Determination of Polycyclic Aromatic Hydrocarbons in Sediment by Pressure-balanced Cold Fiber SPME

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ABSTRACT: Improved performance of the cold fiber solid-phase microextraction (CF-SPME) technique was accomplished with use of the pressure-balanced procedure. In order to obtain a pressure-balanced state during extraction at 200 °C, 7 mL of air volume was withdrawn from 10 mL commercial vials, while 15 mL were withdrawn from vials where 5 μL diethylamine was added as a modifier/displacer. The benefits of the balanced system were demonstrated for determination of polycyclic aromatic hydrocarbons (PAHs) from solid matrices, including sand and certified sediment samples. Results showed the pressure-balanced procedure enhanced the extraction efficiency of the method, especially for high volatility compounds, as the leakage of analytes was mitigated under sample temperature conditions of 200 °C. Analytical precision was also improved, with RSDs ranging from 4% to 8% for all analytes under study. For the determination of PAHs in certified sediment samples, Pressure-balanced CF-SPME yielded more accurate results in comparison to non-pressure-balanced CF-SPME. The proposed methodology provided the additional benefit of improved recoveries at lower pressures.

Owing to its high sensitivity, green technology, and integration of sampling and sample preparation steps, since its introduction in 1990[1], solid phase microextraction (SPME) has been widely used in many fields, including numerous applications in environmental, food, pharmaceutical, biology, toxicology, and metabolomics fields, among others.[2-7] SPME involves two types of extraction modes, direct immersion (DI-SPME) and headspace (HS-SPME) extraction. Since HS-SPME sampling is performed in the headspace above sample matrices, it can be used to extract volatile and semi-volatile compounds from very complex matrices such as sludge, wastewater, and soil.[6,8] In order to improve the extraction efficiency of analytes, researchers attempt to maximize the release potential of analytes from the matrix to the headspace; this can be particularly challenging for soil/sediments samples, in which analytes are bound strongly with matrix. While heating of the matrix can be an effective approach to accelerate the release of analytes to the headspace[9], elevated temperatures also decrease the distribution coefficients of the analytes between the fiber coating and sample matrix, leading to poor extraction results. To overcome this drawback, cold-fiber SPME (CF-SPME) was developed in 1995;[10] CF-SPME allows for simultaneous cooling of the extraction coating and heating of sample matrix. The CF-SPME technique has presented predominant performance for the extraction of volatile and semi-volatile compounds from complex matrices.[11-17]

The extraction efficiency of CF-SPME is mainly dependent on sample temperature, coating temperature, and extraction time. Sample temperature plays an important role in CF-SPME, as the heating of samples can accelerate the release of analytes from complex matrices to headspace. However, increasing sample temperature has been previously found to cause a significant increase in internal vial pressure, resulting in losses of sample vapor during extraction and upon removal of the SPME needle from the vial.[18] Furthermore, increase of internal vial pressure also could cause safety issues.[19] In order to overcome these drawbacks, the use of reduced pressure conditions during CF-SPME sampling should be considered, especially in view of the larger size of the CF-SPME needle in comparison to standard SPME needles, which can lead to larger punctures and faster deterioration of vial septa. Incidentally, the use of reduced pressure has also been demonstrated to assist extraction by increasing mass transfer at the sample gas interface. Darrouzès et al.[20] confirmed the positive effect of reduced pressure on the HS-SPME sampling of ethylated derivatives of butyl and phenyltin compounds, and showed that initiating the derivatization reaction after air evacuation minimized analyte losses and ensured more reproducible conditions for HS-SPME. Psillakis and co-workers[21-24] designed an approach to HS-SPME sampling based on vacuum conditions, leading to greatly increased extraction rates compared to HS-SPME under atmospheric pressure due to the enhancement of evaporation rates in the presence of an air-evacuated headspace. Overall, reducing pressure by evacuating air from the extraction chamber can facilitate the release rate of analytes from matrix to headspace, and minimize the possibility of analyte losses during HS-SPME sampling.

