Validation studies for a new supercritical fluid extraction method for the isolation of hydrophobic organic compounds from filtered suspended solids

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Abstract

A newly developed SFE scheme (consisting of filtration, drying, and extraction steps optimized in two earlier studies) for the isolation of hydrophobic organic compounds from filtered suspended solids has been validated. Accuracy and precision data for the method were obtained for selected polynuclear aromatic hydrocarbons relative to certified and in-house Soxhlet values, using a standard reference material sample (EC-1 from Environment Canada). Compared to in-house results using EPA Method 3561, the recoveries from the optimized SFE step alone were much better, with an overall average accuracy of 101% and precision of 9% R.S.D., versus 74 and 13% for Method 3561, respectively. Unlike most SFE validation studies which validate only the SFE step, this study was able to validate the SFE scheme starting from the drying step to the final SFE step. The combined steps showed an overall average accuracy of 91%, with a precision of 8% R.S.D.. With this accuracy and precision, the newly developed SFE scheme has been proven to be acceptable. © 1997 Elsevier Science B.V.

Keywords: Polynuclear aromatic hydrocarbons; Validation; Extraction methods; Suspended solids

1. Introduction

Method validation is an integral part of the development of an analytical method. It is the process of proving that an analytical method is acceptable for its intended purpose [1]. For supercritical fluid extraction (SFE) methods involving sediments, the two important validation parameters evaluated are accuracy and precision. The accuracy is determined by extracting a standard reference material (SRM) and calculating the percentage recoveries (and precision) relative to the certified values, e.g., [2–4]. Alternatively, the accuracy of a method is determined by comparing the results from the method with in-house results from an existing alternate method that is known to be accurate [1], e.g., sonication or Soxhlet extraction. For example, Lopez-Avila et al. [5] determined the accuracy of their SFE method for polycyclic aromatic hydrocarbons (PAHs) from soils relative to the in-house sonication values. On the other hand, Hawthorne and Miller [6] determined percentage recoveries (of their SFE method to extract PAHs, N- and S-heterocyclics,

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chlorinated phenols and pesticides from soils) relative to in-house Soxhlet values. This approach is also recommended by US Environmental Protection Agency (EPA) Method 3561 (Supercritical Fluid Extraction of Polynuclear Aromatic Hydrocarbons) [7], as an alternative to the use of certified values. A comparison of SFE and in-house Soxhlet data using an environmentally contaminated PAH sample (not spiked) is done to assess the performance of the SFE method.

In the absence of acceptance guidelines for the validation parameters used, one way of assessing the acceptability of a new method is to compare its performance with the validation results from other similar new methods developed by the EPA, such as Method 3561. The validation data found in Method 8270C for EPA Method 3561 was obtained by directly extracting the SRM using the required SFE conditions, without doing the sample preparation steps prior to the SFE step. Such data therefore validate only the SFE step, and not the entire SFE scheme starting from sample collection. However, in this study, an important pre-SFE step (i.e. drying step) of the developed SFE scheme for filtered suspended solids was also validated, but using a sediment SRM instead of a suspended solids SRM, since no SRM specific for suspended solids is available. It should be understood that the "whole" or complete SFE scheme for filtered suspended solids was developed in a series of earlier investigations [8,9], and consists of the following three major optimized steps: (1) filtration of suspended solids sample with MSI TCLP filter (developed and optimized in Ref. [8]), (2) drying of filtered suspended solids using a closed-jar drying method (developed and optimized in Ref. [9]), and (3) extraction of dried filtered suspended solids by SFE using optimum pressure–temperature–modifier (P–T–M) combination (optimized in Ref. [9]). With a sediment SRM, the developed SFE scheme cannot be validated starting from step (1). Once the SRM is mixed with water to simulate a suspended sediment sample to be filtered, the certified values will no longer be valid because fractions of the analytes will be lost by partitioning into the water phase. Thus, method validation with a sediment SRM could only be achieved starting from step (2).

