



Rapid and sensitive method for the simultaneous determination of PAHs and alkyl-PAHs in scrubber water using HS-SPME-GC-MS/MS



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ABSTRACT

Scrubber water, a waste stream generated by ships exhaust gas cleaning systems, may pose a threat when released into the marine environment due to potential contamination with polycyclic aromatic hydrocarbons (PAHs) and their alkyl derivatives (alkyl-PAHs). This study aims to develop a reliable analytical procedure combining headspace solid-phase microextraction (HS-SPME) with gas chromatography coupled to triple quadrupole tandem mass spectrometry (GC-MS/MS) to simultaneously separate and determine target compounds in aqueous samples. Method validation demonstrated good linearity up to 200 ng L⁻¹ ($r^2 > 0.996$) and low limits of detection (0.33 to 1.67 ng L⁻¹, except for naphthalene at 3.3 ng L⁻¹). The method shows good precision (RSD < 20%) and satisfactory analytical recoveries. The methodology was successfully applied to scrubber water samples collected from a container ship and the results highlight the prevalence of naphthalene, phenanthrene, and their alkyl derivatives.

- Rapid and reproducible HS-SPME-GC-MS/MS method for the analysis of PAHs and alkyl-PAHs in scrubber water.
- The capacity of SPME to analyze both filtered and unfiltered samples was assessed, showing that the more hydrophobic PAHs may be lost during filtration.

Specifications table

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More specific subject area:	PAHs and alkyl-PAHs analysis
Name of your method:	Analysis of PAHs and alkyl-PAHs by HS-SPME-GC-MS/MS
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Resource availability:	GC-MS/MS (Thermo Fisher Scientific)

Introduction

Polycyclic aromatic hydrocarbons (PAHs) and alkyl polycyclic aromatic hydrocarbons (Alkyl-PAHs), which originated from petrogenic and pyrogenic activities, are frequent contaminants in the environment. These contaminants are well-known for their potential

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carcinogenic and mutagenic properties, as highlighted by the International Agency for Research on Cancer [1]. In particular, those of major concern are alkyl-PAHs with 3 to 5 rings, which have been pointed out as the main components of oil toxicity to aquatic organisms [2].

Scrubber water has emerged as a significant source of PAHs and their alkyl derivatives into the marine environment, among other compounds, (e.g. metals) [3]. Scrubber water represents a waste stream generated by exhaust gas cleaning systems (EGCs) employed on ships to mitigate gas emissions, especially sulfur oxides. Scrubber water contains substantial quantities of PAHs and alkyl-PAHs, particularly parent PAHs with 2 to 4 rings and their alkyl derivatives, which can extend up to 4 degrees of alkylation, as it has been documented in previous studies [4]. Currently, there are some methods available for the analysis of PAHs and their alkyl derivatives [5–7]. However, to the best of the authors' knowledge, none of them focused on scrubber water samples. Considering the complex PAH assemblages present in scrubber water, and the lack of proper methods, it is necessary to establish comprehensive analytical procedures that allow the determination of PAHs and their alkyl derivatives simultaneously, to conduct regular monitoring programs, allowing for the assessment of the environmental impact of scrubber systems.

For the analytical method, the development of an appropriate extraction technique for the isolation of target compounds and enrichment is essential to obtain reliable information from samples. In this sense, liquid-liquid extraction (LLE) and solid phase extraction (SPE) are the most common procedures used to determine PAHs from water samples. However, both techniques have some drawbacks, such as the need for large organic solvents and sample volumes, respectively, to achieve the required limits of detection [8,9]. Solid phase microextraction (SPME) is a promising alternative to these other methods because it can be easily automated and solventless technique, and the analytes are extracted from the liquid matrix into a non-miscible solid phase, mainly polydimethylsiloxane (PDMS). This allows the simultaneous extraction, concentration, and purification of the samples [10], reaching low limits of detection which are comparable or even lower than those achieved by LLE or SPE. Furthermore, SPME allows the analysis of filtered and un-filtered samples, minimizing the potential losses of the most hydrophobic PAHs and alkyl derivatives [11]. Concerning instrumental analysis, gas chromatography coupled to mass spectrometry (GC–MS) is commonly employed for the identification and quantification of volatile, thermally stable, and non-polar organic pollutants, including PAHs and alkyl-PAHs. However, the efficiency and selectivity of GC–MS methods depends on the level of interferences from the sample matrix, and to achieve lower limits of detection (LODs) an extensive sample clean-up procedure is often required. Gas chromatography coupled to triple quadrupole tandem mass spectrometry (GC–MS/MS) can overcome such limitations and provides a more selective identification of target analytes at trace levels in complex samples, reducing the limits of detection [12–14].

In this study, we developed and validated a rapid and sensitive analytical procedure based on HS-SPME coupled with GC–MS/MS, for the detection of PAHs and alkyl-PAHs in scrubber water. Even though SPME in combination with GC–MS/MS holds great potential, only few studies have used it for the analysis of PAHs and alkyl derivatives in environmental samples [15,16]. The validated method was successfully applied, for the first time, to determine PAHs and their alkyl derivatives in scrubber water samples, demonstrating its suitability for environmental monitoring and research purposes.