However, owing to the larger needle of CF-SPME, keeping the extraction chamber at a sub-ambient pressure could cause ambient air containing organic compounds to be driven into the chamber headspace, thus negatively influencing extraction efficiency. In the current work, Pressure-balanced CF-SPME is proposed for the extraction of polycyclic aromatic hydrocarbons (PAHs) from sediment samples. In this technique, the pressure between the internal vial and ambient air stay the same during the CF-SPME extraction process, while the sample is heated to a high temperature. The extraction efficiency and repeatability of Pressure-balanced CF-SPME and regular CF-SPME were evaluated for 5 PAHs in solid samples.

EXPERIMENTAL SECTION

Instrumental, materials and reagents. A CTC Combi PAL autosampler (Zwingen, Switzerland) with Cycle Composer software, and a Varian 3800 gas chromatography (GC) coupled with flame ionization detector (FID) were used for sand sample analyses. A 30 m × 0.25 mm × 0.25 μm SLB-5 fused silica column from Sigma–Aldrich was used for separations. The carrier gas was helium, and the flow rate was set at 1 mL/min. Oven temperature was initially set at 50 °C for 1 min, increased to 270 °C at a rate of 20 °C/min, then held for 13 min. The injector temperature was set at 270 °C in splitless mode. The detector temperature was set at 300 °C, with gas flows for makeup gas (nitrogen), hydrogen, and high purity air set at 25, 30, and 300 mL/min, respectively.

A GERSTEL® MPS 2 autosampler (GERSTEL, Mülheim an der Ruhr, Germany) and an Agilent 6890 gas chromatograph coupled to a 5973 MSD quadrupole mass spectrometer (Agilent Technologies, Mississauga, ON, Canada) were used for quantitative analysis of sediment samples in this study. In order to avoid any leakages and/or septa coring, SLH from GERSTEL was used for cold-fiber injection and liquid injection. The injector temperature was set at 250 °C. Separations were performed using a SLBTM-5MB (30 m × 0.25 mm × 0.25 μm) fused silica column from Sigma-Aldrich with helium (Praxair Canada, Mississauga, ON, Canada) as carrier gas at a flow rate of 1 mL/min. The oven program was started at 30 °C for 1 min, raised at a rate of 50 °C/min to 120 °C, then further raised at a rate of 4 °C/min to 280 °C, where it was held for 15 min. With the MS operating in electron ionization mode, the transfer line, MS Quad, and MS source were set at 280 °C, 150 °C, and 230 °C, respectively. The spectrometer was operated in single ion monitoring (SIM) mode using the molecular ion (m/z) of each compound (naphthalene: 128; acenapthylene: 152; acenaphthene: 154; fluorene: 166; phenanthrene and anthracene: 178; fluoranthene and pyrene: 202).

A standard vacuum needle gauge was ordered from The Vintner Vault Shop (Paso Robles, CA, USA), and fitted with a thinner needle (O.D. 0.51 mm, I.D. 0.25 mm) at the machine shop at University of Waterloo to fit the pressure measurements of the 10 mL vials. The preparation and design of the cold fiber device used in this study were as previously reported in the literature. [13,15,25] More materials and reagents are shown in Section S1.

Extraction procedure. Sand samples used in regular CF-SPME sampling were prepared by spiking 1 μL standard solution into 10 mL vials loaded with 1 g sand, then capped immediately to prevent any possible losses. After that, spiked sample vials were put on a vortex for 1 min, and analyzed 25 min after spiking. For Pressure-balanced CF-SPME sampling, a specific amount of air volume was withdrawn from a 10 mL vial loaded with 1 g sand with a 30 mL syringe to reduce pressure. Next, samples were spiked with 1 μL standard solution. The vacuumed sand samples were then vortexed for 1 min, and analyzed by GC-FID after 25 min. In addition, to verify the effect of small hole made by syringe during the air withdrawing process on headspace pressure, in-vial pressure was checked using modified needle gauge after air withdrawal of 7 mL, with result that pressure in vial headspace could maintain 2 h without change due to its sufficient thin needle.

The reference-certified sediment samples used in the extraction process were prepared by weighting 0.1 g sediment into 10 mL empty vials. A specific amount of air volume was then withdrawn from the vials to keep the vial pressure balanced. Prior to analysis by GC-MS, 5 μL of diethylamine was added into the vials as a modifier/displacer.