The objective of this study was to evaluate the accuracy and precision of the recoveries from the developed SFE isolation method, using a SRM. Initially, only the extraction (SFE) step was validated, using the determined SFE optimum conditions, to enable comparison of the resulting data to the EPA Method 3561 validation data, which were also based on the extraction step only. However, unlike many SFE validation or recovery studies which evaluate only the SFE conditions without subjecting the SRM to preparation steps prior to SFE, e.g., [2,4,10,11], this study went another step by also evaluating the SFE method starting from the pre-SFE drying step. With the SRM subjected to the drying step before SFE, the losses, if any, arising from drying to the point after SFE could be determined or quantitated, since at the beginning of the drying step, the certified or true values of the PAH analytes in the SRM are still the same. Since the filtration process [step (1)] for the suspended solids using MSI TCLP filter does not contribute to changes in analyte concentration in the suspended solids, as has been shown in a previous filter evaluation studies [8], the accuracy and precision obtained would represent the entire SFE method for filtered suspended solids, from collection by filtration to extraction by SFE.

2. Experimental

2.1. Standard reference material (SRM)

The SRM, EC-1 (National Water Research Institute, Environment Canada, Burlington, Canada), in powdered form and previously freeze-dried, is a lake sediment naturally contaminated with PAHs, and derived from Hamilton Bay, a heavily industrialized location in western Lake Ontario. The certified PAH concentrations in this material (Table 1, colum A) were obtained by over 75 in-house Soxhlet extractions followed by GC–flame ionization detection (FID), GC–MS, or HPLC–UV/fluorescence detection. These values were confirmed by an interlaboratory study involving 15 laboratories across Canada [11].

2.2. Determination of extraction time

A 1.00-g sample of EC-1 was extracted by SFE for 5 min static, followed by 25 min dynamic

Table 1
Recoveries of PAHs from a certified reference sediment (EC-1): comparison of SFE values to certified and Soxhlet values

PAH	(A) certified values[a] (μg/g)	(B) Soxhlet values[b] (μg/g)	(C) SFE values[b] (μg/g)
Naphthalene	–	44.0±5.4	40.7±4.1
2-Methylnaphthalene	–	2.0±0.1	2.0±0.2
Acenaphthylene	–	0.8±0.1	0.8±0.1
Phenanthrene	15.8±1.2	15.5±0.6	16.2±0.2
Anthracene	1.2±0.3	0.9±0.2	1.5±0.1
Fluoranthene	23.2±2.0	25.8±1.0	26.1±0.4
Pyrene	16.7±2.0	23.8±1.3	24.9±1.1
Benz[a]anthracene	8.7±0.8	9.1±0.2	9.3±0.5
Chrysene	9.2±0.9	10.2±0.2	10.2±0.3
Benzo[b]fluoranthene	7.9±0.9	15.8±0.2	14.3±0.6
Benzo[k]fluoranthene	4.4±0.5	5.7±1.3	7.1±1.0
Benzo[a]pyrene	5.3±0.7	5.6±0.1	5.1±0.4
Indeno[1,2,3-cd]pyrene	5.7±0.6	5.1±0.3	4.0±0.7
Dibenz[ah]anthracene	1.3±0.2	2.0±0.3	1.9±0.4
Benzo[ghi]perylene	4.9±0.7	5.2±0.3	3.7±0.6

[a] EC-1 does not have certified values for naphthalene, 2-methylnaphthalene and acenaphthene. Data from Environment Canada.
[b] Average of four results. Quantitative analysis was done by GC–MS.

extraction, using the optimum SFE conditions and modifiers (see Section 2.3). The extract was collected every 5 min (within the 25-min dynamic extraction time) in separate collection tubes, each containing 5 ml of methylene chloride. Each extract solution was concentrated to 1.0 ml, and analyzed by GC–FID for peak profile monitoring.

To determine the appropriate number of sequential extractions required per sample, another 1.0-g sample of EC-1 was extracted sequentially for 3 times, at the same extraction times, and the individual extracts from the 3 extractions were each concentrated to 1.0 ml, and analyzed by GC–FID for peak profile monitoring.

