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Evaluation of selected filters for collection and subsequent supercritical fluid extraction of suspended solids for trace organic analysis

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Abstract

This study evaluated selected filters in order to find an appropriate filter that can be used to separate suspended solids (SS) from the aqueous phase with minimal sorption of the dissolved organic constituents in the aqueous phase, and that is compatible with subsequent supercritical fluid extraction (SFE) of hydrophobic organic compounds (HOCs) from the SS collected onto them. The sorption study for the filters was limited to the use of analytes in aqueous solution with no SS. Membrane filters and a glass-fiber filter with binder showed considerable sorption behaviour during filtration of aqueous solutions consisting of six polynuclear aromatic hydrocarbons (PAHs) as analytes. The extent of sorption of the analytes by the filters increased with the more hydrophobic compounds. A glass-fiber filter with no binder (MSI TCLP) was found to be non-sorbing towards the PAH analytes, and was further shown to be an appropriate filter for a series of 56 base/neutral/acid extractable organic compounds. SFE of the filter as received showed extractable compounds detectable by GC–MS. Thus, pre-cleaning of the filter is required for the removal of SFE-extractable background compounds prior to its use in the collection of SS for subsequent SFE.

Keywords: Filters; Suspended particles; Sample preparation; Supercritical fluid extraction; Polynuclear aromatic hydrocarbons

1. Introduction

The important role that suspended solids (SS) play in the biological and chemical dynamics of an aquatic environment has long been recognized. For example, equilibrium models of the fate of hydrophobic organic compounds (HOCs) always carefully evaluate the SS phase [1]. Suspended solids are principally composed of the fine fraction (<63 μm) of sediment materials [2], and many compounds demonstrate a high affinity for these fine fraction of sediments. Thus, they often can contain a number of contaminants, including complex HOCs such as polynuclear aromatic hydrocarbons (PAHs). Since SS comprise the moving fraction of the solid matrix of water bodies, they act as important components for the transport of contaminants in rivers [3,4]. Also, it is recognized that the bioavailability of HOCs in natural waters may depend upon the soluble 'free' chemical concentration in the aqueous phase [5]. The

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SS can remove the HOCs from solution and decrease bioavailability and lessen toxicity to aquatic organisms. Therefore, to evaluate the hazard of HOCs in aquatic environments, it is necessary to analyze both the soluble and the SS phases after quantitative separation of the phases.

The analysis of organic compounds on SS are usually achieved by extraction with liquid organic solvents using conventional methods, such as Soxhlet extraction [4,6], mechanical shaking [6], ultrasonic extraction [7,8], and homogenization [9]. These methods require a considerable amount of time (e.g. 8–72 h for Soxhlet) and result in different efficiencies. For example, a 24 h Soxhlet extraction achieved 83% average recovery of spiked radiolabelled anthracene from sediment, compared to 73% using mechanical shaking [6].

In recent years, researchers have turned their attention to supercritical fluid extraction (SFE) as a substitute for the conventional methods of extraction. Not only is SFE fast (quantitative SFEs are generally complete within 10–60 min per extraction), but also it employs harmless solvents like carbon dioxide. Furthermore, the properties of supercritical fluids (controllable solvent strength, better mass-transfer characteristics compared to liquid solvents, low-temperature compatibility, many are gases at ambient conditions) make SFE a very attractive alternative to extractions using liquid solvents [10]. Thus, SFE has been used to extract different compounds from a variety of environmental matrices, e.g., PAHs from sediments [11–13] and from urban particulate matter [14], oil, grease, and total petroleum hydrocarbons (TPH) from soil [15], PCBs from river sediment [14], etc. All these various studies point to the potential of SFE as an alternative analytical extraction technique for SS from aqueous systems.

Various techniques are used in the collection of SS for physical or chemical analysis, primarily centrifugation [4,8,9,16] and filtration [6,7,17]. Filtration using membrane or glass-fiber filters with a nominal pore size of 0.45 μm (the conventional boundary between dissolved and particulate phase) to 1.0 μm is a convenient way of collecting SS from the aqueous phase for further analysis by SFE. However, SS have not been collected on filters for subsequent extraction by SFE, and it is not known what problems, if any, will the filter contribute to the entire process, from the filtration step to the final SFE step. For natural waters, a crucial step in the measurement of organic compounds is collecting samples representative of the system at the time of sampling and ensuring that no extraneous materials are introduced or target compounds removed during sampling or transport and storage prior to analysis [18]. The same is true for SS collected by filtration for subsequent SFE.