RESULTS AND DISCUSSION

Pressure in vial headspace. (1) Pressure in vial headspace for sand samples. A modified standard vacuum needle gauge was used to measure pressure changes in sampling vials at various temperatures. As shown in Figure 1, vial pressure decreased as air volume was increasingly withdrawn from the vial. In order to keep the ambient and internal vial pressures balanced, the internal vial pressure had to be maintained at ambient pressure (101.325 KPa). Accordingly, 7 mL of air were withdrawn from the vial using a syringe so as to keep the two pressures balanced for extraction at 200 °C.

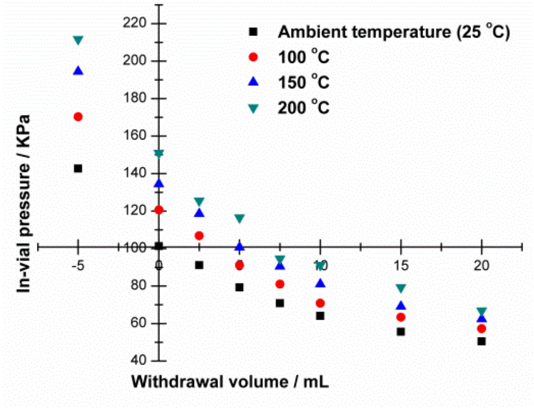

Figure 1. Pressure of in vial headspace in relation to air volume withdrawal at different temperatures.

(2) Pressure in vial headspace for sediment samples. For extraction of PAHs from real sediment samples, certain amounts of diethylamine were added into the samples prior to extraction so as to aid in the recovery by accelerating the release of analytes from the matrix.[15] However, as the addition of diethylamine can affect the internal vial pressure due to its vapor pressure. In addition, water vapor in the sampling vials should be also considered while heating to high temperature. The model of in-vial pressure was developed considering the expansion of air inside the vial stemming from the change in temperature from ambient temperature (25 °C) to 200 °C, and the vapor pressure of diethylamine and water vapor (as shown in Section S2).

Based on the developed model, relationship between liquid volume of diethylamine added into samples (V_W) and volume withdrawn from vial (V_D) can then be depicted by Figure 2, where the volume of air that needs to be withdrawn from the vial increases alongside the amount of diethylamine addition with various water level in samples in order to keep the vial balanced during the extraction process at 200 °C. It can be seen that water level presents an enormous implication on the in vial pressure, which indicates that samples should be dried while be used for extraction with Pressure-balanced CF-SPME procedure. In order to verify the accuracy of the model, pressure in vial without water addition was also measured experimentally after addition of diethylamine with a modified standard vacuum needle gauge, with results presented in Figure S1. In agreement with theoretical results, the experimental results confirmed the relationship between V_W and $V_{D,}$ as shown in Figure 2. Based on the established relationship between V_W and V_D, in order to keep the vial pressure balanced with ambient pressure, the amount of air volume that should be withdrawn from the sampling vials can be obtained when the amount of diethylamine added is known.

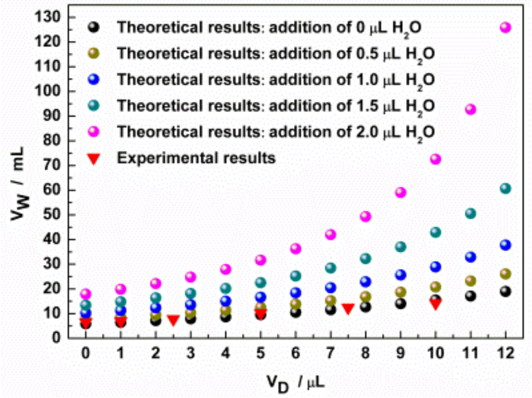

Figure 2. Relationship between V_W and V_D. V_D is liquid volume of diethylamine added into samples; V_W is volume withdrawn from vial.

