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Optimization of a drying method for filtered suspended solids from natural waters for supercritical fluid extraction analysis of hydrophobic organic compounds

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Abstract

This paper describes a closed-jar drying method (with a desiccant), developed specifically for filtered suspended solids, as a more efficient alternative to air-drying or freeze-drying. Supercritical fluid extraction (SFE) recovery studies to evaluate its efficiency were achieved with hydrophobic organic compounds of $\log K_{ow}$ ranging from 3.9 to 5.2, represented by polynuclear aromatic hydrocarbons (PAHs). The PAH analytes were “loaded” onto the suspended solids by sorption to better represent field-collected material. The necessity of drying a sample of filtered suspended solids prior to SFE was confirmed by direct comparison of the SFE recoveries from dry and wet samples. These results indicate that the drying technique is needed to develop reproducible samples to analyze by SFE. An explanation for the effect of water in SFE is proposed. Optimization of SFE parameters for natural filtered suspended solids confirms that the best conditions for SFE of PAHs consist of a pressure of 355 atm, a temperature of 120°C and a modifier consisting of 750 μl of a 1:1:1 (v/v) mixture of water, methanol and methylene chloride.

Keywords: Suspended solids; Sediments; Water analysis; Environmental analysis; Extraction methods; Drying methods; Polynuclear aromatic hydrocarbons

1. Introduction

Suspended solids (or suspended sediments) play an important role in the biological and chemical dynamics of an aquatic ecosystem [1,2]. They are principally composed of the fine fraction ($<63 \mu\text{m}$) of sediment materials [3] and possess larger surface areas for contaminant sorption [4]. They are also

identified as important components in the transport of sorbed hydrophobic organic compounds (HOCs) such as polynuclear aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in surface streams [5,6]. Also, it is recognized that the bioavailability of HOCs in natural waters depend upon the soluble “free” chemical concentration in the aqueous phase [2]. The suspended solids can remove the HOCs from solution and decrease bioavailability and lessen toxicity to aquatic organisms. Therefore, to evaluate the fate or hazards of HOCs in aquatic environments, it is necessary to separately analyze

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both the aqueous and suspended solids phases after quantitative separation of the phases. This work focuses on the analysis by supercritical fluid extraction (SFE) of the mobile fraction of solids, including resuspended solids in aquatic bodies – the suspended solids. A review of the literature indicates that no SFE recovery studies have been done on the suspended portion ($<63 \mu\text{m}$) of solids in the water column; only SFE of bed load sediments has been studied.

Drying is proposed as a necessary step in SFE analyses of suspended solids, as moisture decreases extraction efficiency of sediments, e.g., by 20% for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin as far as time required for achieving an equivalent enrichment [7]. Camel et al. [8] postulated that water usually hinders the extraction of apolar compounds by sheathing the surface of the matrix and acting as a barrier to CO_2 penetration. Roop et al. [9] found that the presence of water decreases the effectiveness of modifiers. Furthermore, restrictor plugging can often occur during off-line SFE when the sample matrices contain high concentrations of water, resulting in poor SFE flow-rates [10]. To avoid such restrictor problems, some workers attempted the use of drying agents (e.g., hydromatrix or pelletized diatomaceous earth [11–14], magnesium sulfate [11,14,15], sodium sulfate [11,16] and calcium chloride [16] used as a “bed” or mixed with the sample to retain the water inside the extraction cell). Burford et al. [11] have identified the problems with drying agents to include: (1) precipitation of the drying agent in the extraction cell outlet frit, restrictor, and/or in the collection solvent, (2) formation of a hard plug which may block the extraction cell, (3) plugging of the frit and restrictor due to removal of fines from the drying agent during SFE and (4) possible reaction with certain modifiers. In this study, the use of such drying agents will be avoided by drying the sample prior to SFE. However, it is not known which drying method is best for suspended solids collected on filters, as no studies have been conducted on drying methods for subsequent SFE. For bottom sediments, drying methods used prior to SFE are air-drying (e.g., [17,18]) and freeze-drying (e.g., [19]). However, air-drying increases potential losses, cross-contamination when drying multiple samples and exposure to air contaminants, while freeze-drying is time

consuming, involves expensive equipment and is not compatible with volatile analytes [20].

In most recovery studies using SFE, the samples or analytes used are either compounds spiked directly into a selected matrix (laboratory-spiked analytes), or natural matrix standard reference materials (SRMs), where the analytes are considered native (e.g., SRMs issued by the National Institute of Standards and Technology, Gaithersburg, MD, USA) [21]. The problem with laboratory-spiked samples is that they give recoveries that may not be representative of recoveries that would be obtained with aged native samples [22]. This is because natural samples have stronger matrix–analyte interactions between the analytes and the active sites in the matrix [23]. Aquatic suspended solids SRMs do not exist and sediment SRMs represent large portions of the particles greater than $63 \mu\text{m}$. The best choice is to “simulate” suspended solids and “load” them with known amounts of analytes through an actual equilibrium sorption process. These “loaded” samples are then collected by filtration (as would an environmental sample) for use in subsequent SFE recovery studies.