2.3. Validation of extraction step (SFE) alone

Four accurately weighed 1.00-g samples of EC-1 SRM were directly extracted (i.e. without being subjected to previous sample handling or preparation step), using a pressure of 355 atm, a temperature of 120°C and a modifier mixture consisting of 250 μl each of water, methanol and methylene chloride. A 2.0-g amount of fine granular copper metal (Mallindkroft, Cat. No. 4649-03) was placed at the bottom of a 10-ml sample cartridge to react with any sulfur from the sample, which could plug the restrictor if allowed to pass through the exit end of the sample cartridge. The SRM samples were enclosed

in a folded MSI TCLP filter, to simulate a filtered suspended solid, rolled to fit the 10-ml sample cartridge, then compacted inside the cartridge. The above-mentioned modifiers were then spiked onto the sample inside the cartridge. A 20-μl volume of surrogate standards (Method 8270 Surrogate Standard, Supelco, Catalog No. 4-7960, diluted to 2000 μg/ml level with methylene chloride), was also spiked onto the compacted sample to monitor the consistency of the extraction. The restrictor temperature was set at 120°C which was within the range of 100–150°C which is recommended in EPA Method 3561 for SFE of PAHs using fixed restrictor and liquid trapping. Each sample was extracted sequentially two times at the above-mentioned pressure and temperature, each for 5 min static and 20 min dynamic extraction, adding the modifiers before each extraction sequence. The extract was collected using an optimized liquid trapping method which uses a C_{18} SPE cartridge (Part No. 51910, Waters Corporation, Milford, MA, USA) as vent trap in a setup similar to that described by Barnabas et al. [12], with 10 ml of pre-chilled methylene chloride as the collection solvent, then concentrated to a final volume of 1.0 ml for subsequent GC–MS analysis.

For comparison purposes, another set of four accurately weighed 1.00-g EC-1 samples were extracted using EPA Method 3561 (SFE-Liquid Trap option) P–T–M combination (a pressure of 300 atm,

a temperature of 80°C and 800 μl of 1:1 v/v mixture of methanol and methylene chloride as modifier), for 60 min dynamic extraction as required, with methylene chloride as the collection solvent. (The modifier volume was equivalent to the 10% concentration recommended, since the void volume of the 10-ml sample cartridge filled with compacted filter with sediment sample was 8 ml).

2.4. Validation of the developed SFE method (starting from the drying step)

Wet MSI TCLP glass filters (previously oven-

with internal standard. All Soxhlet and SFE extracts were directly analyzed for PAHs using either GC–MS or GC–FID [8].

3. Results and discussion

3.1. Monitored extraction time and sequential SFEs

GC chromatograms generated from this preliminary experiment revealed that almost all of the analytes were extracted in the first and second 5 min

most of the analytes are greater than the certified values (column A), indicating a good extraction efficiency. However, four PAHs – pyrene (P), benzo[*b*]fluoranthene (B(b)F), benzo[*k*]fluoranthene (B(k)F) and dibenz[*a,h*]anthracene (D(a,h)A) – have unusually high recoveries (relative to the certified values) of 24.9, 14.3, 7.1 and 1.9 μg/g (or 149, 181, 160 and 147%), respectively. These values could mean that the SFE process is much more efficient than Soxhlet extraction from which the certified values were based, or that this is a result of inter-laboratory differences arising from differences in analysis techniques, standards, or in equipment from laboratory to laboratory ("interlaboratory effect"). To know which is the likely cause, one has to carefully examine the data in Table 2, which shows a compilation of interlaboratory results submitted by 14 Canadian participants [14] for the extraction of PAHs from EC-1, generated by a variety of extraction, cleanup and detection methods.

As shown in Table 2, the range for the concentration of the listed PAH analytes in EC-1 is wide, indicating considerable differences from laboratory to laboratory. For example, the range for benzo[*a*]pyrene is from a low of 2.6 μg/g to a high of 30.0 μg/g. Interestingly, for the four PAH analytes with unusually high SFE percentage recoveries (relative to the certified values), all the concentration values obtained (μg/g) fall within the range given in Table 2. For example, the amount of B(b)F extracted, 14.3 μg/g (or 181% recovery), falls within its range of 3.7–15.2 μg/g in the interlaboratory results. The same is true for the other three PAHs [B(k)F, P and D(a,h)A]. These results indicate that the concentrations of the aforementioned PAH analytes obtained in this study are unusually "high" only when compared to the certified values, but

Table 2
Interlaboratory results (μg/g) on selected PAH in EC-1 (partial list only)[a]

PAH	Range	Median	Mean±S.D.
Pyrene	9.6–26.0	18.5	18.4±5.2
Benzo[*b*]fluoranthene	3.7–15.2	6.8	8.1±3.6
Benzo[*k*]fluoranthene	2.8–16.6	3.6	5.6±4.2
Benzo[*a*]pyrene	2.6–30.0	4.5	6.6±6.8
Dibenz[*ah*]anthracene	1.4–11.0	2.4	3.6±2.4

[a] For a complete listing of available data, refer to Lee et al. [14].