Method details

Reagents and standards

All organic solvents used for the preparation of analytical standards were chromatography grade. In the case of acetone, isooctane, and hexane (GC residue analysis) were purchased from Scharlab, S.L. (Barcelona, Spain) and, methanol and ultrapure water (Optima® LC/MS grade) were purchased from Fisher Scientific S.L. An internal standard mixture containing 5 isotopically labelled PAHs was obtained from Dr. Ehrenstorfer (Augsburg, Germany), including acenaphthalene- d_8 , chrysene- d_{12} , naphthalene- d_8 , perylene- d_{12} , phenanthrene- d_{10} (4000 mg L⁻¹ each in dichloromethane). A working solution was prepared at 20 mg L⁻¹ by appropriate dilution in methanol and finally, an intermediate solution was prepared at 10 µg L⁻¹ in ultrapure water, which was used as a surrogate standard mix. A standard mixture containing the 16 priority PAHs mixture at 2000 mg L⁻¹ of each analyte in benzene:dichloromethane (1:1) was provided by AccuStandard (Connecticut, EE. UU). A working solution was prepared at 10 mg L⁻¹ by appropriate dilution in methanol, and intermediate standard solutions were prepared at 10 µg L⁻¹ and 1 µg L⁻¹ in ultrapure water. Most of the alkyl-PAHs standards were purchased from Chiron Laboratory (Trondheim, Norway) and were: 1,2,5-trimethylnaphthalene, 1,3,7-trimethylnaphthalene, 1,2,5,6-tetramethylnaphthalene, 1-methylfluorene, 3,6-dimethylphenanthrene, 1,3-dimethylphenanthrene, 1,2-dimethylphenanthrene, 2,6,9-trimethylphenanthrene, and 1,2,6,9-tetramethylphenanthrene) and Dr. Ehrenstorfer (Augsburg, Germany) (1-methylnaphthalene, 2-methylnaphthalene, 2,6-dimethylnaphthalene, 1-ethylnaphthalene, 2-ethylnaphthalene, 2,3,5-trimethylnaphthalene, 2-isopropylnaphthalene, 1-methyl-7-isopropylphenanthrene (retene), 1-methylfluoranthene and 1-methylpyrene, except a few, that were purchased from Toronto Research Chemicals (Ontario, Canada), including 1,4,6,7-tetramethylnaphthalene, 1,7-dimethylfluorene and 1,2,6-trimethylphenanthrene. Individual stock solutions were prepared at 1000 mg L⁻¹ in isooctane and a working solution mix was prepared at 10 mg L⁻¹ in hexane. Intermediate standard solutions were prepared a concentration range from 1 µg L⁻¹ to 1000 µg L⁻¹ in acetone. All intermediate working solutions were prepared daily by diluting the working standard solutions. NaOH (ACS, ISO, Scharlau) was used to adjust the pH of scrubber water. Glass fiber filters (GF/F, 47 mm diameter, 0.7 µm mesh size) were obtained from Whatman (Buckinghamshire, UK). SPME fibers of 100 µm PDMS was supplied by Supelco.

HS-SPME-GC-MS/MS analysis

HS-SPME conditions

The optimized extraction methodology has been adapted from an existing in-house protocol that was developed for the analysis of the 16 US EPA priority PAHs in industrial wastewater samples [17]. In the methodology developed herein, besides the 16 priority PAHs, 12 alkyl PAH homologue clusters, representative for 5 different parent PAHs classes, were included. The methodology is based on headspace-solid phase microextraction (HS-SPME) using polydimethylsiloxane (PDMS, 100 μm) coated fibers. For the extraction optimization, the performance of some relevant parameters, including injector temperature, extraction and desorption times was evaluated, while the sample volume, the amount of NaCl and the extraction temperature were those from the original method [17], as they proved to be not as critical parameters as those optimized. The optimization of the extraction parameters was done using a mixture of standards (PAHs + alkyl-PAHs), and isotopically labelled standards, in water (Optima® LC/MS grade), spiked at 100 ng L^{-1} . The parameters tested were: injector temperature (280 and 300 $^{\circ}\text{C}$), extraction time (30, 40, 50 and 60 min) and desorption time (5 and 10 min). The final optimal parameters were further validated with both HPLC grade and sea water. In addition, the performance of the method was also tested with scrubber water, with samples produced from a pilot-scale engine lab operated with sea water samples as inlet water at the Department of Mechanics and Maritime Sciences, Chalmers University of Technology.

In the optimized methodology, HS-SPME analysis was performed in 20 mL amber glass vials equipped with screw caps and PTFE/Silicone septum. 10 mL of samples were transferred into vials containing 3 g of NaCl and adding 100 μL of a 10 $\mu\text{g L}^{-1}$ isotopically labelled standard mixture (acenaphthalene- d_{10} , chrysene- d_{12} , naphthalene- d_8 , perylene- d_{12} , phenanthrene- d_{10}). Conditioning of the fiber was performed at 250 $^{\circ}\text{C}$, during 30 min, following the recommendations of the manufacturer. The extraction temperature used was 90 $^{\circ}\text{C}$, for 40 min, with constant agitation, while the desorption temperature was 300 $^{\circ}\text{C}$ for 5 min. SPME fibre was post-baked at 280 $^{\circ}\text{C}$ for 5 min and several blanks were run periodically to avoid sample carryover. In the case of scrubber water, both filtered and un-filtered samples were analyzed to show the ability of SPME in assessing the PAHs and alkyl-PAHs sorbed onto particulate matter. Prior to the extraction, the pH of the scrubber water (ca. pH of 2.8) was adjusted to 7 with NaOH (1.5 M). Then, a subsample was taken and filtered using 0.7 μm glass fiber filters (Whatman GF/F) pre-combusted at 450 $^{\circ}\text{C}$ for 4 h. Since some compounds may be present at high concentrations jointly with analytes at trace levels in scrubber waters, both diluted (10 times) and undiluted samples are analyzed.