In this study, the filter used to collect the suspended solids was an MSI TCLP ($0.7 \mu\text{m}$ pore size, 142 mm diameter) glass fiber filter (Micron Separations, Westboro, MA, USA), selected in a separate study for filter artifacts and sorption behavior [24]. The analytes used are US Environmental Protection Agency (EPA) priority pollutant PAHs, which are not very volatile, have water solubilities of $>100 \mu\text{g}/\text{l}$ and which could partition onto 2.0 g of suspended solids phase at detectable levels (e.g., 5–100 μg of sorbed amount). Five three-to-four-ringed PAHs, with varying hydrophobicity ($\log K_{\text{ow}}$ 3.9–5.2; K_{ow} =octanol–water partition coefficient) and volatility, were selected as the final analytes (see Table 1).

The primary objective of this work was to determine the optimum method for quantitatively drying filtered suspended solids for the extraction of HOCs by SFE, using suspended solids “loaded” with analytes by actual equilibrium sorption. Closed-jar drying with a desiccant, air-drying and freeze-drying methods were evaluated. A secondary objective was to determine an optimum pressure–temperature–modifier combination

Table 1

Amounts of polynuclear aromatic hydrocarbons (PAHs) sorbed onto 2.0 g of suspended solids (SS) as determined by liquid–liquid extraction of the sorption solutions

PAH (log K_{ow} ; solubility, $\mu\text{g/l}^a$)	Vapor pressure mm Hg ^f (at 218°C) ^e	μg Spiked (in 1.0 l of water)	Aqueous saturation level ^h	Amount in sorption solution (μg)	[R.S.D. (%)]	Residual in sorption solution (μg)	[R.S.D. (%)]	Amount sorbed by 2.0 g SS (μg)	Percent sorbed
Acenaphthene (3.92 ^b ; 3930)	182	357	9.10%	298	(4.4)	288	(2.4)	10	2.7%
Fluorene (4.12 ^c ; 1980)	110	366	18.5	287	(2.9)	276	(1.9)	11	2.9
Phenanthrene (4.57 ^d ; 1290)	42	285	22.1	246	(4.2)	212	(2.0)	34	12
Fluoranthene (5.22 ^e ; 260)	14	195	75.1	197	(5.7)	136	(6.2)	62	32
Pyrene (5.18 ^d ; 135)	6	107	79.0	107	(9.3)	67	(5.9)	39	37

^a Mackay and Shiu [27].

^b Veith et al. [28].

^c Lyman [29].

^d Chiou et al. [30].

^e Carter and Suffet [31].

^f Calculated from the Antoine equation for vapor pressure: $\log_{10}P = a - b/(c + t)$ using the values of constants a , b , and c for the compound [32].

^g Arbitrary temperature. Also the boiling point of naphthalene (i.e., V.P. = 760 mmHg).

^h Relative to solubility values in column 1.

for the SFE of natural samples of suspended solids (filtered and dried).

2. Experimental

2.1. Analytes and GC analysis

All stock mixtures (1000–3000 $\mu\text{g/ml}$) of the PAH analytes (Chem Service, West Chester, PA, USA) were prepared in methanol or acetone (Pesticide Grade, Fisher Scientific, Tustin, CA, USA). All liquid–liquid extractions (LLEs) of aqueous samples were completed with methylene chloride (EM Science, Gibbstown, NJ, USA), as described in a separate study [24].

A Siemens Sischromat 2 capillary GC–flame ionization detection (FID) system (ES Industries, NJ, USA) with an SPB-1 column (60 m \times 0.32 mm I.D. from Supelco, Bellefonte, PA, USA) was used to quantitate the analytes, using peak-height ratios relative to the internal standard [10 μl spike of a mixture (in methanol) of 1000 $\mu\text{g/ml}$ of 1-chlorodecane and 1500 $\mu\text{g/ml}$ of 1-chlorohexadecane

(Aldrich, Milwaukee, WI, USA) into a 1.0-ml sample volume]. The GC conditions included a splitless time of 2.5 min, a temperature program starting at 40°C for 1.5 min and raised to 110°C at a rate of 25°C/min, then held for 1 min, then raised further to 300°C at a rate of 12°C/min and then held at 300°C for 15 min. Injection volume for the sample was 1.0 μl with 0.7 μl of solvent flush.

2.2. Suspended solids simulation and analyte "loading"

Suspended solids were simulated from a natural sediment from Orestimba Creek (San Joaquin Valley, CA, USA). The sediment was air-dried, ground and then sieved through a 63- μm sieve (Fisher Scientific). A 2.0-g sample of the fine sediment fraction [$<63 \mu\text{m}$, Organic Carbon (OC) = 1.0%] was placed in a 50-ml volumetric flask containing distilled water and was ultrasonically dispersed for 10 min. The resulting suspended solids concentrate was added to ultra-pure Milli-Q water (18 M Ω quality) to make a 2.0-g/l suspension of solids. The simulated solids suspension was shaken vigorously to make it

homogeneous. Appropriate volumes of the five-component PAH stock mixture was spiked into each sample containing 1 l solids suspension, to make the resulting PAH aqueous solution less than 80% saturated (see Table 1). The mixture was shaken (Eberbach, Ann Arbor, MI, USA) for 24 h at low speed, to allow sorption of the PAH analytes onto the suspended solids. Solutions without suspended solids were prepared for comparison.