"normal" when compared to the range in the interlaboratory results. This means that certified values from standard reference materials are not always reliable in assessing the accuracy of an analytical method, due to "interlaboratory effect", which could result in differences in analytical results for the same parameter. In fact, Hawthorne and Miller [6], have stated that since the analysis of a standard reference material (as well as extraction) is performed by the certifying agency, differences in both the extraction and analysis between laboratories can contribute to any apparent differences in recoveries. Such differences, unfortunately, were observed in this study, making the use of the certified values (as the basis for the accuracy of the SFE method in this study) an unreliable approach.

3.2.2. Accuracy relative to Soxhlet values

Soxhlet extractions of EC-1 were done in this study, and the results are also shown in Table 1 (column B). Note that the Soxhlet values, especially for the four PAH previously mentioned are much higher than the certified values (e.g., for pyrene: 23.8 μg/g Soxhlet, 16.7 μg/g certified), but in closer agreement with the SFE values (e.g., for pyrene: 23.8 μg/g Soxhlet, 24.9 μg/g SFE). This again confirms the "interlaboratory effect" observed previously. However, as shown in Table 1, most of the SFE recoveries appear to be more realistic when compared to the Soxhlet values than to the certified values. This happens because both the Soxhlet values and the SFE values were obtained in the same laboratory, cancelling out the "interlaboratory effect" responsible for the unexpected differences in recoveries. Thus, the four PAH analytes [P, B(a)F, B(k)F and D(a,h)A] mentioned previously with unusually "high" recoveries relative to the certified values (149, 181, 160 and 147%, respectively) now have "normal" values of 105%, 91%, 123% and 98%, respectively. Thus, with these observations, the determination of the accuracy of the SFE methods evaluated in this study will be based on the in-house Soxhlet values of EC-1, and not on its certified values.

3.2.3. Validation of the SFE step: accuracy and precision data compared to literature values

One way of assessing the performance of a newly

developed method is to compare it to similar methods with available performance data. Table 3 shows a comparison of accuracy (as percentage recovery) and precision (as percentage relative standard deviation) data between the SFE step in this study, and that of EPA Method 3561. However, to understand or appreciate the similarities or differences between results, one must know first the different parameters used to generate these results. Table 4 compares the validation parameters used in this study to those used in EPA Method 3561. Note that EPA Method 3561 has two options, the SFE-solid trap option and the SFE-liquid trap option. Both options have available accuracy and precision data from the literature (in

Table 3) to compare with. From the information given in Table 4, it could be seen that there are many differences between the three methods (pressure, temperature, modifiers, collection solvent and technique, etc.), which could contribute to differences in results. Thus, the following comparison of accuracy and precision will be considered only a "preliminary" comparison of method performance, due to unequal validation parameters.

Using the data in Table 3, this study and EPA Method 3561 (solid trap option) should be compared (column A vs. column B), since both used the same SRM (as well as the same type of extraction fluid) in generating the data. However, all the other validation

Table 3
Accuracy and precision of recoveries of the SFE of PAHs from EC-1: comparison of values obtained in this validation study to literature and in-house values using EPA method 3561 (M3561)[a]