Comparison of extracted amounts of PAHs in sand samples with Pressure-balanced CF-SPME and regular CF-SPME. Since CF-SPME sampling profiles (sample temperature and coating temperature) for determination of PAHs in sand samples have been optimized in previous research,[15] the focus of the current work mainly encompassed an evaluation of extraction performance for Pressure-balanced CF-SPME. As shown in Figure 3, the extracted amounts of PAHs in spiked sand samples were compared at various extraction times for extractions by regular CF-SPME and Pressure-balanced CF-SPME. In the case of regular CF-SPME, the extracted amounts for volatile compounds (naphthalene and acenaphthene) initially stayed at the same levels from 10 min to 30min of extraction time, but then were noted to decrease as extraction time increased. Conversely, extraction by Pressure-balanced SPME was noted to achieve constant extracted amounts within 60 min of extraction time. This phenomenon could be explained as an effect of the increased internal vial pressure during extraction. As the internal pressure of the 10 mL vials reached figures approximating 150.967 KPa at 200 °C, the pressure difference between the inside of the vial and ambient air gave rise to gas leakages stemming from the tiny holes made by the needle. As extraction time increased, more analytes escaped the vial, being released to ambient air. The decrease that caused by leakage was verified in Section S3 and Figure S2. However, when pressure was kept balanced between the inside of the vial and ambient air, decreases in extracted amounts of naphthalene and acenaphthene were not observed within 60 min of extraction. Similarly results were obtained for regular CF-SPME extraction of anthracene, where the maximum extracted amount was achieved at 40 min of extraction time, then noted to slightly decrease as extraction time increased; as observed with volatile analytes, extraction of anthracene remained constant when the pressure-balanced approach was used. For extraction of heavier compounds (fluorathene and pyrene) by regular CF-SPME, the extracted amounts were noted to increase along with extraction time, while for Pressure-balanced CF-SPME, these compounds reached equilibrium at 30 min. Pressure-balanced CF-SPME also presented higher extracted amounts than regular CF-SPME owing to the reduced in-vial pressure, which can facilitate the release of analytes from the solid matrix, and consequently, yield higher extraction efficiencies.

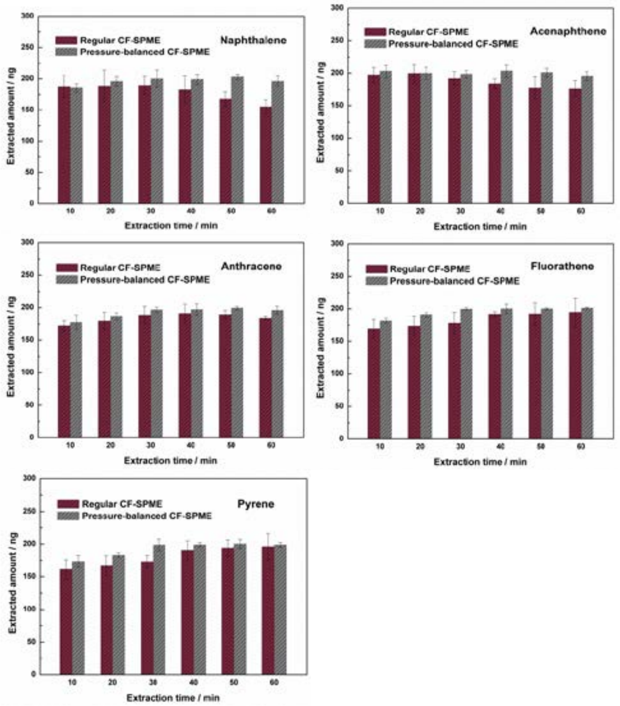

Figure 3. Extracted amounts of 5 PAHs in sand samples with various extraction times for regular CF-SPME and Pressure-balanced CF-SPME. Experiments were carried out at temperatures of 200 °C for samples, and 30 °C for coatings.

The effect of reduced and increased pressure on CF-SPME sampling from spiked sand samples was also investigated as shown in Section S4 and Figure S3. Results showed that reduced pressure in the vial headspace enhanced extraction efficiency as expected, while increased pressure decreased the extracted amount of PAHs and yielded poor RSD values, especially for the higher volatility analytes naphthalene and acenaphthene (Figure S3-a). In comparison to pressure-balanced extraction, sampling under sub-ambient pressure conditions, accomplished by withdrawing 20 mL of air from the vial, yielded almost the same extraction efficiency for naphthalene, acenaphthene and anthracene, while obtained a slight increasing for fluorathene and pyrene. However, extraction under sub-ambient pressure conditions could also lead to ambient air entering the vial headspace due to pressure differences, and as such, influence the accuracy and precision of the method. It is worth noting that pressure-balanced extraction achieved the best RSD results among the tested conditions (Figure S3-b).