2.3. Collection of suspended solids by filtration

After shaking for 24 h, each suspension was filtered through a Millipore Filtration System (142 mm filter diameter, Cat. No. YT30 142HW; Millipore, Bedford, MA, USA) which uses positive pressure of 20–40 psi from an inert gas. The filter used was an MSI TCLP glass fiber filter, 142 mm, oven-baked overnight at 150–175°C, as described in a separate study [24]. The early portion of the filtrate (≈ 200 ml) was used to rinse the container in order to collect particles that remained in the bottle, and then was poured back into the main suspension inside the filtration system. The final filtrate was observed to be clear from fine particles. To partially remove bulk water remaining on the filter, the applied pressure was increased to 60 psi for 5 min before final depressurization. The wet filter containing suspended solids was then folded in half and placed inside a wide-mouth 250-ml jar for storage in a freezer.

2.4. Drying methods

Contamination during air-drying in a desiccator or in a hood can occur. Even if the filter used is non-sorbing, such as the MSI TCLP glass fiber filter, contamination from the surrounding air may still result if collected suspended solids which contain active sorption sites are on the filter. To eliminate, or minimize, this problem, a closed-jar drying method specific to a wet filter containing filtered suspended solids was developed. Different desiccants were evaluated (in duplicate) to determine the optimum drying agent for a wet filter containing filtered suspended solids using the closed-jar method. The anhydrous drying agents studied were calcium chloride, 8 mesh (Spectrum Chemicals, Gardena, CA, USA), calcium sulfate, 4 mesh (W.A. Hammond

Drierite, Xenia, OH, USA), magnesium sulfate, powder (Fisher Scientific, Fair Lawn, NJ, USA) and sodium sulfate, 10–60 mesh (Fisher Scientific). Wet filters containing 2.0 g of filtered suspended solids were positioned inside each jar for drying. The masses of the filters were monitored every day for seven days. All the filters were then dried to constant mass at 110°C to determine the dry mass and the water content.

Each closed-jar drier consisted of a 500-ml (16 oz) wide-mouth short jar (Industrial Glassware, Milville, NJ, USA) with 100 g of freshly dried (at 110–120°C) desiccant placed at the bottom. Then, two clean and dry 10 ml test tubes were placed inside each jar at an “X” position relative to each other. The filter sample was then placed on top of the tubes, as the “X” position provided support. The glass support was needed to prevent the wet filter from coming into contact with the desiccant, otherwise the filter would stick to the desiccant by caking. After drying agent optimization, subsequent closed-jar drying experiments used the optimum desiccant, for at least 15 h of drying time.

Air-drying of the filters was done by exposing the wet filters in a hood overnight for at least 15 h. Freeze-drying was done for at least 15 h, using a three-piece (750 ml capacity) Virtis Freeze-Dryer Jar (Virtis, Gardiner, New York, USA), attached to the freeze-dryer port by means of a Labconco glass adapter (19/38 to 3/4 in. port; 1 in. = 2.54 cm) with a 90° bend (Labconco, Kansas City, MO, USA).

2.5. Supercritical fluid extraction of filtered suspended solids

The SFE experiments were done using a Model SFX 2-10 Supercritical Fluid Extractor (ISCO, Lincoln, NE, USA), with carbon dioxide as the solvent. The dried filter with suspended solids was compacted in a 10-ml sample cartridge. Surrogate standard (20 μg) (2,2'-difluorobiphenyl in methylene chloride) was then spiked into the sample. Then, 250 μl of acetonitrile was added as the modifier, based on the work of Langenfeld et al. [25]. The SFE conditions were 200 atm (1 atm = 101 325 Pa) and 50°C (supercritical CO_2 density = 0.79 g/ml) for 5 min static and 25 min dynamic extraction, at flow-rates of between 1.2 to 1.5 ml/min, using ISCO's coaxially-heated

restrictor, set to a temperature of 50°C by a Restrictor Temperature Controller (ISCO, Lincoln, NE, USA). The extracts were collected in 12 ml of methylene chloride contained in a 30-ml round bottomed culture tube with a screw cap. Methylene chloride has been shown by Langenfeld et al. [26] to be the best overall collection solvent for SFE of semi-volatile pollutants. During extraction, the bubbling of CO₂ into the collection solvent caused most of it to evaporate to 1–2 ml. The final volume was adjusted to exactly 0.5 ml by gently blowing nitrogen over the surface of the sample, followed by spiking of the internal standard. Exhaustive SFE of the analytes that remained sorbed on the dried sample was completed using two sequential extractions. After the first extraction, the sample cell was depressurized, 250 µl of modifier was again added, and the sample was re-extracted.

2.6. Soxhlet extraction

The Soxhlet extraction [33] of filtered suspended solids was performed for 20 to 24 h using 300 ml of methylene chloride at a cycle time of ≈13–15 min. The sample was placed inside a Pyrex glass extraction thimble (125×45 mm O.D.) with fritted disc sealed in. The Soxhlet extraction set-up consisted of a 1-l Kimax flask (24/40), Pyrex Soxhlet extractor (55/60 top; 24/40 bottom) and a Pyrex extraction condenser (55/60 bottom). After extraction, the extract was concentrated to 0.5 ml using a Kontes Kuderna-Danish apparatus consisting of a 10-ml concentrator tube (19/22) attached to a 500-ml evaporation flask (24/40 top; 19/22 bottom) with a three-ball Snyder column (24/40).

