemicals from wood may require modifications to the solvent selection and extraction strategies successful for other matrices (e.g., soil or sediments) while applying general EPA methods. To the best of our knowledge, no comprehensive studies have been performed on hydrocarbon extraction from wood.

The objective of this study was to develop an effective strategy and protocols for extraction of fuel oil hydrocarbons (i.e., non-swelling polar contaminants) from aged contaminated wood, while attempting to get insights into the nature of interactions between the entrapped chemicals and wood matrix. *n*-Hexadecane, a water-insoluble, non-polar, and non-volatile chemical (comprising ca. 13% of all fuel oil GC-detectable hydrocarbons in our samples, not shown) was used as a representative fuel oil hydrocarbon. Extraction method development was addressed for the entire range of pertinent analyte concentration (from micrograms to decigrams of the analyte per gram of wood) because pertinent concentration ranges may vary for different applications (e.g., toxicology vs. monitoring decontamination). Southern yellow pine softwood was selected because it is most commonly used in home construction in the USA (27).

EXPERIMENTAL

Reagents

Standard #2 heating fuel oil was obtained locally (Vilandre Inc., Grand Forks, ND, USA). All other chemicals used were of reagent grade. Radiolabeled *n*-hexadecane-1-^{14}C was purchased from Sigma-Aldrich (St. Louis, MO, USA) and diluted 65-fold with non-labeled *n*-hexadecane to yield a scintillation counting rate of 3.40×10^4 DPM/μL (15.3 nCi/μL). Unlabeled *n*-hexadecane and fuel oil samples were used as neat liquids in selected experiments.

Contaminated Wood Sample Preparation

Southern yellow pine sapwood boards were obtained locally (Menards, Grand Forks, ND, USA) and sawed into $6 \times 6 \times 20$ mm^3 samples. For consistency, only samples with a density of 0.43 ± 0.02 g/cm^3 were used. Measured amounts of neat *n*-hexadecane (either labeled or non-labeled, depending on the method of detection; the concentration ranges are provided in the corresponding sections) and non-labeled fuel oil were applied longitudinally, i.e., parallel to the direction of wood cells.

Two different types of wood samples were used. In the experiments under "ambient" conditions, wood samples were not further treated. Otherwise, wood samples were submerged in a beaker containing a sterile aqueous medium (3.8 g/L of sodium chloride in distilled water). To prevent microbial biodegradation of the contaminant, 5.0 mM sodium azide was added.

To prepare aged contaminated wood, samples were stored at room temperature and ambient air humidity (ca. 80%) for 21 days followed by their extraction. Further extension of the aging time up to 200 days did not result in alteration of extraction efficiencies beyond the margin of statistical error (not shown).

Solvent Extraction Procedure

The entire wood samples were used for extraction. To increase the surface area for the analyte extraction, contaminated aged wood samples were cut into small pieces of less than 3-mm size (largest dimension) using a wire cutter, then ground and milled to the maximum 0.2 mm^2 size using a ball mill. Three different liquid-solid extraction procedures were tested.

Cold Solvent Extraction

Samples were placed in 22 mL vials covered with screw top solid caps with Teflon liners and extracted with 10.0 mL of solvent for 4 days (i.e., 96 ± 1 hours, unless indicated otherwise) on a rotary shaker (100 rpm, room temperature). Due to formation of turbid suspensions, extracts were subjected to centrifugation (15 min at 3,200 rpm) immediately after the extraction followed by filtration using Whatman paper filters #5 (Whatman Int., Maidstone, UK).

Soxhlet Extraction

Samples were homogenized with anhydrous Na_2SO_4 (1:1, w:w, to remove moisture) and placed into cellulose extraction thimbles (Whatman Int., Maidstone, UK). Extraction was carried out using 100 mL of a solvent (or

a mixture of solvents) for 24 h unless indicated otherwise. The resulting extract was concentrated by evaporation on a rotavapor to about 15 mL, followed by centrifugation and filtration as described above. No analyte loss due to evaporation was observed (confirmed by scintillation counting).

Ultrasound Extraction

Samples were placed in 22 mL vials covered with screw top solid caps with Teflon liners and sonicated with 20 mL of a solvent for 4–24 hours in a 42 kHz Branson 2510 Ultrasound Cleaner (Branson Ultrasonics Corp., Danbury, CT, USA), followed by centrifugation and filtration as described above.