In a study involving chlorinated biphenyls (CBs), the membrane filters appeared to adsorb all freely dissolved CBs, while the glass-fiber filters showed a limited adsorption [19]. Another work [20] reported that adsorption of colloidal and dissolved organic matter (DOM) onto glass-fiber filters resulted in an overestimate of the organics associated with particulate matter. DOM adsorption onto glass-fiber filters has been shown to be up to 35% ([21], as cited in [19]). Such adsorption by filters during sample filtration could contribute positive errors in the SFE analysis of organic compounds in the SS phase (since the SS are to be extracted together with the filter), and losses of solutes in the corresponding aqueous phase. This point is important especially in the determination of real-world partition coefficients. Most pitfalls in methodology of sampling and the determination of partition coefficients appear to origin from adsorption [22]. Also, if the filter shows incompatibility with SFE by contributing artifacts or background compounds during SFE, interferences will occur. For example, organic membrane filters may release organic compounds, sometimes initially present as preserving agents [23]. This work addresses these problems. Although a few other studies on different filters used for collection of SS had been conducted [24,25], none involved evaluation of filters for their suitability in subsequent SFE. In fact, a literature review indicates that no SFE studies have been attempted on SS collected on filters.

The objective of this work was to find an appropriate filter that can be used to separate SS from the aqueous phase without sorption of the dissolved organic constituents in the aqueous phase, and is compatible with SFE of hydrophobic organic compounds from SS collected onto them. An appropriate pre-cleaning method was developed. The test analytes used is a series of PAH probes of varying polarity (with log K_{ow} of 3.36–5.18, where K_{ow} is the

Table 1
Percent recoveries [a] (and percent relative standard deviations) from the liquid–liquid extraction of the aqueous PAH solutions after filtration

PAH ($\log K_{ow}$; solubility [c], μg/l)	%Saturation of PAH solutions [g]	Reference (blank) solution (no filter) [b]		Supor-450 filtrate		Nuclepore filtrate		Gelman Extra Thick filtrate		MSI TCLP filtrate		Whatman filtrate	
		Mean (%)	R.S.D. (%)	Mean (%)	R.S.D. (%)	Mean (%)	R.S.D. (%)	Mean (%)	R.S.D. (%)	Mean (%)	R.S.D. (%)	Mean (%)	R.S.D. (%)
Naphthalene (3.36 [d]; 31 700)	0.2	79	5	67	5	78	6	63	2	75	3	74	9
2-Methylnaphthalene (4.11 [d]; 25 400)	0.2	79	4	62	7	78	1	52	4	74	1	73	5
Acenaphthene (3.92 [e]; 3930)	1	89	4	71	6	87	4	56	8	84	3	84	2
Fluorene (4.12 [f]; 1980)	2	90	6	62	5	89	7	44	10	92	8	90	7
Anthracene (4.54 [d]; 73)	44	88	6	35	10	73	15	31	16	89	9	83	9
Pyrene (5.18 [d]; 135)	47	92	6	<dl [h]	–	77	11	<dl	–	88	12	85	11

[a] Mean of 6 trials for the reference solution (2 trials/round) and 3 trials for the filtrates (1 trial/round).
[b] The blank solution was passed through the filtration system without the filter.
[c] [26].
[d] [27].
[e] [28].
[f] [29].
[g] Based on the following amounts spiked into 2.0 l of water: naphthalene=121 μg; 2-methylnaphthalene=110 μg; acenaphthene=106 μg; fluorene=90 μg; anthracene=64 μg; pyrene=127 μg.
[h] <dl=less than detection limit.

octanol–water partition coefficient) and volatility (see Table 1) which represent many hydrophobic organic compounds in the aquatic environment, and a series of 56 basic/neutral/acidic (BNA) organic compounds.

2. Experimental

2.1. PAH analytes and preparation of aqueous PAH solutions

Table 1 lists the PAHs (Chem Service, West Chester, PA, USA) used in this study and their relevant properties. Primary individual PAH stock solutions (5000–10 000 μg/ml) were prepared in methanol or acetone (Pesticide Grade, Fisher Scientific, Tustin, CA, USA). From the stock solution, a secondary stock mixture in methanol containing all the PAHs was prepared such that a 25-μl spike of the mixture into 1.0 ml solvent results in an analyte concentration of 15–30 μg/ml for the different PAHs. A calibration curve was prepared by GC–FID analysis of different dilutions of the stock mixture.

Before preparing the aqueous PAH solutions, a trial 25-μl spike of the prepared 6-solute PAH mixture in methanol was made into 1.0 ml of methylene chloride for quantitation by GC–FID. From the calculated concentration, the spike volume of the stock solution into 2.0 l of water was then determined to ensure that the saturation level of the most insoluble compound will not exceed 80%, to prevent it from possible precipitation due to temperature fluctuations. Aqueous PAH solutions were then prepared by spiking the desired volume (e.g., 100 μl) of the PAH stock mixture into 2.0 l of ultra pure Milli-Q water (18 MΩ quality). The resulting PAH solution was swirled to ensure dissolution of the solutes. Table 1 also shows the saturation levels of each analyte from the spike volume used in the experiment.