PAH	A This study: SFE-liquid trap method for filtered SS[b]		B M3561: SFE-solid trap option[c] (literature values)		C M3561: SFE-liquid trap option[d] (literature values)		D M3561: SFE-liquid trap option[e] (in-house values)	
	%Rec[e]	%R.S.D. (n=4)	%Rec[f]	%R.S.D. (n=6)	%Rec[f]	%R.S.D. (n=4)	%Rec[f]	%R.S.D (n=4)
Naphthalene	93	10	(148)	9	91	11	96	9
2-Methylnaphthalene	100	9	NA[h]	–	122	2	91	8
Acenaphthylene	107	13	(112)	11	NA	–	51	13
Acenaphthene	ND[h]	–	(100)	5	91	3	NA	–
Fluorene	ND	–	(102)	12	87	3	NA	–
Phenanthrene	105	1	102	11	79	3	91	2
Anthracene	156	9	(88)	18	95	3	81	8
Fluoranthene	101	2	104	9	80	5	94	5
Pyrene	105	4	103	11	88	3	93	5
Benz[a]anthracene	103	5	101	11	89	5	81	10
Chrysene	99	3	(86)	11	95	4	80	5
Benzo[b]fluoranthene	91	4	108	13	86[g]	11	76	9
Benzo[k]fluoranthene	123	14	91	12	–	–	82	13
Benzo[a]pyrene	90	9	96	12	60	7	60	16
Indeno[1,2,3-cd]pyrene	78	18	91	12	NA	–	46	26
Dibenz[ah]anthracene	98	18	88	12	NA	–	47	32
Benzo[ghi]perylene	71	15	(85)	18	NA	–	41	33
Overall average	101	9	100	12	89	5	74	13

[a] Refer to next Table 4 for the validation parameters used.
[b] SS=suspended sediments.
[c] Data from Table 13, EPA Method 8270C, Rev. 3, January, 1995.
[d] Data from Table 15, EPA Method 8270C, Rev. 3, January, 1995.
[e] Relative to in-house Soxhlet values of EC-1.
[f] Relative to certified values of EC-1. However, values in parentheses were compared to Soxhlet extraction results which were not certified.
[g] Sum of benzo[b]fluoranthene and benzo[k]fluoranthene.
[h] ND=not detected; NA=not analyzed.

Table 4
Comparison of SFE validation parameters used in this study to those in EPA method 3561[a]

Validation parameters	A This study (SFE-liquid trap method for filtered SS)[b]	B EPA Method 3561 (SFE-solid trap option)	C EPA Method 3561 (SFE-liquid trap option)
SFE instrument used	ISCO SFX 2-10	Hewlett-Packard Model 7680	Dionex Model 703-M
SRM used	EC-1[c]	EC-1[c]	SRS103-100[d]
Extraction fluid	CO_2	CO_2	CO_2
SFE conditions:			
Pressure (P)	355 atm	$P_1 = 1750$ p.s.i. (120 bar) $P_2 = 4900$ p.s.i. (338 bar)	300 atm
Temperature (T)	120°C	$T_1 = 80$°C; $T_2 = 120$°C	80°C
CO_2 density (d)	0.66 g/ml	$d_1 = 0.30$ g/ml; $d_2 = 0.63$ g/ml	0.75 g/ml
Modifier (M)	250 µl each of H_2O, CH_3OH and CH_2Cl_2	5% 1:4 (v/v) $CH_3OH–CH_2Cl_2$	10% 1:1 (v/v) $CH_3OH–CH_2Cl_2$
Restrictor type	Fixed	Variable	Fixed
Restrictor temperature	120°C	80°C	120°C
Collection technique	Liquid trapping	Solid trapping	Liquid trapping
Collection medium	Methylene chloride	Octadecylsilane (ODS) trap	Chloroform
Extraction mode	Sequential (2)	Sequential (3)	Single
Extraction time	5 min static; 20 min dynamic for each of two sequential extractions	Extr. 1: 10 min static, 10 min dynamic at 1750 p.s.i. and 80°C. Extr. 2: 10 min static, 30 min dynamic at 4900 p.s.i. and 120°C. Extr. 3: 5 min static, 10 min dynamic at 4900 p.s.i. and 120°C.	60 min dynamic

[a] EPA Method 3561 (Revision 0, January, 1995): Supercritical fluid extraction of polynuclear aromatic hydrocarbons (from soils, sediments, fly ash and other solid materials amenable to extraction with conventional solvents).
[b] SS=suspended sediment.
[c] From Environment Canada (Burlington, Ont. L7R 4A6, Canada).
[d] From Fisher Scientific (Tustin, CA, USA).