GC-MS/MS analysis

Instrumental analysis was performed in a Trace 1300 Series GC, with a TriPlus™ RSH autosampler coupled to the triple quadrupole tandem mass spectrometer (TSQ9000) (Thermo Fisher Scientific). The GC was equipped with a TraceGOLD TG-1701MS capillary column (30 $\text{m} \times 0.25 \text{ mm} \times 0.5 \mu\text{m}$ film thickness, Thermo Fisher Scientific). Samples were injected in splitless mode, to achieve maximum sensitivity. The carrier gas was helium at a constant rate (1.0 mL min^{-1}). The oven temperature program was held at 50 $^{\circ}\text{C}$ for 1 min and it was increased to 180 $^{\circ}\text{C}$ at a rate of 25 $^{\circ}\text{C min}^{-1}$, then it was further raised with a step of 6.5 $^{\circ}\text{C min}^{-1}$ to 280 $^{\circ}\text{C}$ and these conditions were held for 5 min and finally, there was a further increase of 10 $^{\circ}\text{C min}^{-1}$ to 320 $^{\circ}\text{C}$ and the temperature was kept for 8 min. The transfer line and ion source temperatures were 300 $^{\circ}\text{C}$. The detection was performed by mass spectrometry using electron impact ionization of 70 eV in the multiple reaction monitoring mode (SRM). Detection of analytes (PAHs + alkyl PAH standards) was done by monitoring two transitions per compound (from precursor ion to two specific fragment ions) and quantified by the most intense transition, as indicated in Table S1. The SRM transitions used for the identification of the alkyl-PAHs cluster are those optimized by Sorensen et al. [14] and indicated in Table 1. These transitions cover the losses of characteristic fragments with different degrees of alkylation ($[\text{M}-\text{H}]^+$, $[\text{M}-\text{CH}_3]^+$, $[\text{M}-\text{C}_2\text{H}_5]^+$, $[\text{M}-\text{C}_3\text{H}_7]^+$). The transition corresponding to the loss of methyl ($[\text{M}]^+ \rightarrow [\text{M}-\text{CH}_3]^+$) records homologues having ethyl, methyl, isopropyl and t-butyl substituents, while the transitions corresponding to the loss of ethyl ($[\text{M}]^+ \rightarrow [\text{M}-\text{C}_2\text{H}_5]^+$) and propyl ($[\text{M}]^+ \rightarrow [\text{M}-\text{C}_3\text{H}_7]^+$) records n-propyl and isobutyl groups, respectively. Nevertheless, in all cases, semi-quantification was conducted using the transition with the highest contribution, SRM 1, as shown in Table 1. Besides the specific SRM transitions, alkyl derivatives were also identified by their specific chromatographic pattern recognition, taken from the literature [4]. For the quantification of the different alkyl-PAHs, and to define the chromatographic retention time window of each cluster, analytical standards that cover various alkylation levels were selected as representative standards. This selection was based on the approach by Yang et al. [5], who evaluated the performance of a wide range of alkylated compounds as proper standards for the quantification of the different homologue clusters. The detection of these standards was done by SRM mode as well, monitoring two transitions per compound, as indicated in Table S1.

The quantification of the 16 parent PAHs was performed by using linear regression calibration curves and the internal standard approach, to account for possible matrix effects and recovery losses during the SPME process. However, for alkyl-PAHs, semi-quantification was done, and the analytes were quantified according to relative response factors (RRFs), using the aforementioned standards and after normalizing to appropriate internal standards, as indicated in Table S2. In case that more than one quantification standard was available for the alkylated homologues, as is the case for naphthalene-C3, naphthalene-C4, phenanthrene-C2, phenanthrene-C3, phenanthrene-C4 and fluoranthene/pyrene-C1 clusters, the average RRF value, obtained by using each individual standard, was used to quantify the corresponding clusters.

System control and data acquisition were achieved with the Xcalibur 4.1 software, and the acquired data was processed using TraceFinder software (Thermo Fisher Scientific).

Table 1

Selected SRM transitions for the analysis of alkylated PAHs homologue clusters, and the standards used for their quantification.