2.2. Filters and filtration of aqueous PAH solution

The five filters selected in this study are comprised of two membrane filters [Supor-450 (polysulfone, 0.45 μm pore size, 142 mm diameter, Gelman Sciences, Ann Arbor, MI, USA) and Nuclepore (polycarbonate, 0.40 μm pore size, 142 mm diameter, Costar Corp., Cambridge, MA, USA)] and three glass-fiber filters [Gelman Extra Thick (borosilicate glass fiber with acrylic binder, 1.0 μm pore size, 127 mm diameter, Gelman Sciences, Ann Arbor, MI, USA); MSI TCLP (borosilicate glass fiber with no binder, 0.7 μm pore size, 142 mm diameter, Micron Separations Inc., Westboro, MA, USA); and Whatman GF/B (borosilicate glass fiber with no binder, 1.0 μm pore size, 125 mm diameter, Whatman, Maidstone, UK)]. These filters were selected based on availability, type of media, pore size at or near 0.45 μm, and diameter at or near 142 mm.

A Millipore Filtration System (teflon-lined, 142 mm filter diameter, Cat No. YT30 142HW, Millipore, Bedford, MA, USA) which uses positive pressures of <700 kPa from an inert gas was used in the filtration process. A series of 2.0-l aqueous PAH solutions was prepared in 2.5-l bottles as described previously. The prepared solutions were then filtered one after the other, changing the type of filter after each 2.0-l filtration. Each filtrate was collected in 4.0-l amber solvent bottles with teflon-lined caps. A 2.0-l aqueous PAH solution as reference (blank) was also passed through the filtration system without any filter. The different filters were folded and placed inside wide-mouth jars, and were stored in the freezer before subsequent drying and SFE. The entire series of filtration using the selected filters was done in three rounds to represent triplicate experiments for each filter. The pH of the solutions after filtration was monitored using an Accumet pH Meter 925 (Fisher Scientific, Tustin, CA, USA). All the filtrates showed practically the same pH range (6.8–7.0) as that of the reference solution.

2.3. Liquid–liquid extraction (LLE) and analysis of aqueous PAH solutions

Each filtrate (500 ml), including the reference (blank) aqueous PAH solutions, was extracted following a modified version of the batch shaking LLE technique described in Method 6440B [30], using 30 ml methylene chloride solvent (EM Science, Gibbstown, NJ, USA) per extraction. Surrogate standards [10 μl; a mixture of 1000 μg/ml difluorobiphenyl and 2000 μg/ml decafluorobiphenyl (Chem Service, West Chester, PA, USA) in methylene chloride] was

spiked into the sample prior to extraction. The sample was extracted in a 1-l Wheaton bottle, using 5 min magnetic stirring that produced a vortex effect, resulting in good mixing of the two phases [31]. Separation of the phases was achieved by pipetting out the organic layer, using a transfer pipette, into a separatory funnel. After three serial extractions, the combined extract was transferred for concentration in a micro Kuderna–Danish (K–D) apparatus (Kontes, Vineland, NJ, USA) consisting of a 5-ml concentrator tube (14/20) [where 14/20 is a designation for the joint size number of interchangeable joints, indicating that the computed diameter at the large end of the ground zone is 14 mm, and that the approximate length of the ground zone is 20 mm (Kontes Catalog, 1996)] attached to a 125-ml evaporative flask (14/20 at bottom, 24/40 at top), and a three-ball Snyder column (24/40). The sample was concentrated as described in Method 6440B to a final volume of 1.0 ml, spiked with 10 μl of internal standard, and analyzed by GC–FID.

2.4. Filter drying and supercritical fluid extraction

All the filters were dried at the same time inside an aluminum cabinet desiccator with a gentle nitrogen flow for 48 h. To ensure a uniform exposure of the filter surface, the filters were unfolded and suspended from paper clips hanging from the inside top of the desiccator.

The SFE of the different filters used to filter the aqueous PAH solutions was done using a Model SFX 2-10 Supercritical Fluid Extractor (ISCO, Lincoln, NE, USA) by compacting the air-dried filter in a 10-ml sample cartridge. The surrogate standard solution previously described was then spiked into the sample in the cartridge at a ratio of 10 μl per 1.0 ml final volume of extract. Then 50 μl of methanol was added as modifier. The filters were extracted with supercritical CO_2 at previously determined optimum conditions consisting of 200 atm pressure and 50°C temperature (density=0.79 g/ml) for 5 min static and 20 min dynamic extraction, at flow-rates between 1.2 and 1.5 ml/min. (These conditions were previously determined to be sufficient for the type of matrix and analytes involved.) The extracts were collected in a 10-ml initial volume of methylene chloride contained in 30-ml round bottom culture tubes with screw cap. During extraction, the bubbling of CO_2 into the collection solvent caused most of it to evaporate to around 1 or 2 ml. The final volume was adjusted to exactly 0.5 ml by gently blowing nitrogen over the surface, followed by spiking of the internal standard. The sample was then analyzed by GC–FID.