parameters are different, especially the P–T–M combination (Table 4). Despite the differences in many of the parameters, the overall accuracy of the two methods was high and similar (101% vs. 100%), but the overall precision in this study was better than in the EPA Method (9% vs. 12%). On an analyte-to-analyte basis, four of the analytes – anthracene, chrysene, benzo[k]fluoranthene and dibenz[ah]anthracene – had significantly higher percentage recoveries in this study (98–156%) than in the EPA method, while another four – naphthalene, benzo[b]fluoranthene; indeno[1,2,3-cd]pyrene and benzo[ghi]perylene – had significantly higher recoveries in the EPA method (85–148%) than in this study. The analyte with lowest percentage recovery in this study was benzo[ghi]perylene (71%), which was also the lowest in the EPA method (85%). The other

PAHs analyzed in both methods had very similar recoveries in the vicinity of 100%. This indicates that in general, the SFE step in this study is as accurate as the SFE step in the EPA method, but with a better overall precision.

A more interesting comparison should be between this study and EPA Method 3561, liquid trap option (column A vs. column C), because both methods use liquid trapping as the analyte collection technique (as well as the same supercritical fluid and restrictor type). Having these parameters equal in both methods will help point to the difference in the SFE P–T–M combination as the most likely source of difference in recoveries, although the type of collection solvent (methylene chloride vs. chloroform) could also have some influence (Table 4).

Table 3 shows that the SFE recoveries of PAHs in

this study are higher (71–156%) than the recoveries in the EPA SFE-liquid trap method (60–122%). While the overall average percentage recovery in this study was 101%, the EPA method had only 89%. In terms of precision, the EPA method had a better precision (5% R.S.D.), while this study had 9% R.S.D., which could still be considered a good precision. In general, the SFE step in this study is more accurate than in EPA Method 3561 (SFE-liquid trap method) for all the PAHs analyzed in both methods. However, this conclusion is based on data generated not only by different SFE conditions, but also from different laboratories, where "interlaboratory effect" could contribute to the differences in results. As such, the conclusion needs to be confirmed by data generated in the same laboratory. This is discussed in Section 3.2.4.

3.2.4. Single laboratory accuracy and precision: comparison between this study and EPA Method 3561

Table 3 (Columns A and D) shows a comparison of accuracy and precision data between the SFE step in this study and that of EPA Method 3561, done in the same laboratory using identical analysis conditions. This ensures that the differences in resulting recoveries can be attributed only to differences in the SFE conditions between the two methods. As shown in the table, the SFE step in this study is more accurate than in EPA Method 3561. The overall percentage recovery from the former was 101%, compared to only 74% from the EPA method. The precision was also better in the former (9% R.S.D.) compared to 13% R.S.D. in the latter. Note that very low recoveries (41–60%) were achieved from the EPA method for the last four analytes in the list (benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene and dibenz[ah]anthracene), indicating that the SFE conditions in the EPA method are not sufficient to solubilize these highly hydrophobic compounds. On the other hand, the corresponding range from this study was 71–98%. Since the results from both methods being compared were generated in the same laboratory using the same analysis conditions, the differences observed confirm that the optimum SFE P–T–M combination of this study yields more accurate and more precise recoveries

than the P–T–M combination suggested in EPA Method 3561.

3.3. Validation of the SFE method starting from the drying step

3.3.1. SFE with closed-jar drying step vs. SFE without drying step

Table 3 (column A) also shows accuracy and precision data from direct SFE recoveries (i.e. without the drying step before SFE). On the other hand, Table 5 (column A) shows accuracy and precision data from SFE recoveries starting from the drying step (using the closed-jar drying method). Since the only difference between the two methods is the presence or absence of the drying step, the differences in recoveries can therefore be attributed only to the drying step. Thus, the data also validates the developed closed-jar drying method [9] as a sample preparation step in the SFE of filtered suspended solids.

The closed-jar drying step resulted in losses from a number of analytes (e.g., naphthalene, 2-methylnaphthalene, acenaphthylene, anthracene, benzo[k]fluoranthene), as shown by significantly lower percentage recoveries compared to those from the method without the drying step. However, the majority of the PAH analytes did not show significant losses due to the closed-jar drying step. In fact, the method with the drying step resulted in an overall average recovery of 91% (which is a fairly high recovery despite the inclusion of the drying step) compared to 101% when there was no drying step. The precision of the method with the drying step was also slightly better if not practically the same, 8% R.S.D., compared to 9% R.S.D. when there was no drying step.