3. Results and discussion

3.1. Sorption or “loading” of PAH analytes onto simulated suspended solids

Table 1 shows the amounts of analytes sorbed onto the suspended solids during the 24-h contact period. Any loss of analyte not due to sorption (e.g., volatilization during the contact period, filtration or extraction) was accounted for by the fact that all the suspended solids mixtures and the reference aqueous

solution (no suspended solids) were subjected to the same shaking, filtration and extraction procedures. The data in Table 1 show excellent precision; the relative standard deviation (%) range was 2 to 9%. The extent of sorption is a function of hydrophobicity; the less hydrophobic analytes (lower K_{ow}) are less sorbed. This dependence of the amount sorbed on the hydrophobicity is supported by a straight-line relationship with a correlation coefficient (r^2) of 0.95, for a plot of percent sorbed versus log K_{ow} .

3.2. Closed-jar drying with a desiccant: optimization of drying agent

Fig. 1 shows the profile of water removal during seven days of drying. The fastest removal was achieved by anhydrous calcium chloride, which removed 99.8% of the water content after only one day. Thus, all subsequent closed-jar drying experiments were done using calcium chloride as the desiccant.

3.3. Evaluation of efficiency of drying using multiple sequential supercritical fluid extraction

The purpose of the drying recovery studies was to evaluate the efficiencies of different drying methods when applied to suspended solids collected on a glass fiber filter. Two sequential SFEs were used to

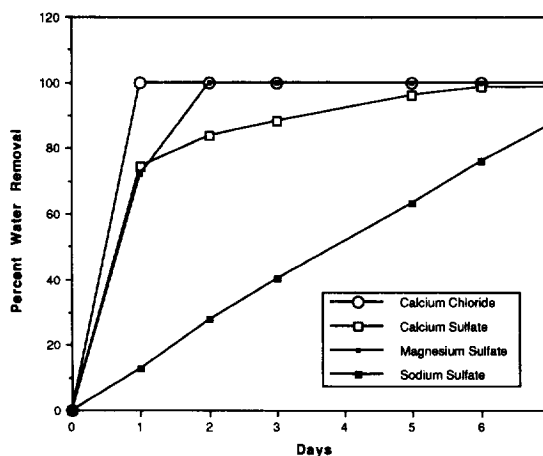


Fig. 1. Profile of water removal by different desiccants during closed-jar drying. Samples were wet MSI TCLP glass fiber filters containing 2.0 g of collected suspended solids.

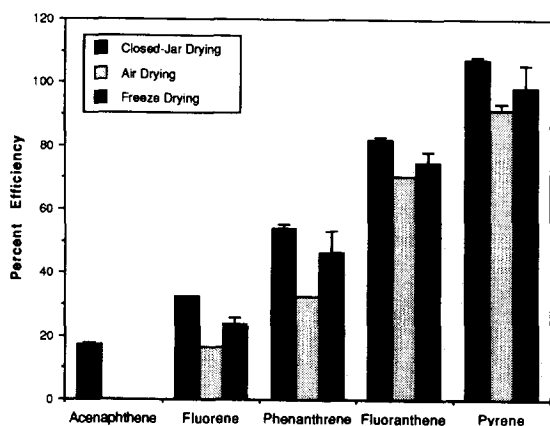


Fig. 2. Average recovery efficiencies of different drying methods for sorbed polynuclear aromatic hydrocarbons on filtered suspended solids. Error bars (standard deviations) are shown for triplicate analysis. Drying time was at least 15 h. Complete extractions were achieved using two sequential SFEs per sample. SFE conditions: CO₂ pressure=200 atm; temperature=50°C; modifier=250 μl of acetonitrile; time=5 min static, 25 min dynamic; collection solvent=methylene chloride.

ensure complete extraction of the analytes, as initial experiments showed that small amounts were detected in the second extract. Completeness was confirmed by a Soxhlet extraction after a second sequential SFE of another sample. The Soxhlet extract did not show any analytes.

Fig. 2 shows the results of the drying experiments. Air-drying has the lowest efficiency for all the analytes (0–91%), with the more volatile chemicals having the lowest recoveries. The most volatile

analyte, acenaphthene, was totally lost (100%) during the drying process, while the least volatile analyte, pyrene, still lost about 9%. Thus, air-drying should be avoided, although it is used in sediment analysis (e.g., [17,18]). Air-drying has also been shown to result in contamination of field samples with air contaminants, particularly PCBs [34]. Closed-jar drying and freeze-drying have better and similar recoveries for the most hydrophobic and non-volatile PAH analyte, pyrene. However, as volatility increases, more losses were incurred in freeze-drying than in closed-jar drying. The most volatile PAH analyte, acenaphthene, resulted in 100% loss by freeze-drying while closed-jar drying still retained 18%.

These results can be explained by the quicker volatility of a compound in an open system where there is air flow through the system. Freeze-drying has a constant “flow” pulling moisture away from the sample during the drying process and equilibrium is not achieved by the compounds. Closed-jar drying is a static drying method inside an air-tight system and the compounds are able to equilibrate according to their vapor pressures within the system. If the target analytes include volatile compounds, closed-jar drying is a convenient, more efficient and less expensive alternative to freeze-drying.