Scintillation Counting Analysis

Analyses of extracts containing radiolabeled chemicals were carried out on a Beckman 7000 liquid scintillation counter (Beckman Coulter, Inc., Fullerton, CA, USA). 1-mL aliquots were added into standard plastic vials with 5.0 mL of Econo-safe scintillation cocktail (RPI, Mt. Prospect, IL, USA). The original readings were taken in counts per minute (CPM), which were then converted to DPM, calculated as CPM/quenching efficiency. Quenching efficiencies were determined in each system upon calibration with stock solutions containing known DPM amounts. Prior to counting, freshly prepared samples were set on a bench for 60 minutes to reduce the level of chemiluminescence (which was negligible after this treatment).

The radioactivity measured in the extracts was validated by performing control experiments in which wood samples were spiked with the analyte and then extracted and analyzed immediately. Radioactivity monitored in this manner was proportional to the analyte concentration. In selected experiments, *n*-hexadecane was determined, in parallel, by gas chromatography (GC, see next section). Numerical values obtained using these two methods were similar, within the margin of statistical error. However, those obtained using GC had consistently higher statistical variance (by 10–25% as compared to those using scintillation counting). This observation led to the selection of scintillation counting as the primary analytical method when applicable.

The measured radioactivity was recalculated to the precisely measured final volume of the extraction solvent. Extraction efficiency values were calculated as $\text{Recovery} = (\text{DPM}_t/\text{DPM}_0) \cdot 100\%$, where DPM_t is the reading of the extract after an aging time of 21 days whereas DPM_0 is that of the initially applied radioactivity.

Gas Chromatographic Analysis

Analyses of fuel oil extracts were carried out on an HP (Hewlett-Packard Co., Avondale, PA, USA) 5890 II gas chromatograph equipped with a flame-ionization detector (FID). A DB-1 15 m long, 0.32 mm ID, 0.25 μm film thickness capillary column (J&W Scientific, Folsom, CA, USA) was used. The temperature program was as follows: 40°C, held for 1 min, ramp to 280°C at a rate of 10°C/min, with a final hold of 10 min. The splitless injection volume was 1.0 μL. The splitless time was 0.2 min. The injector temperature was 250°C and the detector temperature was 330°C. Zero grade helium was used as a carrier gas with a head pressure of 4 psi. Hydrogen flow rate was 25 mL/min and the air flow rate was 250 mL/min.

The protocol used allowed for the separation of principal peaks of non-branched alkanes identified by matching the peak retention times with those of pure hydrocarbon standards. Extraction efficiencies were calculated in a similar way as for scintillation counting while using peak areas instead of DPM. External standard calibration was used for quantification.

All experiments in this study were conducted in triplicate unless indicated otherwise. Results were presented as mean values ± standard deviation. Standard t-tests were used to assess whether the differences in extraction efficiencies were statistically significant.

RESULTS AND DISCUSSION

n-Hexadecane Extraction from Ambient Wood

Cold (Room Temperature) Solvent Extraction of n-Hexadecane at Low Concentrations

Experiments were conducted with a small analyte amount (1.00 mg/g of wood) to simulate the worst-case scenario (from the extraction perspective) when a significant fraction of the analyte is bound to a few high-affinity sites. First, cold extraction efficiency was assessed for a variety of commonly used solvents with varied polarity, hydrogen bonding ability, molecular size (molar volume), and wood swelling coefficient (26, 28–30). Acetone, benzene, dichloromethane, and *n*-hexane were selected as EPA-recommended solvents (31, 32).

Effect of extraction time on the analyte recovery is shown for a few selected solvents in Fig. 1; other solvents used in this study exhibited similar trends. The use of extraction time below 3 days (<72 hours) resulted in a decline in analyte recovery. However for extractions of 3 days and longer, the analyte recovery leveled off; further increase of the extraction time to 10 days or increase of the solvent volume did not result in any increase

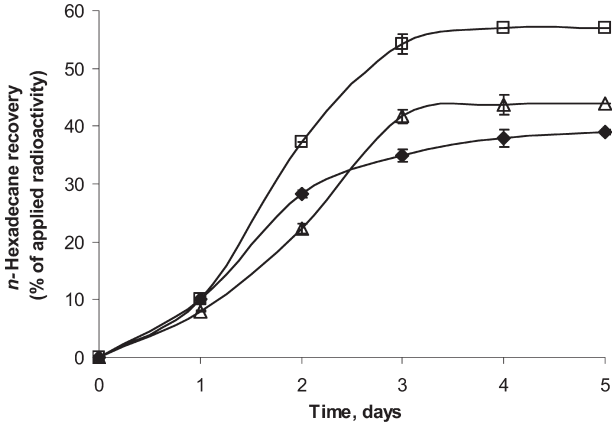

Figure 1. Effect of the extraction time on *n*-hexadecane recovery from aged (21 days) wood samples under ambient conditions; 1.00 mg analyte/g of wood was applied. ◆-acetone, □-*n*-pentane, △-acetone + *n*-pentane (1:1).