2.5. GC–FID and GC–MS analyses

A Siemens Sichromat 2 capillary GC–FID (ES Industries, Berlin, NJ, USA) with an SPB-1 column [60 m×0.32 mm I.D., coated with 100% poly(dimethylsiloxane), 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 μg/ml 1-chlorodecane and 1500 μg/ml 1-chlorohexadecane (Aldrich, Milwaukee, WI, USA) into 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 25°C/min, then held for 1 min, then raised further to 300°C at 12°C/min, and held at 300°C for 15 min. The injection volume for the sample was 1.0 μl with 0.7 μl of solvent flush.

A Finnigan 9610 gas chromatograph with data acquisition on a Finnigan 4000 mass spectrometer was used for GC–MS analysis of selected extracts, following the EPA 525/625 methodology as modified in the US EPA Contract Laboratory Program (CLP), August 1991, Statement of Work for organic compounds. The method was upgraded by using a capillary GC column, and by adding more analytes to the quantification list. The gas chromatograph used a 30 m narrow bore (0.25 mm) DB-5MS (J&W Scientific, Folson, CA, USA) fused-silica capillary column. The helium carrier gas flow-rate was 40 cm/s. The initial column temperature was 30°C for 4 min, programmed at 6°C/min to 300°C, and held at that temperature for 30 min. Data were acquired (Superincos Data System, Finnigan) and stored over the mass range m/z 35–500 with a total scan cycle time of 1 s. Five or more spectra were measured during the elution of each GC peak. Compounds were identified by comparing their measured spectra and retention times to reference spectra in a database compiled by the user from the measurement of

authentic standard compounds under the same conditions used for the samples. Calculation of the target analyte concentrations was made by the Autoquan Software package (Finnigan, Cincinnati, OH, USA) using a linear fit of the three closest points in the multi-point response list for each analyte from the plot of area of unknown/area of standard versus amount of standard.

3. Results and discussion

3.1. Liquid–liquid extraction of aqueous PAH solutions

Table 1 shows the mean percent recoveries and relative standard deviations obtained from the LLE of the aqueous mixture of selected PAHs (32–63 μg/l) before and after filtration. The percent relative standard deviations show that the analysis method has good reproducibility. The recoveries from the reference (blank) solution (which was passed through the filtration system without any filter) reflect the maximum recoveries from the filtrates and represent no sorption of solutes. Thus, the degree of sorption of PAHs from aqueous solution onto a filter was determined by difference relative to the reference solution concentrations.

Fig. 1 shows the percent sorption of the PAH analytes onto the selected filters, calculated from the recovery data in Table 1. The figure shows that the membrane filter Supor-450 has considerable sorptive capacity. The most hydrophobic of the analytes, pyrene, is completely removed from the solution by the Supor-450. The Nuclepore filter also exhibits sorption towards the more hydrophobic analytes, although at a much lesser degree than the Supor-450. Among the glass-fiber filters, the Gelman Extra Thick filter, which has 5% acrylic binder, shows the largest sorption capacity compared to all the filters. In both membrane and glass-fiber sorbing filters, the extent of sorption generally increases with hydrophobicity; the more hydrophobic, the greater the amount sorbed. The other two glass-fiber filters, MSI TCLP and Whatman GF/B have no binders in them, and show less than 8% sorption of the selected PAHs from the aqueous solution. The glass-fiber filter MSI TCLP shows the best performance with less than 6% sorption of any solute. Since these values are rather small, they can be interpreted as mainly due to experimental error, and not due to actual sorption. Thus, both Whatman GF/B and MSI TCLP glass-fiber filters are considered non-sorbing. To confirm this, the filters used were extracted by SFE as discussed in the next section.

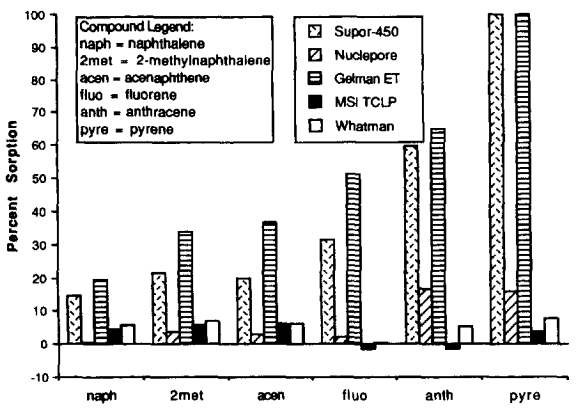

Fig. 1. Profile of percent sorption of PAH analytes onto selected filters after filtration of aqueous PAH solutions. Calculated from the data in Table 1. %Sorption=$[(A-B)/A]\times 100$, where A=%recovery from reference (blank) solution, B=%recovery from filtrate.