3.4. SFE of dry and wet filtered suspended solids

Dry and wet samples were extracted under the same SFE conditions. The dry samples were dried

Table 2

Sequential SFE recoveries^a of PAH analytes sorbed onto simulated suspended solids: comparison between dry and wet samples

PAH	Dry sample recoveries			Wet sample recoveries		
	First extraction (%)	Second extraction ^b (%)	Total (%)	First extraction (%) (moisture = 68.5%)	Second extraction ^c (%) (moisture = 63.2%)	Total (%)
Acenaphthene	19	0	19	23	24	47
Fluorene	31	0	31	29	34	63
Phenanthrene	52	6.6	59	18	27	45
Fluoranthene	66	12	78	10	21	31
Pyrene	96	5.6	102	8.5	20	29

^a Average of duplicate results based on the calculated amounts sorbed.

^b The third extraction did not show detectable analytes.

^c The third extraction showed more detectable analytes, indicating extraction was not complete after the second extraction.

using the closed-jar method. Recoveries from two sequential SFEs are shown in Table 2. The first extraction achieved better recoveries (19–96%) with dry samples than with wet samples (9–29%). For example, the recovery of pyrene from a dry sample was 96%, ten times greater than from wet sample. Also, the second extraction with dry samples gave smaller recoveries (0–12%) relative to the first extraction recoveries, indicating almost complete extraction. However, for wet samples, the second extraction gave recoveries from 20–34%, which are higher than the first for all the analytes. These results indicate a slower kinetics of dissolution by the supercritical fluid solvent when water is present. Thus, after two sequential extractions, the recovery of pyrene from the wet sample was only 29%, compared to 102% from the dry sample. This suggests that much more time is needed to completely extract pyrene from the wet sample and this also confirms the need to dry a sample prior to extraction. However, as volatility increased, the recoveries from the dry sample decreased due to losses during the drying process, while the recoveries from the wet sample increased, especially for the more volatile analytes, like acenaphthene and fluorene. This could imply that volatile compounds could be more efficiently recovered, albeit at a slower rate, when the sample is not subjected to any drying process.

3.5. Exhaustive sequential SFE of wet filtered suspended solids

Fig. 3 shows the results of seven sequential SFEs of pyrene from a wet suspended solids sample. The amount extracted from the wet sample first reached a maximum at the second extraction, then slowly decreased after the succeeding extraction. Apparent complete extraction was achieved only after the sixth extraction, as indicated by the absence of pyrene in the seventh extraction. This again supports the idea that water has to be removed from a matrix by drying in order to achieve complete extraction of higher molecular mass (non-volatile) compounds within a shorter time. Although drying is achieved at the expense of losing the low molecular mass (volatile) analytes, such loss is relatively small when closed-jar drying is used.

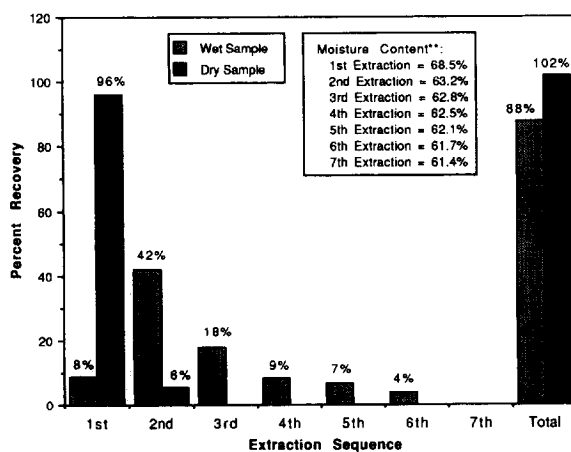


Fig. 3. Exhaustive multiple sequential SFE of pyrene from wet suspended solids: comparison to dry sample. Percent recovery is relative to the following amounts: dry=39.3 μ g; wet=37.9 μ g. SFE conditions are the same as in Fig. 2. **Moisture content was determined before the corresponding extraction.

3.6. Explanation of the effect of water on SFE

This study indicates that the effect of water is to slow down the kinetics of dissolution of an analyte in the supercritical fluid. Hitchen and Dean [35] described the mechanism of SFE of a solid matrix as a two-step process: (1) initial displacement of the analytes from the sample matrix, followed by (2) diffusion of the analytes from the sample matrix into the bulk of the fluid. In this mechanism, the rates of extraction are ultimately limited by the rate with which the analyte molecules are transported by step 2. This is assuming that step 1 occurs with no hindrance. Since step 1 involves interaction with the matrix, it becomes more important when the matrix contains natural organic matter (NOM) as sorption sites. In this case, the supercritical fluid must be able to compete effectively with a dried gel-like layer of NOM [36]. However, when water is present, a sheathing effect can result, whereby the water hinders the extraction by sheathing the hydrophobic surface of the gel-like organic matrix and acting as a barrier to supercritical fluid penetration [8]. Also, the gel-like matrix is not a pure solid with specific sites for sorption [36]. This makes the displacement of the analytes from the gel-like matrix more complicated than when there is no water present. Apparently, the

presence of modifier (acetonitrile) did not help to overcome the water sheathing effect or its interaction with the gel-like matrix. In this situation, step 1 of the mechanism appears to become the rate-determining step. As shown in Fig. 3, only 8% of the pyrene was extracted in the first extraction from the wet sample, compared with 90% from the dry sample. After two sequential extractions, recovery of pyrene from the dry sample was complete (102%), while that from the wet sample was only 50%. These results indicate that this drying technique is needed to develop reproducible samples to analyze by SFE.