Effect of vacuum procedure. Owing to their high volatility, lighter compounds in sand sample can be lost when withdrawing air from sample vials. Therefore, two kinds of vacuum procedures were investigated in this research: $1^{\#}$-withdrawal of 7 mL of air from vials containing spiked sand samples; $2^{\#}$-spiking of PAHs after withdrawal of 7 mL air from vials with sand only. As shown in Figure S4, no differences were observed for extracted amounts of acenaphthene, anthracene, fluoranthene, and pyrene with either vacuum procedure. However, owing to its high volatility, naphthalene was noted to be lost during vacuum procedure 1 in comparison to vacuum procedure $2^{\#}$. In order to avoid loss of high volatility analytes, vacuum procedure $2^{\#}$ was used for the remainder of this research with sand samples. However, for the real sediment samples, procedure $2^{\#}$ is impractical. In view of this, effect of air withdrawal on naphthalene loss in different matrix was investigated (Section S5). Results in Figure S5 showed that there was no loss for naphthalene in sediment sample when withdrawing 7 mL of air at ambient temperature (≈25 °C), due to its high affinity and adsorption. Therefore, pressure-balanced condition can be achieved for real sediment samples.

Table 1. Precision test for regular CF-SPME and Pressure-balanced CF-SPME

	Regular CF-SPME		Pressure-balanced CF-SPME	
	Average / ng	RSD / % (n=10)	Average / ng	RSD / % (n=10)
Naphthalene	189	18	196	7
Acenaphthene	200	11	200	5
Anthracene	179	10	187	6
Fluorathene	174	5	191	4
Pyrene	167	10	185	8

Evaluation of analytical precision for Pressure-balanced CF-SPME. Analytical precision for Pressure-balanced CF-SPME and regular CF-SPME was defined as the relative standard deviation (RSD) calculated from 10 samplings of sand samples spiked with 200 ng of 5 PAHs. Extractions were carried out for 30 min, with temperatures set as 200 °C for samples, and 30 °C for coatings. As shown in Table 1, the resulting RSD values for 5 PAHs ranged from 5% to 18% with regular CF-SPME. With the exception of fluoranthene, RSD values for all compounds were equal to, or higher than 10%. The worst precision was obtained for naphthalene, possibly due its comparative high volatility in relation to other PAHs, and consequently the higher possibility of leakage during the extraction process. Furthermore, analytical precision was much improved with the Pressure-balanced procedure during CF-SPME sampling, which yielded RSD values of less than 8% for all compounds. The results are presented in Table S1 and summarized in Table 1. Improvement of precision for Pressure-balanced CF-SPME method can be attributed to the fact that keeping pressure balanced between the extraction vials and ambient air mitigated the possibility of analytes leaking during the extraction process.

Determination of PAHs in sediment samples. In comparison to extraction from sand samples, exhaustive extraction of PAHs from sediment samples can be harder to achieve due to the strong interactions occurring between analytes and matrix. To address this challenge, Guo et al.[15] investigated the addition of organic modifier/displacers to facilitate analyte release from soil matrix, finding that diethylamine enhanced extraction efficiency significantly. It is anticipated that the mode of action of diethylamine displaced PAHs from the sorption sites of sediment, and release them from the carbon-rich matrix. Therefore, 5 μL of diethylamine as organic modifier/displacer was used in the extraction of PAHs from sediment samples. Water level in the certified sediment sample is 0.8 % in weight, indicating that for one trial 0.1 g sample contains 0.8 μL water. In accordance with Figure 2, 15 mL of air was chosen as the quantity to be withdrawn from the sampling vial to keep the pressure balanced during extraction. Figure 4 summarizes the extraction results of 8 PAHs from a certified sediment sample using regular CF-SPME and Pressure-balanced CF-SPME sampling procedures. For comparison, the certified values of the sediment sample were also given in the same figure. Use of the Pressure-balanced procedure resulted in improved extraction efficiency compared to regular CF-SPME. The recovery of eight PAHs ranged from 60 to 109 % for regular CF-SPME sampling, while recoveries from 82% to 109% were obtained for Pressure-balanced CF-SPME. In comparison to regular CF-SPME, Pressure-balanced CF-SPME yielded extractions that matched more closely to the certified sediment reference figures.