of the analyte recovery (not shown). This indicates a near-the-limit partitioning of the analyte between the matrix and extraction solvent. This assumption limits the factors affecting the extraction efficiency to those of thermodynamic rather than kinetic nature.

Based on these results, a four-day incubation time was selected for use in subsequent solvent extraction experiments. The recoveries of *n*-hexadecane from ambient wood upon a four-day extraction with various solvents are listed in Table 1. These recoveries did not exceed 40% and were not significantly different for a number of chemically different solvents with a notable exception of dichloromethane and *n*-pentane (which are discussed below). Repeating the extraction with the same solvent did not yield any significant increase in extraction recoveries ($<2-5\%$ of the first extraction recovery). The observed incomplete extraction of *n*-hexadecane with single non-polar solvents is consistent with our prior transport study in which evidence was obtained for the existence of two analyte fractions differing in their strength of binding to the matrix (i.e., loosely and strongly adsorbed/absorbed) (9). Apparently, the former are readily extractable whereas the latter are not.

One unexpected effect is that the application of non-polar solvents was not successful to release all of the adsorbed analyte. If kinetic limitations are excluded, this may mean that the hydrocarbon binding is not entirely hydrophobic in its nature, i.e., it may be based on physical entrapment. Confirming this hypothesis, a small molecular size solvent, CH_2Cl_2, yielded an elevated analyte recovery (Table 1). Similarly, when a homology series of hydrocarbons (C_5-C_{12}) were used as single extraction solvents, *n*-pentane, having the smallest size, showed a greater analyte recovery (Table 1).

Table 1. Cold solvent extraction of *n*-hexadecane (1.00 mg analyte/g of wood) from aged (21 days) samples under ambient conditions (4 days for each solvent). Results are presented as mean values ± standard deviation, the number of replicated experiments (n) is 3 unless indicated otherwise

	Recovery,%		
Extraction solvent	1st solvent	2nd solvent	Total
Acetone	38 ± 6[b]	NA[a]	38 ± 6
Acetone followed by 2-propanol	38 ± 6[b]	7 ± 1	41 ± 1
Acetone followed by *n*-pentane	38 ± 6[b]	55 ± 3	92 ± 2
Acetone + *n*-pentane (1:1)	43 ± 7	NA[a]	43 ± 7
Carbon disulfide	21 ± 7	NA[a]	21 ± 7
Dichloromethane	53 ± 3	NA[a]	53 ± 3
Dichloromethane followed by *n*-pentane	53 ± 3	11 ± 2	64 ± 2
n-Dodecane	47 ± 3	NA[a]	47 ± 3
n-Hentane	45 ± 5	NA	45 ± 5
n-Octane	43 ± 2	NA	43 ± 2
2-Propanol	37 ± 4[b]	NA[a]	37 ± 4
2-Propanol followed by *n*-pentane	37 ± 4[b]	7 ± 1	41 ± 3
2-Propanol followed by acetone	37 ± 4[b]	1 ± 0	38 ± 1
n-Pentane	57 ± 3[b]	NA[a]	57 ± 3
n-Pentane followed by acetone	57 ± 3[b]	6 ± 1	63 ± 3
n-Pentane followed by 2-propanol	57 ± 3[b]	8 ± 2	57 ± 6

[a]NA–not applicable, extraction was performed with a single solvent.

[b]Average for all experiments using this extraction solvent as a first solvent (n = 9); thus, the mean value of the total 2-solvent extraction efficiency differs from the sum for two sequentially applied solvents.

These results suggest that it is the size of the solvent molecules, rather than their polarity, that is a critical factor in releasing the strongly adsorbed *n*-hexadecane.

The use of binary mixtures instead of single solvents did not result in any significant improvement over single solvent extractions. By contrast, a much greater recovery (92%) was observed when a sequential extraction (with acetone followed by *n*-pentane) was used, this order of application of the solvents being essential for the improvement of analyte recovery.