3.3.2. Closed-jar drying vs. air drying

To further validate the closed-jar drying method as a preparation step in the developed SFE scheme, its performance was compared to that of a common drying method, e.g., air drying. Table 5 is a comparison of accuracy, precision and drying loss data, between closed-jar drying and air drying (column A vs. column B). Much lower recoveries from air drying compared to closed-jar drying for all the analytes was observed. While closed-jar drying had

Table 5

Accuracy and precision of recoveries for the SFE of PAHs from a certified reference sediment (EC-1) which was previously subjected to drying step before extraction: single laboratory performance comparison between closed-jar drying and air drying

PAH	A Closed-jar drying[a] (followed by SFE-liquid trap method for filtered SS)[b]			B Air drying[a] (followed by SFE-liquid trap method for filtered SS)[b]		
	SFE recovery[c] (%)	SFE R.S.D. (n=4) (%)	Drying loss[d] (%)	SFE recovery[c] (%)	SFE R.S.D. (n=4) (%)	Drying loss[d] (%)
Naphthalene	83	10	10	68	3	26
2-Methylnaphthalene	69	9	31	53	5	47
Acenaphthylene	80	3	25	47	13	55
Phenanthrene	97	3	8	73	6	30
Anthracene	129	8	17	96	5	39
Fluoranthene	99	3	2	85	5	15
Pyrene	99	6	6	78	7	25
Benz[a]anthracene	96	3	6	75	12	27
Chrysene	97	8	3	76	6	23
Benzo[b]fluoranthene	96	10	0	75	15	18
Benzo[k]fluoranthene	106	10	14	73	13	41
Benzo[a]pyrene	91	2	0	56	13	38
Indeno[1,2,3-cd]pyrene	77	12	1	37	16	52
Dibenz[ah]anthracene	80	20	19	39	14	60
Benzo[ghi]perylene	72	10	0	36	11	49
Overall average	91	8	9	65	10	36

[a] Before drying, wetness of sample was first simulated by enclosing it in a wet MSI TCLP filter like a real sample of filtered suspended sediment. Drying of the sample means drying of the wet filter with enclosed EC-1 sample.
[b] SFE conditions are given in Table 4.
[c] Relative to Soxhlet value.
[d] Relative to the SFE value with no drying (Table 1, column C).

an overall average recovery of 91%, that of air drying was only 65%. Overall precision was also slightly better with closed-jar drying (8% R.S.D.) than with air drying (10% R.S.D.).

Table 5 also shows the losses from both drying methods relative to the SFE value without the drying step. The results further confirms the high efficiency of closed-jar drying (as a preparatory step before SFE) compared to air drying. The overall average losses resulting from closed-jar drying is only 9%, compared to 36% from air drying. Thus, the closed-jar drying step in the SFE method for filtered suspended solids is an acceptable sample preparation step, which is necessary to achieve a good extraction accuracy and precision. Also, being able to quantitate the losses of certain analytes during the drying step means that proper corrections, if necessary, can be applied to the recoveries of these analytes from environmental samples to account for the losses from

the drying step, thereby achieving more accurate and reliable results.

4. Conclusions

This study has validated a newly developed SFE method for the isolation of hydrophobic organic compounds from filtered suspended solids. The complete method consists of three optimized steps: filtration step (using MSI TCLP glass fiber filter), drying step (using closed-jar drying method) and the extraction (SFE) step. Compared to results from EPA Method 3561, the recoveries from the optimized SFE step alone were much better, with an overall average accuracy of 101% and precision of 9% R.S.D., versus 74 and 13% for Method 3561, respectively. More significantly, the overall performance of the developed SFE method has also been validated

starting from the drying step, and the combined methods (steps) showed an overall average accuracy of 91%, with a precision of 8% R.S.D.. Since previous study has shown that the filtration step to collect the suspended solids does not result in changes in analyte concentration in the suspended solids, such accuracy of 91% and precision of 8% R.S.D. can be considered a reasonable measure of the overall accuracy and precision of the complete SFE method for filtered suspended solids, from sample collection by filtration to final extraction by SFE. With such accuracy and precision, the newly developed SFE method has been proven to be acceptable.

Acknowledgments

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