3.2. Supercritical fluid extraction of filters

One purpose of this study is to identify the problems that the use of filters as collection media will contribute to the SFE of SS for analysis of trace organics. Table 2 shows the amounts of PAH analytes sorbed onto the filters and also the amounts subsequently extracted from the filters by SFE. These results confirm the presence on the filter of the solutes that were sorbed from the corresponding aqueous solution by the filter during the filtration process. Thus, filters for use in the SS analysis by SFE should not be sorbing filters. On the other hand, the data in Table 2 also confirms the absence of PAH analytes from the filters shown to be non-sorbing. No PAH analytes were detected in the SFE extracts from Whatman GF/B and MSI TCLP glass-fiber filters.

Furthermore, Table 2 shows that the amounts extracted from the sorbing filters were either greater than or less than the calculated amounts sorbed during filtration. For example, the Gelman Extra

Table 2
Calculated PAH amounts sorbed onto the selected filters after filtration and amounts subsequently extracted from the filters by SFE [a]

PAH	Reference (blank) solution	Supor-450		Nuclepore		Gelman Extra Thick		MSI TCLP		Whatman	
	Total μg [b]	μg sorbed [c]	μg extr.[g]	μg sorbed	μg extr.[g]	μg sorbed	μg extr.	μg sorbed	μg extr.	μg sorbed	μg extr.
Naphthalene	95	14	23	1	<dl [e]	19	<dl	4	<dl	6	<dl
2-Methylnaphthalene	86	18	33	3	19	29	<dl	5	<dl	6	<dl
Acenaphthene	94	19	27	3	13	35	10	6	<dl	6	<dl
Fluorene	82	26	38	2	24	42	29	−2 [f]	<dl	<1	<dl
Anthracene	56	33	nq [d]	9	nq	36	nq	−1 [f]	nq	3	nq
Pyrene	116	116	77	18	23	116	499	4	<dl	9	<dl

[a] SFE conditions: pressure=200 atm; temperature=50°C; extraction time=25 min; collection solvent=methylene chloride; modifier=methanol (50 μl).
[b] Based on LLE recoveries from reference (blank) PAH solution in Table 1.
[c] μg sorbed=(%Sorption)×total μg in reference (blank) solution.
[d] Not quantitated due to interference from the SFE system. Later GC–MS analysis of the SFE system blank confirmed that the SFE system impurity at the retention time of anthracene was actually *n*-octadecane.
[e] <dl=less than detection limit.
[f] Negative sorption is interpreted as being due to experimental error, and should indicate zero sorption.
[g] extr.=extracted.

Thick filter sorbed 116 μg of pyrene, but the amount extracted from it was much greater, 499 μg, while the Supor-450 also sorbed 116 μg of pyrene, but the amount extracted was much less, 77 μg. For fluorene, the amount extracted from the Nuclepore membrane (24 μg) was much greater than the amount sorbed (2 μg), while the amount extracted from the Gelman Extra Thick filter (29 μg) was much less than the amount sorbed (42 μg). The most likely explanation for these observations should be the interaction with the surroundings. Since the individual filters in each study were dried at the same time in the same desiccator before extraction, the sorbing filters may have sorbed more of the compounds during the drying stage, either from neighbouring filters through volatilization and re-adsorption, or from contaminants in the surrounding air environment. These data may, therefore, indicate that sorbing filters have the ability to desorb or resorb contaminants to or from the surrounding air, and, thus, should never be used for SFE of SS. Even if the filter is non-sorbing from the air or water phases, contamination from the surrounding air is still a problem if the filter contains SS which have available sorption sites. This indicates the necessity for the development of an alternative drying technique where the filter is isolated from all sources of contamination. An individual filter drying technique reported by the authors has solved this problem [32].

3.3. SFE-extractable organic compounds from filters

Another concern in the use of filters as an SFE substrate is the presence of SFE-extractable organic compounds which may interfere with the analysis or contribute positive errors to it. GC–MS analyses of the SFE extracts of the individual filters in this study have shown detectable amounts of BNA organic compounds. The data obtained indicate that each type of filter, sorbing or non-sorbing, has some SFE-extractable compounds detectable by GC–MS. For example, the following compounds were detected in the extract of the Supor-450 membrane filter (but not in the SFE system blank) at <0.5 μg amounts: butylbenzyl phthalate, 4-chlorophenyl-phenyl ether, diethyl phthalate and naphthalene, while the MSI TCLP glass-fiber filter had benzopyrene (<0.5 μg), butylbenzyl phthalate (2 μg), diethyl phthalate (2 μg) and naphthalene (<0.5 μg). The most ubiquitous are phthalates, especially di-*n*-butyl phthalate and bis(2-ethylhexyl) phthalate which were detected in all the filters and in the SFE system blank at amounts ranging from 0.5 μg to 9

μg per filter. Of the target PAHs, naphthalene is the most prevalent, being detected in 3 out of 5 filters at <0.5 μg per filter. Of great importance, the glass-fiber filters primarily contain phthalates. Therefore, the data indicate that a pre-cleaning procedure is needed prior to the use of filters in SFE. This was developed for the filter of choice in the later part of this study.