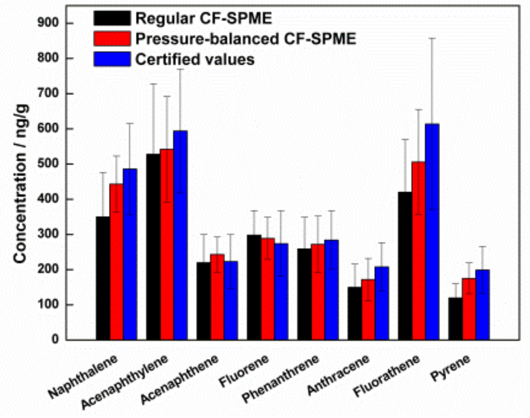

Figure 4. Analysis results of extracted PAHs from certified sediment samples using regular CF-SPME and Pressure-balanced CF-SPME after addition of 5 μL diethylamine. Extractions were carried out for 30 min under temperatures of 200 °C for samples and 30 °C for coatings.

Table 2. Z-test of PAHs results in sediment samples between experimental values and certified values at 95% confidence

	Z-values with regular CF SPME	Z-values with Pressure-balanced CF SPME
Naphthalene	-1.49	-0.47
Acenaphthylene	-0.75	-0.42
Acenaphthene	-0.05	0.38
Fluorene	0.37	0.23
Phenanthrene	-0.43	-0.21
Anthracene	-1.19	-0.73
Fluorathene	-1.12	-0.62
Pyrene	-1.67	-0.51

Z_{crit}=1.96, 2-tailed

In addition, a Z-test was used to evaluate differences between experimental data and certified values (results are shown in Table 2). As all experimental Z values are between -1.96 and 1.96, the 95% confidence Z_{crit} range assuming normal distribution of the population mean (certified value), the null hypothesis can be accepted, allowing for the conclusion that the sample mean is not statistically different from the certified value at a 95% level of confidence. Notably, the Z-values generated using the Pressure-balanced CF-SPME method ranged from -0.73 to 0.38, a decided improvement in comparison to figures generated with regular CF-SPME, which ranged from -1.67 to 0.37.

CONCLUSION

The proposed Pressure-balanced CF-SPME was found to achieve higher extraction efficiency and precision for all studied PAHs compounds in comparison to regular CF-SPME. High pressure conditions in the vial headspace at high temperature sampling conditions negatively impacted enrichment of PAHs onto the cold fiber due to losses via leakage of analytes, especially for volatile compounds owing to their higher headspace concentration. The pressure-balanced procedure effectively mitigated analyte leakage during extraction at high temperatures with use of commercial vials. Pressure-balanced CF-SPME can be applied for extraction of volatile and semi-volatile compounds from complex solid matrices, achieving extraction recoveries higher than those obtained by regular CF-SPME for certified sediment samples, and similar to certified values. Considering that Pressure-balanced CF-SPME is a “green” alternative to solvent extraction technologies, and that the method can be conveniently automated using commercially available autosamplers, these results open new possibilities for applications of Pressure-balanced CF-SPME in different fields as an alternative, greener analysis methodology.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Sections of (1) supplementary materials and reagents, (2) model of in-vial pressure with addition of diethylamine (3) quantification of PAHs in vials after heating to 200 °C, (4) effect of change in pressure as a function of in vial air volume, (5) effect of air withdrawal on naphthalene loss in different matrix; figures of (1) in vial pressure after addition of diethylamine at 200 °C, (2) PAHs amounts in vials after heated to 200 °C for 30 min, (3) comparisons of extracted amounts from spiked sand samples for different withdrawn volumes of air from vial headspace, (4) extracted amounts of 5 PAHs in sand samples with different vacuum procedure for Pressure-balanced CF-SPME, (5) effect of air withdrawal on naphthalene amount in different matrix; table of RSD results for regular CF-SPME and Pressure-balanced CF-SPME (PDF)

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The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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