Perhaps, the most unexpected effect observed was that the replacement of acetone with a solvent of a similar polarity, 2-propanol, in a similar two-step extraction was, by far, less successful (as well as other solvent combinations—no improvement was observed as compared to single solvents). It appears that the first (specific, polar) and second (non-polar) solvents play different roles in analyte extraction. The former, specifically acetone, seems to make the adsorbed fraction of *n*-hexadecane more available for removal by the latter. Since acetone and 2-propanol have similar wood swelling

abilities (26, 28–30), reversing the analyte absorption in cellulose/hemicellulose tracheid walls does not appear to be a critical factor.

The observed specific effect of acetone may be due to the disruption of the hydrogen-bonded aqueous network surrounding the analyte binding sites. 2-Propanol, as an alcohol, tends to make strong interactions with water (which is present in ambient wood up to 40–60% (30)) by hydrogen bonding. By contrast, acetone exhibiting only a moderate hydrogen bonding strength (26, 28, 30) cannot donate protons and may thus dissolve the aqueous layer rather than contributing to it. Cellulose and hemicelluloses chains also may be linked together by 2-propanol (simulating water) but not by acetone. The 1:1 mixture of acetone with *n*-pentane failed to achieve the extraction efficiency comparable to that of the sequential extraction (Table 1). It appears that this mixture is not polar enough to disrupt the aqueous hydrogen bonds sufficiently to make the strongly adsorbed *n*-hexadecane available for extraction. The proposed mechanism corroborates the earlier observation that wood pretreatment with ketones rather than alcohols improves the extraction efficiency for pinosilvine (8).

The information obtained in cold solvent extraction experiments leads to the following hypothesis for the mechanism of extraction of non-swelling contaminants from wood. The matrix interactions with *n*-hexadecane on high-affinity adsorption sites may be viewed as entrapment of the hydrocarbon into hydrophilic/hydrated "pockets" near the surface of hydrated carbohydrate polymers; perhaps, size-specific, like the inclusion of foreign molecules in polydextrine moieties (33, 34). Thus, the proposed sequential two-solvent extraction may be essential when the contribution of such a strong adsorption is significant. By contrast, whenever this contribution is less significant, the use of either single solvents or their mixtures may be sufficient. This postulated mechanism and proposed extraction strategy were tested in subsequent experiments as described below.

Ultrasound and Soxhlet Extraction

To reduce the total extraction time, other extraction techniques, i.e., ultrasound-assisted (sonication) and Soxhlet extractions were tested (Table 2). These treatments are known to disrupt the analyte-matrix interactions thus emulating the observed effect of the first solvent in sequential two-step cold extraction (35). As a result, the equilibrium establishes faster, analyte becomes accessible, and the solvent selection becomes less important. Indeed, ultrasound-assisted extraction was shown to be more effective than cold extraction of a similar duration, yielding about 65% recovery in the first 30 min and then remaining constant for longer incubations, up to 12 hours (thus indicating the achievement of near-the-limit partitioning). Contrary to the two-step extraction, the analyte recovery was

Table 2. Comparison of different extraction techniques for *n*-hexadecane extraction (1.00 mg analyte/g of wood) from aged (21 days) samples under ambient conditions (4 days for each solvent, in triplicate). Results are presented as mean values ± standard deviation

Technique	Duration	Extraction solvent	Recovery,%
Cold extraction	24 hours	*n*-Pentane (10 mL)	10 ± 2
		Acetone (10 mL)	10 ± 1
		n-Pentane:Acetone (5 mL:5 mL)	8 ± 1
Sonication extraction	24 hours	*n*-Pentane (20 mL)[a]	69 ± 5
		Acetone (20 mL)[a]	65 ± 7
		n-Pentane:Acetone (10 mL:10 mL)[a]	68 ± 2
Soxhlet extraction	24 hours	*n*-Pentane:Acetone (50 mL:50 mL)[a]	91 ± 7
Sonication followed by soxhlet	24 hours (sonication), 24 hours (soxhlet)	*n*-Pentane:Acetone (50 mL:50 mL)[b]	97 ± 6

[a]In sonication and Soxhlet extraction experiments, large volumes of solvent were used for convenience purposes only. Decrease in solvent volume to 10 mL did not affect recovery as shown in selected experiments.