3.4. MSI TCLP glass-fiber filter study 1: sorption behaviour towards BNA organic compounds

The filter of choice, the MSI TCLP glass-fiber filter, was further tested for its sorption behaviour towards an aqueous mixture of 56 BNA organic compounds. A 300-μl aliquot of 160 μg/ml BNA stock solution was spiked into 1.5 l of distilled water in a 2.0-l volumetric flask, and the resulting solution was swirled vigorously to dissolve the compounds. Because many of the components in the mixture have very low water solubilities, the resulting solution contained undissolved constituents. To remove these undissolved constituents, the mixture was filtered using an MSI TCLP glass-fiber filter into a 2.0-l volumetric flask, and the filter was discarded. The filtered solution was then diluted to 2.0 l to bring all the constituents down to unsaturated levels. Another 2.0-l solution was prepared in the same manner, and the two filtered unsaturated solutions were combined in a 4.0-l amber solvent bottle to make a composite solution. A 2.0-l portion of the composite solution was then filtered using another MSI TCLP glass-fiber filter to further test its sorption behaviour. The filtrate (labelled as Solution B) was collected in a 2.5-l bottle. The remainder of the composite solution was poured directly into another 2.5-l bottle without further filtration (labelled as Solution A). Aliquots (500 ml) of Solutions A and B were extracted, using the procedure for LLE described earlier. Each 500-ml aliquot was spiked with 10 μl of BNA surrogate standard mixture (Cat. No. 4-8925, Supelco). The extracts from each solution were concentrated to a final volume of 0.5 ml, and stored in a 2-ml vial for subsequent GC–MS analysis. The filter used was dried, then extracted using SFE following the methods previously described in the main study. The filter extract was adjusted to a final volume of 0.5 ml, and also stored in a 2-ml vial for subsequent GC–MS analysis.

Table 3 shows the results of this additional filter sorption study. In general, the results show two major points. First, that the filter has no sorption ability towards majority (at least 95%) of the compounds, as shown by their percent sorption values and confirmed by their absence (not detected) in the extract of the filter used. Note that all the PAH analytes previously studied were also not sorbed, confirming the previous results. Second, the filter apparently shows significant sorption towards certain highly polar compounds [marked with asterisk, notably benzoic acid (64%), carbazole (19%), and 3-nitroaniline (38%)]. However, their sorption on the filter used was not confirmed in the SFE extract of the filter. The only compounds (butylbenzyl phthalate, diethyl phthalate, di-*n*-butyl phthalate, isophorone, naphthalene and phenol) which were detected on the filter used were also detected in the unused filter (blank) and/or in the SFE system blank, all in trace amounts (<1 μg). Thus, these compounds are part of the system or filter impurities and are not considered as being sorbed by the filter from the aqueous solution. These observations also suggest that optimization of quality-assurance procedures is required when analysing filtered SS samples for trace organic compounds.

3.5. MSI TCLP glass-fiber filter study 2: filter pre-cleaning for SFE

As another consequence of the findings in this study, a filter cleanup experiment was conducted on the filter of choice, the MSI TCLP glass-fiber filter, to minimize the presence of SFE-extractable compounds in the extracts. Previous workers [24,25] performed filter cleanup procedures for glass-fiber filters using overnight heating in a furnace at 550°C and sonification with methylene chloride, respectively, but not in relation to SFE. For this study, two cleanup methods were tried. First, sonification with solvent of different polarities (hexane, methylene chloride and methanol). Second, overnight heating in an oven. The first method was done by folding the filter and placing it inside a 60-ml jar filled with the solvent, and sonifying it for 15 min. Fine particles from the filter were observed at the bottom of the jar

Table 3
Sorption behaviour of MSI TCLP glass-fiber filter towards an aqueous mixture of 56 BNA organic compounds