Alkyl PAH homologue cluster	Reference Standard for quantification	MW (g/mol)	SRM 1 (m/z)	CE (eV)	SRM 2 (m/z)	CE (eV)	SRM 3 (m/z)	CE (eV)	RT window (min)
Naphthalene-C2 ^a	Naphthalene-2,6-dimethyl	156	156–141	15					8–9
Naphthalene-C3 ^a	Naphthalene-1,3,7-trimethyl Naphthalene-2,3,5-trimethyl Naphthalene-1,2,5-trimethyl	170	170–155	15	170–141	15			8–11
Naphthalene-C4 ^a	Naphthalene-1,4,6,7-tetramethyl Naphthalene-1,2,5,6-tetramethyl	184	184–169	15	184–155	15	184–141	15	10–13
Fluorene-C1 ^b	Fluorene-1-methyl	180	180–165	15	180–179	15			11–13
Fluorene-C2 ^b	Fluorene-1,7-dimethyl	194	194–179	15	194–165	15			12–14
Phenanthrene-C1 ^b	Phenanthrene-1-methyl	192	192–191	15					14–16
Phenanthrene-C2 ^b	Phenanthrene-3,6-dimethyl Phenanthrene-1,2-dimethyl Phenanthrene-1,3-dimethyl	206	206–191	15					15–18
Phenanthrene-C3 ^b	Phenanthrene-1,2,6-trimethyl Phenanthrene-2,6,9-trimethyl	220	220–205	15	220–191	15			16–20
Phenanthrene-C4 ^b	Retene Phenanthrene-1,2,6,9-tetramethyl	234	234–219	15	234–205	15	234–191	15	17–22
*Fluor/Pyr-C1 ^b	Fluoranthene-1-methyl Pyrene-1-methyl	216	216–215	20					16–21

Superscripts indicate surrogate internal standards used for quantification.

^a naphthalene-d8^b phenanthrene-d10

Method validation

The performance of the analytical method was characterized through the estimation of the linearity of the calibration curve, limits of detection (LOD) and quantification (LOQ), and extraction recoveries. Method validation was done using the inlet water used for scrubber water production, sea water. This selection was made because the concentrations of some analytes in scrubber water are too high for assessing extraction recoveries and sea water is considered a representative matrix as the inlet scrubber water. Furthermore, evaluating the extraction performance in scrubber water solely based on the labeled standards would lead to erroneous results, attributable to the signal variability inherent in the solid phase microextraction.

Linearity of the analytes was established by analyzing, in duplicate, the calibration curve prepared with ultrapure water spiked at seven concentration levels (1, 5, 10, 20, 50, 100, 200 ng L⁻¹). Each calibration standard was spiked with an internal standard mixture, at a final concentration of 100 ng L⁻¹, to account for possible matrix effects and recovery losses during the SPME process. Calibration curves were injected at the beginning and the end of each sequence, and one calibration standard was measured repeatedly throughout the sequence to check for signal stability. Method blanks were performed to account for any background levels of the analytes investigated. LOD and LOQ were estimated by two different approaches, depending on the occurrence of the target compounds in the analytical blanks. For instance, naphthalene was ubiquitous in the analytical blanks and LODs and LOQs were calculated as: $LOD/LOQ = Y(\text{blank}) + S(\text{blank}) * k$; $k = (3 \text{ and } 10)$, where Y is the concentration of the analytes in the blank, S is the standard deviation of various replicates in the blanks, and k is a factor applied, which is 3 for LOD and 10 for LOQ. For the compounds that were not present in the analytical blanks, LODs were estimated as $LOQ/3$, where the LOQ represented the lowest calibration level giving a signal-to-noise (S/N) of 10.

The precision (%relative standard deviation of the extraction recoveries) and accuracy (% recovery) were determined by spiking PAH-free sea water samples at 20 and 100 ng L⁻¹ with a mixture containing PAHs and the representative alkyl-PAHs standards. Relative recoveries were calculated by comparing the concentration before and after the whole analytical extraction procedure. Concentrations were calculated by an internal calibration curve using standards in ultrapure water. Repeatability and reproducibility were estimated through the calculation of both the intra-day (the injection of five standard replicates within the same day) and

inter-day precision (the injection of standard replicates within three consecutive days). The performance of the method was further tested by spiking scrubber water samples produced by a pilot scrubber system, at 100 ng L^{-1} concentration level.

Scrubber water sample collection

Scrubber water samples were collected from a container ship during the fall of 2021. Samples were taken along the journey of the vessel, covering different geographical regions with intense marine traffic. The scrubber process was carried out by pumping seawater to the scrubber unit to neutralize and remove the pollutants from exhaust gases. In this study, 6 representative samples were analyzed to assess the performance of the analytical method developed. Scrubber water samples were mostly collected manually from the outlet of the open-loop system (STI Marine, Seoul, South Korea), close to the discharge point, into 1-L amber glass bottles and stored onboard at $4 \text{ }^\circ\text{C}$ in the dark. All samples were shipped refrigerated to ICRA, where they were kept at $4 \text{ }^\circ\text{C}$ in the dark until analysis. At the time of sample collection, the ship used heavy fuel oil (HFO) with a sulphur content of approximately 2.4%.

Method discussion

Optimization of SPME conditions

The evaluation of the injector temperature, extraction time, and desorption time was performed through a sorption profile analysis. This analysis aimed to establish an optimized extraction methodology for both parent and alkylated PAHs. Through this evaluation, it was possible to determine the maximum amount of target analyte that the fiber can extract by measuring the peak area as a function of exposure time. The fiber was exposed to the headspace of ultrapure water during four extraction periods, as depicted in Fig. 1.

Fig. 1A illustrates that the sorption profile between the parent and its alkyl derivatives changes as the degree of alkylation increases. For low-molecular-weight PAH derivatives like naphthalene and fluorene, the extraction yield decreases with longer extraction times. Conversely, for medium-molecular-weight PAH derivatives such as phenanthrene, fluoranthene and pyrene, longer extraction times are required to reach the equilibrium. Given this contrasting behavior, and to achieve a compromise, an extraction time of 40 min was selected as the optimal value.