[b]Sonication was done with 20 mL mixture of *n*-pentane: acetone (1:1); then, 80 mL of the same mixture were added and samples were submitted to Soxhlet extraction.

not affected by solvent selection; either *n*-pentane or acetone, or their 1:1 mixture yielded similar analyte recoveries (Table 2). This implies that a fraction of the matrix-analyte interactions remained undisrupted after sonication due to relatively high binding energies. When a higher-temperature (i.e., energy-intensive) Soxhlet extraction was employed instead of ultrasound-assisted extraction, the analyte recovery (with a similar duration of extraction) increased to nearly 90% (Table 2) thus corroborating with this hypothesis.

The best results were achieved when sonication and Soxhlet extraction were combined in a two-step procedure (97 ± 6%, i.e., virtually quantitative recovery). Thus, it appears that the thermal treatment (Soxhlet) and ultrasound-assisted extraction disrupt different (although, overlapping) matrix-analyte interactions. At higher temperature, desorption is favored, even for high-energy bonding; this may explain a slightly greater extraction efficiency for the sonication/Soxhlet treatment. In practical applications, the choice between this protocol and cold solvent extraction may be dictated by the number of samples to be analyzed and availability of multiple Soxhlet extraction apparatuses.

Cold Extraction of Higher Concentrations of *n*-Hexadecane (2–100 mg/g of Wood)

The proposed mechanism of extraction assumes adsorption of a certain fraction of the analyte on some specific sites on the surface of wood cells which can be reversed by solvents. This assumption implies a limited number of those specific sites so that the reduction of *n*-hexadecane recovery due to its adsorption would be negligible for larger amounts of the analyte. Indeed, when larger amounts of *n*-hexadecane were applied on wood and then aged as in previous experiments, the hydrocarbon was extracted from this aged sample almost quantitatively with acetone as a sole solvent (Fig. 2). Comparable analyte recoveries were achieved with 2-propanol or *n*-pentane (data not shown); i.e., extraction of large analyte amounts (e.g. 60–100 mg/g of wood) is not solvent-specific, reaffirming the insignificance of analyte-matrix interactions under these conditions.

The data in Fig. 2 show that the analyte binding within the wood is determined by the analyte-wood mass ratio rather than by the absolute amount of *n*-hexadecane. When the amount of applied *n*-hexadecane was less than ca. 60 mg/g, the portion of *n*-hexadecane remaining in wood was large and concentration-dependent. By contrast, when the concentration of applied *n*-hexadecane exceeded this threshold, the amount of *n*-hexadecane that remained in the wood (i.e., bound on high-affinity adsorption sites) was nearly constant (within statistical limits), 5–10 mg/g (becoming statistical zero for samples for which these amounts of *n*-hexadecane were statistically insignificant as compared to the amount

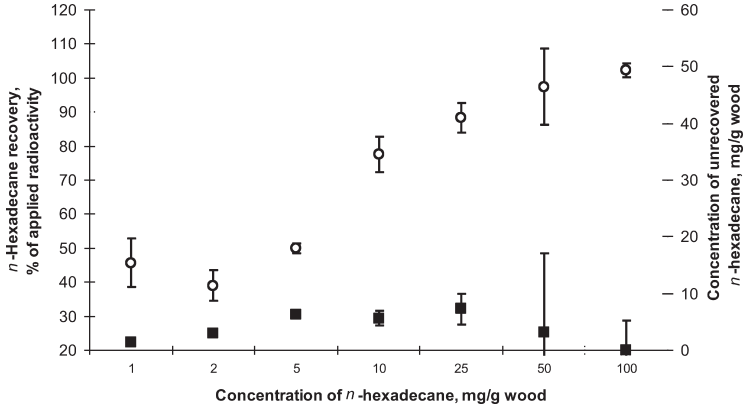

Figure 2. Effect of the concentration of applied *n*-hexadecane on its recovery upon a cold solvent extraction (4 days with acetone as a single solvent) from aged (21 days) ambient wood. ○-relative amount of recovered *n*-hexadecane, mg/g wood; ■-relative amount of unrecovered *n*-hexadecane, mg/g wood.

applied). As a result, significantly greater extraction recoveries (measured as a fraction of the original analyte) were achieved for larger analyte concentrations. Apparently, the number of high-affinity adsorption sites is constant and these sites are "titrated" by the applied amounts of a hydrocarbon until their saturation is achieved.