The recovery from the second extraction of the wet sample (42%) was much greater than from the first extraction (8%). The likely reason is that during the first extraction, some of the water in the sample was mainly swept out (not dissolved) by the supercritical fluid, resulting in a decrease in the moisture content of the wet sample, from 68.5 to 63.2%, for the first and second extractions, respectively. The decrease in the amount of water in the matrix meant that less sheathing of the matrix and an initial breakup of the organic gel-like structure of the NOM occurred. This, in turn, allowed easier penetration by the supercritical fluid, resulting in a faster displacement of analyte from the matrix and greater extraction. However, in succeeding extractions, the decrease in moisture content from the previous extraction was not significant (e.g. 62.5 versus 62.1% for the 4th and 5th extractions, respectively). This indicates that little "sweepable" water was in the sample, only "residual" water was present and that the slight decrease was due primarily to dissolution of minute amounts of residual water by the supercritical fluid. Also, the gel-like structure of the NOM would change minimally and maintain its sorption sites.

Water solubility in supercritical carbon dioxide is approximately 0.3% ([37], as cited in [38]). Even in the 7th extraction, the moisture content was still very high (61.4%). Thus, the inability of a supercritical fluid to remove residual water from a wet sample and break the gel-like structure results in incomplete extraction, as shown in Fig. 3, where pyrene was still detected even in the 6th extraction. The rate of dissolution of pyrene in the supercritical fluid is slower when moisture is present. The 7th extraction did not show any more pyrene extracted but this may

not indicate complete extraction, since the grand total extracted was only 88%, compared to 102% for the dry sample after two extractions. This implies that when moisture is present, there is a "residual" amount of analyte which may remain unextractable and is probably part of the organic gel-like NOM material.

3.7. Selection of optimum SFE conditions for dry suspended solids collected on an MSI TCLP glass fiber filter

An optimum set of SFE conditions that could be used for extraction of PAHs from environmental samples of filtered suspended solids was developed. Four different studies in the literature [17,19,23,39], each using a different set of SFE conditions (Table 3), were selected based on extraction of PAHs from soil or sediment. The SFE conditions for pressure, temperature and modifier (P-T-M) in these studies were tested to find out which P-T-M was most "potent" and could result in the highest percentage extracted after a certain time period, thus the optimum condition (fastest extraction).

The samples used in this investigation were filtered suspended solids previously loaded with PAHs. The samples were dried using the closed-jar drying method for 15–24 h. The dry sample was compacted in a 10-ml sample cartridge and extracted by SFE, using the different P-T-Ms (see Table 3). Initially, a 10-min extraction time was used, but this resulted in complete extraction of some analytes, so an extraction time of 5 min (dynamic extraction) was used. (It would not be possible to ascertain which P-T-M was fastest if two or three P-T-Ms all gave 100% recoveries for the same analytes). The restrictor temperature was set at 75°C. The extracts were collected in 5 ml of methylene chloride, concentrated to 0.5 ml, spiked with internal standard and were then analyzed by GC-FID. Table 3 shows the percentage recoveries calculated relative to the total amounts obtained by duplicate 24 h Soxhlet extractions. The fastest extraction was achieved by Study 1 which gave recoveries ranging from 91–102% after 5 min. Surprisingly, Study 3, which corresponds to the highest pressure (400 atm) and the highest temperature (140°C), resulted in only 60–88% recoveries.

Table 3
Comparison of recoveries^a of PAH analytes after 5 min SFE using different pressure–temperature–modifier (P–T–M) combinations from selected studies

PAH	Percent recoveries [recovery (%)] and relative standard deviations [R.S.D. (%)]							
	Study 1 [19]		Study 2 [39]		Study 3 [17]		Study 4 [23]	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
Acenaphthene	102	(1.2)	93	(23)	87	(7.0)	88	(7.8)
Fluorene	95	(3.9)	68	(24)	79	(21)	85	(4.5)
Phenanthrene	93	(4.2)	66	(7.5)	79	(18)	81	(1.3)
Fluoranthene	92	(8.4)	61	(4.0)	67	(11)	79	(8.9)
Pyrene	91	(6.0)	60	(2.2)	60	(14)	76	(9.2)
<i>P</i> (atm), <i>T</i> (°C), <i>d</i> (g/ml) ^b	355, 120°C, 0.66		350, 90°C, 0.76		400, 140°C, 0.64		395, 80°C, 0.82	
Modifier (volume)	1:1:1 mixture ^c (750 μl)		methylene chloride (2 ml)		toluene (1 ml)		methanol (200 μl)	

^a Percent recoveries are relative to 24 h Soxhlet extraction.

^b Supercritical CO₂ density was determined using the ISCO SF Solver, Jr. (ISCO, Lincoln, NE, USA).

^c Mixture of water, methanol and methylene chloride.

Table 4

Relative recoveries of PAH analytes after 5 min SFE using different combinations of pressure, temperature and modifier: comparison of effect of toluene modifier and mixture^a modifier

	A	B	C
Pressure	400 atm	400 atm	355 atm
Temperature	140°C	140°C	120°C
Modifier	toluene (1 ml)	mixture (750 μ l)	mixture (750 μ l)
PAH	Recoveries ^b (%)		
Acenaphthene	102	123	152
Fluorene	99	106	140
Phenanthrene	82	71	88
Fluorene	74	80	91
Pyrene	69	84	93

^a Mixture of water, methanol and methylene chloride (1:1:1, v/v).