Desorption parameters, including injector temperature and time were also optimized to ensure the complete desorption of analytes from the fiber. In this study, the desorption process was carried out by inserting the fiber into the injector at temperatures of $280 \text{ }^\circ\text{C}$ and $300 \text{ }^\circ\text{C}$, with desorption times of 5 and 10 min (see Fig. 1B and C). Although no significant differences were observed between the temperatures (Fig. 1B), we chose $300 \text{ }^\circ\text{C}$ as the optimum desorption temperature, to ensure a complete desorption of the high molecular weight PAHs. The selection of this parameter matches with previous studies, where an injector temperature of $300 \text{ }^\circ\text{C}$ has been also used [16]. For the desorption time, it is worth mentioning that the sensitivity of the method decreased with longer desorption times, particularly for alkyl derivatives, except for fluorene homologues (Fig. 1C). Consequently, the optimum desorption time was set at 5 min.

Validation of the SPME-GC-MS/MS method

The performance of the analytical method was characterized through the linearity of the calibration curve, extraction recoveries, LODs and LOQs. The results for the method validation parameters are presented in Table 2 and S2.

Recoveries were satisfactory for most compounds, generally ranging from approximately 60 to over 120%. The overall method precision, calculated as the relative standard deviation (%RSD) of the extraction recoveries was also satisfactory, below 20% (Table 2). Linearity was tested using spiked ultrapure water at seven different concentration levels in duplicate. The calibration curves demonstrated good fits ($r^2 > 0.996$) over the established concentration points, ranging from 1 to 200 ng L^{-1} , except for some compounds, such as naphthalene ($10\text{--}200 \text{ ng L}^{-1}$) or chrysene ($1\text{--}100 \text{ ng L}^{-1}$) (Table S2). LODs and LOQs ranged from 0.33 to 1.67 ng L^{-1} and from 1 to 5 ng L^{-1} , respectively. Slightly higher LODs and LOQs were achieved for naphthalene, as this is a semi-volatile compound that is ubiquitous in the method blanks, and LODs and LOQs ranged from 3.3 to 10 ng L^{-1} , respectively (Table 2). It is important to highlight that these LODs are slightly lower than those obtained by previous HS-SPME-GC-MS methods ($1\text{--}29 \text{ ng L}^{-1}$) [18]. This might be attributed to the enhanced selectivity and sensitivity of MS/MS detection, compared to single GC-MS instruments. In comparison with other studies based on SPE-GC-MS/MS, Martínez et al. [8] and Qiao et al. [9] achieved limits of detection within the same range for most compounds ($0.1\text{--}15 \text{ ng L}^{-1}$ and $0.02\text{--}6.3 \text{ ng L}^{-1}$, respectively). Even though LODs might be lower for some compounds, it is important to mention that the SPE procedures require large sample volumes, that must be filtered prior to the extraction, leading to more time-consuming methodologies. Furthermore, SPE could lead to considerable losses of target compounds, particularly the more hydrophobic ones. In contrast, SPME not only overcomes these limitations but also operates as an automated process that integrates sample clean-up and preconcentration into a single step, thereby reducing analysis time and enhancing the accuracy of the analysis [19].

The results obtained suggest that the methodology presented in this study is robust and sensitive enough to detect and quantify PAHs and their alkyl derivatives at levels within the maximum permitted concentration limits specified by Directive 2013/39/UE. An exception to this is benzo[*g,h,i*]perylene, for which the maximum permissible concentration is 0.82 ng L^{-1} , a value that falls close to the limit of detection of 1.67 ng L^{-1} . However, the concentrations of PAHs detected in scrubber water are in the 10 to 2800 ng L^{-1} range, which are several orders of magnitude higher than the method limit of detection. This is also the case for benzo[*g,h,i*]perylene, which is usually found at 20 ng L^{-1} [3], and this concentration remains above the LODs.