n-Hexadecane Extraction from Water-Submerged Wood

Experiments on the extraction of low amounts of *n*-hexadecane (1.00 mg/g of wood) were repeated for water-submerged wood with the single solvents and mixtures listed in Table 1. The major results are summarized in Table 3. These results indicate that analyte recovery is usually lower for water-submerged wood compared to the corresponding ambient wood samples (Table 1). This may be due to a greater aqueous barrier separating the hydrocarbon and extraction solvent. One exception is that the strategy proposed in the previous sections, i.e., sequential two-solvent extraction (with acetone followed by *n*-pentane), resulted in nearly quantitative recovery not affected by wood moisture content. This is consistent with the proposed extraction mechanism in which the role of acetone as a first solvent is the removal of the aqueous barrier surrounding the adsorbed analyte (plus collection of the weakly adsorbed analyte). Then, the extraction of a more tightly-bound *n*-hexadecane fraction (now exposed as a result of the first solvent application) is achieved with a non-polar second solvent.

Table 3. Cold solvent extraction of low amounts of *n*-hexadecane (1.00 mg/g of wood) from aged (21 days) water-submerged wood samples under ambient conditions (4 days for each solvent, in triplicate). Results are presented as mean values ± standard deviation.

	Recovery,%		
Extraction solvent	1st solvent	2nd solvent	Total
Acetone	29 ± 3	NA[a]	29 ± 3
Acetone followed by *n*-pentane	29 ± 3	64 ± 2	93 ± 5
Acetone + *n*-pentane (1:1)	28 ± 5	NA[a]	28 ± 5
Dichloromethane	35 ± 4	NA[a]	35 ± 4
n-Pentane	21 ± 3	NA[a]	21 ± 3
2-Propanol	76 ± 4	NA[a]	76 ± 4
2-Propanol followed by *n*-pentane	76 ± 4	10 ± 5	86 ± 3

[a]NA–not applicable, extraction was performed with a single solvent.

Extraction of Fuel Oil Hydrocarbons (200 mg/g of Wood)

To test the applicability of the developed methods to other fuel oil aliphatic hydrocarbons (its major components), the same protocols were used for extraction of fuel oil from aged water-submerged wood (inundation of samples in water prevented the unwanted evaporation of light hydrocarbons). Chromatograms of the fuel oil before its application on wood and after its extraction from 21-day aged wood were nearly identical (not shown), with 95% of C_{10}–C_{23} hydrocarbons being recovered with acetone or 2-propanol as single solvents, Table 4. Recoveries were slightly higher for smaller hydrocarbons (C_{10}–C_{13}), apparently, due to the difference in volatility.

The applied amounts of fuel oil (200 mg/g of wood) significantly exceeded the threshold for the saturation of adsorption sites (ca. 60 mg *n*-hexadecane/g of wood) thus explaining the observed near-quantitative recovery (Table 4). In select experiments, >95% analyte recovery was observed for higher concentrations of fuel oil or hexadecane, up to the wood pore saturation limit of 320 ± 90 mg/g wood (determined gravimetrically, measuring the mass difference of wood samples before and after submerging them into pure *n*-hexadecane for 21 days). Thus, the suggested extraction protocols are applicable within the entire range of pertinent analyte concentrations.

Table 4. Cold solvent extraction of major fuel oil hydrocarbons (200 mg/g of wood) from aged (21 days) ambient wood samples by shaking with a solvent for 4 days. Results of the experiments performed in triplicates are presented as mean values ± standard deviation

	Recovery, %	
Alkane	Acetone	2-Propanol
n-$C_{10}H_{22}$	107 ± 8	90 ± 9
n-$C_{11}H_{24}$	108 ± 9	96 ± 4
n-$C_{12}H_{26}$	91 ± 21	95 ± 6
n-$C_{13}H_{28}$	101 ± 12	94 ± 6
n-$C_{14}H_{30}$	103 ± 15	90 ± 13
n-$C_{15}H_{32}$	95 ± 16	92 ± 8
n-$C_{16}H_{34}$	100 ± 22	100 ± 8
n-$C_{17}H_{36}$	97 ± 12	96 ± 7
n-$C_{18}H_{40}$	96 ± 20	95 ± 10
n-$C_{19}H_{42}$	94 ± 17	96 ± 12
n-$C_{20}H_{44}$	95 ± 13	95 ± 6
n-$C_{21}H_{46}$	99 ± 6	96 ± 7
n-$C_{22}H_{48}$	99 ± 4	94 ± 8
n-$C_{23}H_{50}$	97 ± 12	87 ± 14

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