^b Calculated relative to amounts extracted by Soxhlet for 24 h. Recoveries much greater than 100% are due to evaporation losses of the more volatile analytes during Soxhlet extraction.

Table 3 also shows that Study 4 has higher pressure (395 atm) and higher CO₂ density (0.82 g/ml) than has Study 1 (355 atm; 0.66 g/ml), yet it achieved lower recoveries. Also, Study 3 has a higher temperature (140°C) than Study 1 (120°C), yet it also achieved lower recoveries. These results indicate that higher pressure or higher temperature alone (or greater density alone) does not guarantee the highest extraction efficiency. It is the combination of pressure, temperature and modifier which determines the optimum extraction efficiency. Most importantly, the identity of the modifier has been shown to have a larger impact in boosting the extraction efficiencies of PAHs and PCBs than does the modifier concentration [31]. This is shown by the P–T–Ms of Studies 1 and 3. These pressure and temperature combinations correspond to similar CO₂ densities (0.66 vs. 0.64 g/ml), thus similar solvent strength. However, Study 1 used water–methylene chloride–methanol (1:1:1, 750 μ l mixture) as the modifier, while Study 3 used toluene (1 ml) as the modifier. The results showed that the 1:1:1 mixture of modifier was much better than toluene in boosting extraction efficiencies (91–102% vs. 60–87%). Thus, this study indicates that the 1:1:1 mixture of modifier is the best at helping to displace PAHs from the NOM dried-out gel matrix.

To confirm this point, more experiments were done where the two modifiers (toluene and the 1:1:1 mixture) were used with the same P–T combination, and the resulting recoveries after 5 min of SFE were compared (Table 4). Using the P–T combination of

Study 3 (400 atm; 140°C), toluene (1 ml) was used as the modifier in one extraction (column A), and the 1:1:1 mixture (750 μ l) was used in another (column B). Higher recoveries were achieved with the mixture modifier than with toluene for most of the analytes (e.g., 84% vs. 69% for pyrene). However, between the P–T combination of Study 3 using the 1:1:1 mixture as the modifier (column B) and the Study 1 P–T–M (column C), the latter was still the best P–T–M among those being evaluated, since it resulted in the greatest recoveries (e.g., 93% for pyrene). This confirms the earlier finding indicating that the Study 1 P–T–M is the best among the SFE conditions being evaluated. Thus, these conditions are recommended in the supercritical fluid extraction of PAHs and other HOCs from filtered and dried samples of suspended solids from the natural water environment.

4. Conclusions

SFE recovery studies for filtered suspended solids were achieved using selected PAH analytes previously sorbed or “loaded” onto simulated suspended solids by equilibrium sorption. Filtration of the mixture of suspended solids, using a non-sorbing 0.7 μ m glass fiber filter (MSI TCLP), allowed the quantitative separation of the suspended solids phase from the aqueous phase.

A drying method using a closed-jar with a drying agent inside it was developed specifically for drying

filtered suspended solids for subsequent SFE. Optimization studies identified calcium chloride as the optimum drying agent. Closed-jar drying is the optimum drying method, especially when the target analytes include volatile PAH compounds. In addition, closed-jar drying is comprised of a sealed system, preventing contamination from the surroundings.

The necessity of drying filtered samples of suspended solids prior to SFE has been confirmed for PAH compounds by this study. The primary effect of water was to slow down the rate of dissolution of the PAH analytes from the gel-like NOM. A proposed explanation for this phenomenon is that the water sheaths the surface of the matrix, making it difficult for the supercritical fluid to penetrate the matrix, and the gel-like matrix must be dehydrated to allow displacement of the analytes. The key SFE parameter appears to be the modifier type to interact with the collapsed gel-like NOM. These results indicate that the drying technique is needed to develop reproducible samples to analyze by SFE. The conditions recommended in the SFE of PAHs from filtered and dried samples of suspended solids from the natural water environment are as follows: pressure of 355 atm, temperature of 120°C and a modifier containing 750 μ l of water–methanol–methylene chloride (1:1:1, v/v).