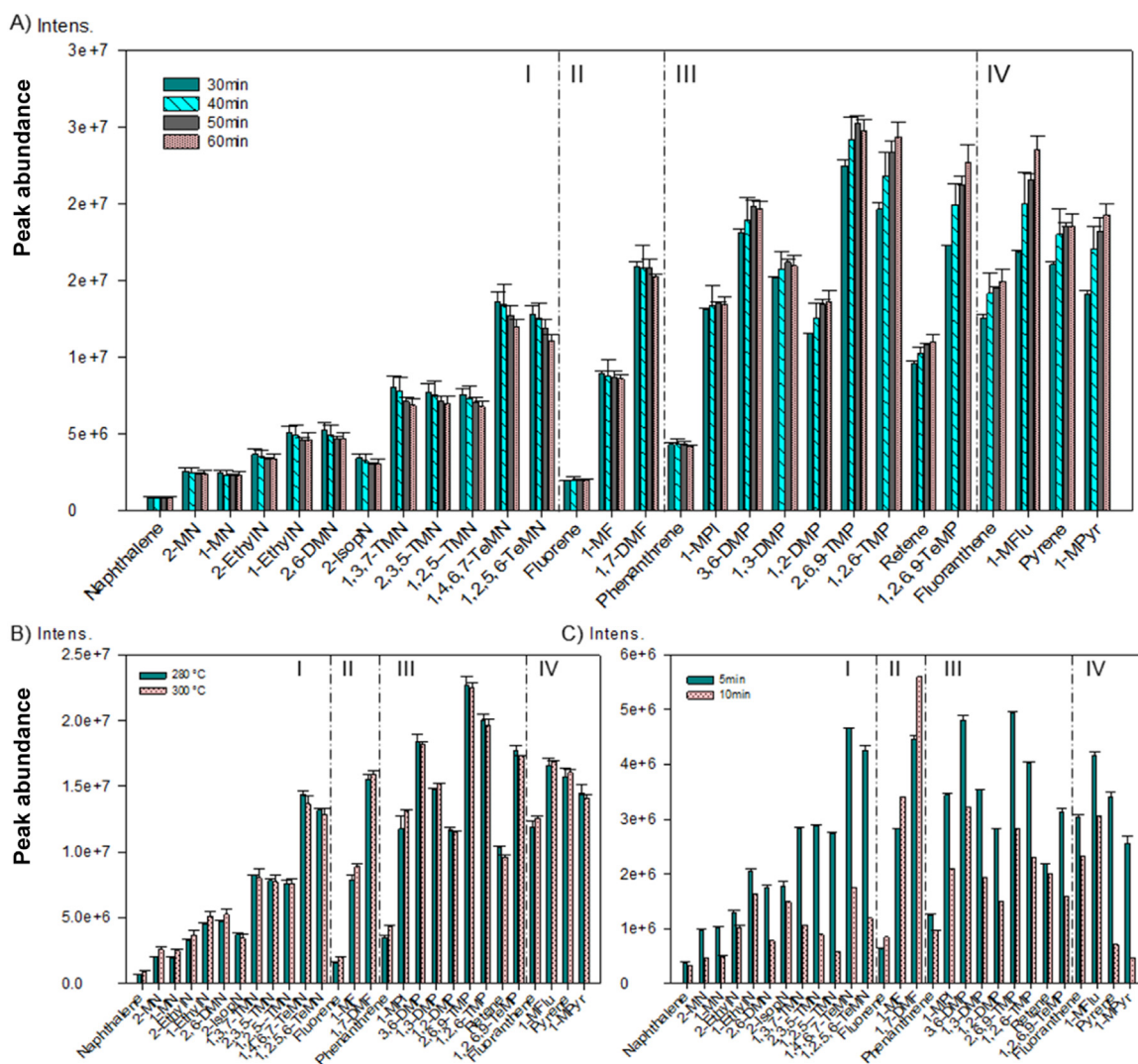


Fig. 1. Effects of the extraction time (A), the desorption temperature (B) and the desorption time (C) during the optimization of the HS-SPMEGC-MS/MS parameters for the determination of alkyl-PAHs. All these graphs are divided into four regions that define naphthalene (I), fluorene (II), phenanthrene (III) fluoranthene and (IV) pyrene and their derivatives.

Regarding the performance of the analytical standards used for the quantification of alkyl PAHs, the relative response factors estimated using different standards for the quantification of isomers within the same homologue group revealed no remarkable differences among them (Table S2). Yet, in our study, compounds were quantified using average RRF values, to increase the precision in the quantification.

As previously mentioned, and as part of further validation to ensure the robustness of the method, extraction recoveries were also estimated using scrubber water spiked at 100 ng L^{-1} . The average recoveries were between 60 and 100%, for parent PAHs, and from 50 to 100% for alkyl PAHs, both with a precision $<20\%$ (Table S3). Notably, lower recoveries were observed for PAHs with higher molecular weight and for alkyl-PAHs with a higher degree of alkylation.

Application to real samples: scrubber water analysis

The analytical methodology described above was applied to the analysis of PAHs and their alkyl derivatives in scrubber water collected from a container ship. Both filtered and un-filtered samples were analyzed to show the possibility of the developed methodology in assessing the compounds sorption onto particulate matter. The concentrations of PAHs and alkyl-PAHs detected in the samples are detailed in Table S4, where it is shown that scrubber water samples contain high concentrations of the target compounds, especially alkyl-PAHs, which, in some cases, are more prominent than the parent compounds.

Table 2
HS-SPME-GC–MS/MS method performance parameters (recoveries, LOD and LOQ).