Compound [a]	Amount (μg) dissolved in 2.0 l (before filtration)	Estimated % sorption [b]	Compound [a]	Amount (μg) dissolved in 2.0 l (before filtration)	Estimated % sorption [b]
Acenaphthene	21	0	Dinitrotoluene, 2,4-	22	−9
Acenaphthylene	40	1	Dinitrotoluene, 2,6-	27	−9
Anthracene	14	−8	Fluoranthene	11	7
Azobenzene	26	−8	**Fluorene**	22	2
Benz[*a*]anthracene	2	7	Hexachlorobenzene	3	7
Benzoic acid*	4	64	Hexachlorobutadiene	3	9
Benzyl alcohol	12	0	Hexachloroethane	5	4
Bis(2-chloroethoxy)methane	32	−3	Isophorone	36	−4
Bis(2-chloroethyl) ether	26	−2	Methyl-4,6-dinitrophenol, 2-	16	9
Bis(2-chloroisopropyl) ether	26	9	**Methylnaphthalene, 2-**	21	−4
Bromophenyl phenyl ether, 4-	16	3	Methylphenol, 2-	23	−1
Butyl benzyl phthalate	16	0	Methylphenol, 4-	20	1
Carbazole *	59	19	*N*-Nitrosodi-*n*-propylamine	26	1
Chloro-3-methylphenol, 4-	33	−6	*N*-Nitrosodiphenylamine	73	10
Chloroaniline, 4-	26	−54	**Naphthalene**	25	−2
Chloronaphthalene, 2-	19	3	Nitroaniline, 2-	41	3
Chlorophenol, 2-	25	0	Nitroaniline, 3- *	30	38
Chlorophenyl phenyl ether, 4-	16	−4	Nitroaniline, 4-	9	−41
Di-*n*-butyl phthalate	18	−7	Nitrobenzene	34	−3
Dibenzofuran	21	1	Nitrophenol, 2-	31	−6
Dichlorobenzene, 1,2-	11	−3	Nitrophenol, 4-	14	9
Dichlorobenzene, 1,3-	9	2	Pentachlorophenol	26	7
Dichlorobenzene, 1,4-	10	0	Phenanthrene	18	−3
Dichlorobenzidine, 3,3'-	19	−3	Phenol	10	−2
Dichlorophenol, 2,4-	30	−4	**Pyrene**	11	−4
Diethyl phthalate	31	−3	Trichlorobenzene, 1,2,4-	13	1
Dimethyl phthalate	28	−2	Trichlorophenol, 2,4,5-	25	−9
Dimethylphenol, 2,4-	53	−4	Trichlorophenol, 2,4,6-	26	5

[a] Names in bold are the PAH analytes used in the main study; names with an asterisk are compounds considered significantly sorbed onto the filter.

[b] Estimated %Sorption=$[(A-B)/A]\times 100$, where A=amount (μg) before filtration, B=amount (μg) remaining after filtration.

of each solvent, indicating a slight degradation of the filter during sonification. Cloudiness was apparent in the methanol solvent only. The solvent was then poured off, and the filter was rinsed with a fresh portion of the solvent, then removed from the jar, air-dried flat on an aluminum foil in the hood for an hour before SFE. The second method was performed by placing the filter flat on a stainless-steel pan layered with aluminum foil and heating in an oven at 150–175°C overnight. The treated filters were extracted using the same SFE conditions as before, and the extracts were analyzed by GC–FID. A filter fresh from the manufacturer which was not subjected to any cleanup method was also extracted for comparison. A blank extraction was performed to check the system contribution to the background.

Fig. 2 shows the results of the MSI TCLP glass-fiber filter cleanup experiments. For comparison, the chromatograms of the untreated filter (A) and of the SFE system blank (F) are shown. The system blank shows the peaks of the internal standards used (labelled s) and the FID-detectable system impurity (labelled x). Note that all treated filters showed relatively clean chromatograms compared to the untreated filter. However, comparison of the chromatograms point to either sonification with methanol (D) or overnight oven heating at 150–175°C (E) as the best cleanup procedure for the filter