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References

- [1] I.G. Droppo and E.D. Ongley, *Water Res.*, 28 (1994) 1799.
- [2] I.H. Suffet, C.T. Jafbert, J. Kukkonen, M.R. Servos, A. Spacie, L.L. Williams and J.A. Noblet, in J.L. Hamelink, P.F. Landrum, H.L. Bergman and W.H. Benson (Editors), *Bio-availability — Physical, Chemical, and Biological Interactions*, Lewis Publishers, Ann Arbor, MI, 1994, p. 93.
- [3] A.J. Horowitz, *A Primer On Sediment-Trace Element Chemistry*, Lewis Publishers, Michigan, 2nd ed., 1991, p. 136.
- [4] I.G. Droppo and C. Jaskot, *Environ. Sci. Technol.*, 29 (1995) 161.
- [5] R.P. Eganhouse and R.K. Kaplan, *Environ. Sci. Technol.*, 15 (1981) 310.
- [6] Y.L. Lau, B.G. Oliver and B.G. Krishnappan, *Environ. Toxicol. Chem.*, 8 (1989) 293.
- [7] F.I. Onuska and K.A. Terry, *J. High Resolut. Chromatogr.*, 12 (1989) 357.
- [8] V. Camel, A. Tambute and A. Caude, *J. Chromatogr.*, 642 (1993) 263.
- [9] R.K. Roop, R.K. Hess and A. Akgerman, in K.P. Johnston and J.M.L. Penninger (Editors), *Supercritical Fluid Science and Technology*, American Chemical Society, Washington, DC, 1989, p. 468.
- [10] M.D. Burford, S.B. Hawthorne and D.J. Miller, *J. Chromatogr.*, 609 (1992) 321.
- [11] M.D. Burford, S.B. Hawthorne and D.J. Miller, *J. Chromatogr. A*, 657 (1993) 413.
- [12] M.L. Hopper and J.W. King, *J. Assoc. Off. Anal. Chem.*, 74 (1991) 661.
- [13] N.L. Porter, A.F. Rynaski, E.R. Campbell, M. Saunders, B.E. Richter, J.T. Swanson, R.B. Nielsen and B.J. Murphy, *J. Chromatogr. Sci.*, 30 (1992) 367.
- [14] V. Lopez-Avila, J. Benedicto, N.S. Dodhiwala, R. Young and W.F. Beckert, *J. Chromatogr. Sci.*, 30 (1992) 335.
- [15] S.E. Eckert-Tilotta, S.B. Hawthorne and D.J. Miller, *Fuel*, 72 (1993) 1015.
- [16] W.H. Griest, R.S. Ramsey, C.H. Ho and W.M. Caldwell, *J. Chromatogr.*, 600 (1992) 273.
- [17] A. Meyer and W. Kleiböhmer, *J. Chromatogr. A*, 657 (1993) 327.
- [18] S. Bøwadt and B. Johansson, *Anal. Chem.*, 66 (1994) 667.
- [19] H. Lee, T.E. Peart, R.L. Hong-You and D.R. Gere, *J. Chromatogr. A*, 653 (1993) 83.
- [20] T. Greibrokk, *J. Chromatogr.*, 626 (1992) 33.
- [21] S.A. Wise, M.M. Schantz, R.M. Parris, R.E. Rebbert, B.A. Benner and T.E. Gills, *Anal. Mag.*, 20 (1992) M57.
- [22] B.E. Richter, in T. Cairns and J. Sherma (Editors), *Emerging Strategies for Pesticide Analysis, Modern Methods for Pesticide Analysis Series*, CRC Press, Boca Raton, FL, 1992, p. 51.
- [23] S. Reindi and F. Höfler, *Anal. Chem.*, 66 (1994) 1808.
- [24] M.B. Capangpangan, J.A. Noblet and I.H. Suffet, *J. Chromatogr. A*, in preparation.
- [25] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller and J. Pawliszyn, *Anal. Chem.*, 66 (1994) 909.
- [26] J.J. Langenfeld, M.D. Burford, S.B. Hawthorne and D.J. Miller, *J. Chromatogr.*, 594 (1992) 297.
- [27] D. Mackay and W.Y. Shiu, *J. Chem. Eng. Data*, 22 (1977) 399.
- [28] G.D. Veith, K.J. Macek, S.R. Petrocelli and J. Carroll, in J.G. Eaton, P.R. Parrish, and A.C. Hendricks (Editors), *Aquatic Toxicology*, ASTM STP 707, American Society for Testing and Materials, 1980, p. 116.
- [29] W.J. Lyman, in W.J. Lyman, W.F. Reehl and D.H. Rosenblatt

- (Editors), Handbook of Chemical Property Estimation Methods – Environmental Behavior of Organic Compounds, McGraw-Hill, New York, 1982, Ch. 2, p. 52.
- [30] C.T. Chiou, D.W. Schmedding and M. Manes, *Environ. Sci. Technol.*, 16 (1982) 4.
- [31] C.W. Carter and I.H. Suffet, in R.L. Swann and A. Eschenroeder (Editors), Fate of Chemicals in the Environment. Compartmental and Multimedia Models for Predictions, ACS Symposium Series 225, American Chemical Society, Washington, DC, 1983, p. 215.
- [32] J.A. Dean (Editor), Lange's Handbook of Chemistry, McGraw-Hill, New York, 13th Ed., 1985.
- [33] U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, Washington, DC, 3rd Ed., 1986.
- [34] R.E. Alcock, C.J. Halsall, C.A. Harris, A.E. Johnston, W.A. Lead, G. Sanders and K.C. Jones, *Environ. Sci. Technol.*, 28 (1994) 1838.
- [35] S.M. Hitchen and J.R. Dean, in J.R. Dean (Editor), Applications of Supercritical Fluids in Industrial Analysis, CRC Press, Boca Raton, FL, 1993, p. 1.
- [36] J. Pawliszyn, *J. Chromatogr. Sci.*, 31 (1993) 31.
- [37] M.S. Kuk and J.C. Montagna, in M.E. Paulitis, J.M. Penninger, R.D. Gray, and K.P. Davidson (Editors), Chemical Engineering at Supercritical Fluid Conditions, Ann Arbor Science, Ann Arbor, MI, 1983, p. 101.
- [38] V. Janda, K. Bartle and A.A. Clifford, in J.R. Dean (Editor), Applications of Supercritical Fluids in Industrial Analysis, CRC Press, Boca Raton, FL, 1993, p. 159.
- [39] V. Lopez-Avila, R. Young, J. Tehrani, J. Damian, S. Hawthorne, J. Dankers and C. van der Heiden, *J. Chromatogr. A*, 672 (1994) 167.