Target compound	IS	LOD (ng L ⁻¹)	LOQ (ng L ⁻¹)	% Recovery (%RSD)	
				20 (ng L ⁻¹)	100 (ng L ⁻¹)
Naphthalene	Naphthalene-D8	3.33	10.0	86.8 (13.1)	93.6 (6.15)
Acenaphthylene	Acenaphthalene-D10	1.67	5.00	102 (7.35)	107 (6.06)
Acenaphthalene	Acenaphthalene-D10	1.67	5.00	97.4 (1.53)	98.2 (1.61)
Fluorene	Acenaphthalene-D10	0.33	1.00	101 (9.83)	101 (0.49)
Phenanthrene	Phenanthrene-D10	0.33	1.00	91.6 (1.76)	94.9 (1.11)
Anthracene	Phenanthrene-D10	1.67	5.00	96.2 (4.38)	95.5 (1.40)
Fluoranthene	Phenanthrene-D10	0.33	1.00	87.4 (1.76)	90.1 (3.07)
Pyrene	Chrysene-D12	1.67	5.00	116 (0.23)	96.1 (1.71)
Benzo(a)anthracene	Chrysene-D12	1.67	5.00	96.6 (4.98)	97.1 (3.22)
Chrysene	Chrysene-D12	0.33	1.00	112 (8.73)	95.6 (1.64)
Benzo(b)fluoranthene	Chrysene-D12	0.33	1.00	103 (2.49)	101 (6.09)
Benzo(k)fluoranthene	Chrysene-D12	0.33	1.00	109 (4.83)	95.9 (1.51)
Benzo(a)pyrene	Chrysene-D12	1.67	5.00	114 (3.41)	107 (5.80)
Indeno(1,2,3-cd)pyrene	Perylene-D12	1.67	5.00	73.9 (11.3)	70.7 (5.69)
Dibenzo(a,h)anthracene	Perylene-D12	1.67	5.00	68.7 (10.5)	66.5 (5.05)
Benzo(g,h,i)perylene	Perylene-D12	1.67	5.00	87.5 (14.0)	86.3 (7.67)
Naphthalene-2-methyl	Naphthalene-D8	0.33	1.00	82.3 (9.12)	102 (3.46)
Naphthalene-1-methyl	Naphthalene-D8	0.33	1.00	92.3 (8.32)	99.5 (2.22)
Naphthalene-ethyl	Naphthalene-D8	0.33	1.00	83.3 (7.84)	98.9 (3.56)
Naphthalene-2,6-dimethyl	Naphthalene-D8	0.33	1.00	81.8 (7.95)	97.9 (3.75)
Naphthalene-2-Isopropyl	Naphthalene-D8	0.33	1.00	76.3 (1.39)	75.6 (4.29)
Naphthalene-1,3,7-Trimethyl	Naphthalene-D8	0.33	1.00	95.0 (8.85)	102 (1.47)
Naphthalene-2,3,5-Trimethyl	Naphthalene-D8	0.33	1.00	97.8 (7.79)	102 (2.09)
Naphthalene-1,2,5-Trimethyl	Naphthalene-D8	0.33	1.00	102 (7.69)	104 (2.36)
Naphthalene-1,4,6,7-Tetramethyl	Naphthalene-D8	0.33	1.00	97.1 (5.20)	99.3 (3.16)
Naphthalene-1,2,5,6-Tetramethyl	Naphthalene-D8	0.33	1.00	104 (7.43)	104 (4.48)
Phenanthrene-1-methyl	Phenanthrene-D10	0.33	1.00	87.9 (3.75)	92.0 (3.35)
Phenanthrene-3,6-dimethyl	Phenanthrene-D10	0.33	1.00	80.7 (5.59)	84.7 (3.25)
Phenanthrene-1,3-dimethyl	Phenanthrene-D10	0.33	1.00	86.1 (3.64)	79.6 (2.75)
Phenanthrene-1,2-dimethyl	Phenanthrene-D10	0.33	1.00	87.0 (4.22)	80.5 (3.40)
Phenanthrene-2,6,9-trimethyl	Phenanthrene-D10	0.33	1.00	80.1 (4.85)	77.2 (3.39)
Phenanthrene-1,2,6-trimethyl	Phenanthrene-D10	0.33	1.00	85.8 (5.83)	82.5 (3.49)
Phenanthrene-1,2,6,9-tetramethyl	Phenanthrene-D10	0.33	1.00	81.4 (4.55)	82.0 (3.68)
Retene	Phenanthrene-D10	0.33	1.00	51.5 (4.27)	43.8 (3.25)
Fluorene-1-methyl	Phenanthrene-D10	0.33	1.00	85.0 (5.02)	91.9 (4.04)
Fluorene-1,7-dimethyl	Phenanthrene-D10	0.33	1.00	78.5 (8.01)	83.9 (3.61)
Fluoranthene-1-methyl	Phenanthrene-D10	0.33	1.00	89.4 (5.90)	95.2 (4.33)
Pyrene-1-methyl	Phenanthrene-D10	0.33	1.00	99.9 (6.61)	110 (3.48)

Among the 16 priority PAHs, naphthalene and phenanthrene are the compounds present at the highest concentrations, ranging from 3 to 13 $\mu\text{g L}^{-1}$. Fluorene and acenaphthene are also found at relevant concentrations, approximately from 0.3 to 1.6 $\mu\text{g L}^{-1}$, followed by fluoranthene and pyrene, which are in the range of approximately 0.1 to 0.9 $\mu\text{g L}^{-1}$. On the other hand, compounds like acenaphthylene and chrysene are detected at lower levels, typically around 0.02 to 0.3 $\mu\text{g L}^{-1}$. As depicted in Fig. 2A, the concentration profile of the scrubber water is predominantly characterized by low molecular weight PAHs. These findings match well with the study by Lunde Hermansson et al. [3], that evaluated the presence of the 16 priority PAHs in scrubber systems. Their study revealed that low molecular weight PAHs were present at higher concentrations than the high molecular weight compounds, with naphthalene and phenanthrene being the dominating substances, in terms of frequency of detection and concentration.