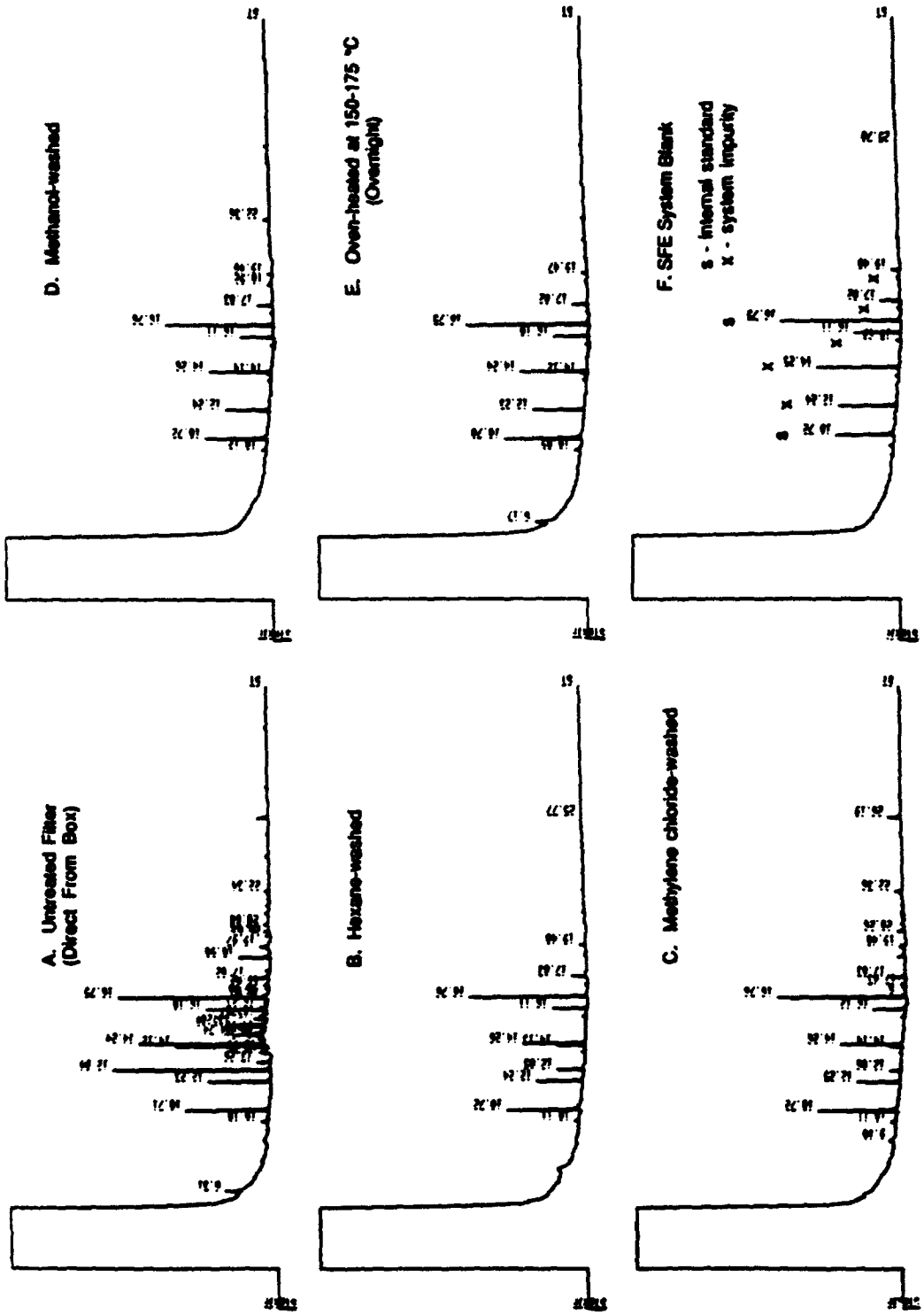

Fig. 2. GC–FID chromatograms of SFE extracts from MSI TCLP glass-fiber filters after different cleanup methods. SFE conditions are the same as in Table 2.

at the SFE conditions used. Chromatograms from both methods are the closest match to that of the system blank (F). For ease and convenience, overnight oven-heating at 150–175°C is the suggested method. Higher temperatures are not necessary. Furthermore, it does not result in filter degradation unlike sonification with solvents. However, it should be emphasized that a clean filter at certain SFE conditions may still give out extractables at different SFE conditions. Thus, cleanup experiments for a filter should be done for every set of SFE conditions used. For example, if heating in an oven at 150–175°C is not sufficient at stronger SFE conditions, then cleanup combustion of the glass-fiber filter at higher temperatures in a furnace (up to 15 h at 450°C [20]) should be considered.

4. Conclusions

This study has shown that there is a need to test filters intended for use in the collection of suspended solids for subsequent SFE. The sorption behaviour of certain filters towards hydrophobic organic compounds is considerable during filtration and subsequent air drying. Membrane filters in this study have all been found to be sorbing. The presence of binder in glass-fiber filters makes the filter more sorbing. The degree of sorption by the filters increases with the more hydrophobic compounds. The sorbing filters have also been found to sorb more of the analytes from the surrounding air during the drying stage of the filter before SFE. This suggests that the drying of filters containing collected suspended solids should be done in a closed system, which is the subject of another study [32]. The presence of SFE-extractable compounds from a virgin filter is another major concern. Such compounds may interfere with the analysis or contribute positive errors to it. This study has shown that even the non-sorbing filters in this study have SFE-extractable compounds (BNAs) that could affect an analysis.

The sorption experiments in this study were limited to the use of analytes in aqueous solution with no suspended solids. However, from the results of this study, the non-sorbing MSI TCLP glass-fiber filter was chosen to be the most appropriate filter to use for analysis of HOCs from suspended solids by SFE. To remove or minimize background compounds from this filter, a cleanup procedure using overnight oven-heating at 150–175°C or higher is recommended before use in an SFE analysis.

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