In the case of alkyl PAHs, several clusters of alkyl derivatives were identified. The compounds most widely detected were related to the most ubiquitous parent PAHs, such as naphthalene and phenanthrene, and covered up to four alkylation levels, as shown in Fig. 2B. Among them, C1-C4 naphthalene derivatives were the most relevant in the samples reaching a concentration between approximately 1 to 15 $\mu\text{g L}^{-1}$. Additionally, C1-C4 phenanthrene, C1-C2 fluorene, and C1-fluoranthene/pyrene derivatives were detected. However, their concentrations were a bit lower than those in the naphthalene cluster, generally below 5 $\mu\text{g L}^{-1}$. It is important to highlight that the concentrations decreased as the level of alkylation increased, and consequently, as the molecular weight increased, as occurred with the parent PAHs.

Remarkable differences in the concentration of both PAHs and alkyl homologues were observed when comparing filtered and unfiltered samples, showing the potential of SPME to assess PAHs partitioning. As expected, higher concentrations were found in most of the un-filtered samples, and those differences were more pronounced for the high molecular weight PAHs and alkyl derivatives with higher levels of alkylation, as depicted in Fig. 3.

The sorption percentages of PAHs onto particulate matter vary, ranging from approximately 20% for more volatile compounds like naphthalene to 86% for medium molecular weight compounds such as chrysene. This pattern is also observed for alkyl derivatives, where the C1-C4 phenanthrene clusters serve as a clear illustration, with sorption percentages ranging from 36 to 89%. Notably,

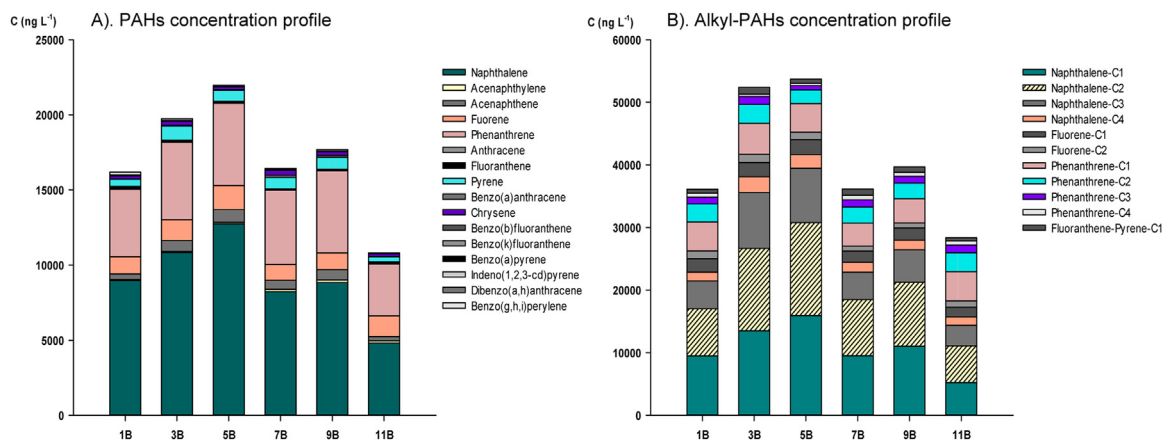


Fig. 2. Concentration profile of parent PAHs (A), and their alkyl derivatives (B) in scrubber water.

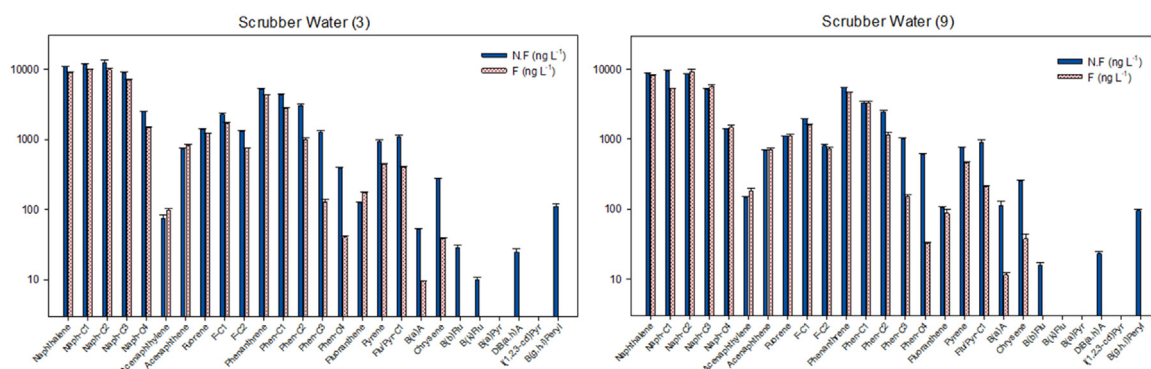


Fig. 3. Concentration of PAHs and their alkyl derivatives in filtered (F) and un-filtered (N.F) scrubber water samples collected at sampling points 3 and 9.

high molecular weight PAHs were entirely lost after the filtration step. These results highlight the importance of considering the particulate matter in PAHs and alkyl-PAHs analysis, especially for high molecular weight compounds.

Data availability

Data will be made available on request.

CRediT authorship contribution statement

Elisa García-Gómez: Conceptualization, Methodology, Software, Validation, Visualization, Writing – original draft. **Sara Insa:** Methodology, Software, Supervision. **Meritxell Gros:** Conceptualization, Writing – review & editing. **Mira Petrović:** Funding acquisition, Conceptualization, Writing – review & editing.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.mex.2024.102589](https://doi.org/10.1016/j.mex.2024.102589).

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