Pressurised fluid extraction of polycyclic aromatic hydrocarbons and their polar oxidation products from atmospheric particles

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An effective method utilising pressurised fluid extraction (PFE) to simultaneously extract polycyclic aromatic hydrocarbons (PAHs) and their polar oxidation products from atmospheric particulate matter (PM) is presented. The PFE method is advantageous over the traditional Soxhlet extraction due to its lower solvent consumption (9 mL compared to 90 mL) and shorter extraction time (15 min versus 18 h). Seventy compounds including PAHs and polar PAH oxidation products containing carbonyl (oxy-PAHs), hydroxyl (hydroxy-PAHs), and carboxylic acid (carboxy-PAHs) groups were targeted in the extraction of two different PM matrices: wood smoke (WS) and diesel exhaust (DE) PM. The PFE method was optimised and then compared to Soxhlet extraction for both PM matrices. The overall amounts of PAHs and their derivatives extracted from WS PM were slightly higher for the optimised PFE method (1849 ± 21 and 1863 ± 25 µg g⁻¹ with dichloromethane (DCM) and methanol (MeOH), respectively) than those obtained with Soxhlet extraction (1726 ± 33 and 1769 ± 22 µg g⁻¹ with DCM and MeOH, respectively). For DE PM (standard reference material (SRM) 2975) the overall amounts extracted by both methods were similar (average of 165 ± 6 µg g⁻¹), agreeing with previously published values. The detailed evaluation of extraction efficiencies for WS PM showed similar amounts for unfunctionalised PAHs (1100 µg g⁻¹) for both methods and solvents. For DE PM the mass yields for PAHs using PFE with DCM (62 ± 1 µg g⁻¹) were the highest and nearly 20% higher than those obtained with MeOH (53 ± 2 µg g⁻¹). The total mass yields of carboxy and hydroxy-PAHs from WS PM were also similar (412 ± 18 and 407 ± 11 µg g⁻¹) for PFE and Soxhlet with MeOH, and higher than when DCM was used (371 ± 5 and 379 ± 12 µg g⁻¹ for PFE and Soxhlet, respectively). For both matrices, the PFE yields for oxy-PAHs were higher than those obtained with Soxhlet.

Keywords: PFE; PAHs; oxy-PAHs; hydroxy-PAHs; carboxy-PAHs; particulate matter

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have long been recognised as environmental pollutants that also exhibit pro-mutagenic and carcinogenic properties [1]. The fate of these PAH species in the atmosphere and their occurrence in atmospheric particulate matter (PM) has been studied extensively, resulting in the discovery of specific oxidation pathways that lead to products containing various polar functional groups [2–12]. These polar derivatives, which include species with carbonyl (oxy-PAHs), hydroxyl (hydroxy-PAHs) or carboxylic acid (carboxy-PAHs) groups, have been found to induce either similar or more adverse health effects compared to their PAH precursors [1,9,13].
Oxy-PAHs are either emitted directly through incomplete combustion processes or formed via photochemical reactions in the troposphere with hydroxyl radicals, nitrate radicals or ozone \[3,7,11,14,15\]. Alternatively, PAHs may be oxidised to hydroxy-PAHs through hydroxyl radical (OH) initiated reactions with NO\(_2\) followed by HONO loss \[16\]. Carboxy-PAHs have also been observed in various ambient PM samples, with a major formation pathway being the reaction of H\(_2\)O with photochemically produced peroxy radicals to form either aldehydes or mono-carboxylic acids \[16\].

Various extraction methods, including Soxhlet which is regarded as a standard extraction technique, have previously been employed to extract PAHs or selected polar PAH derivatives from PM \[17–26\]. However PFE, a modern technique which is commercially referred to as accelerated solvent extraction, is advantageous due to its reduced solvent consumption and total extraction time \[27\]. Studies utilising PFE for the extraction of PAHs or nitro-PAHs from PM matrices showed increased extraction efficiency over other techniques such as Soxhlet and ultrasonic extraction, depending on the solvent used \[17,18,28–30\]. However, in those studies only PAHs or a specific class of polar PAH derivatives (such as nitro-PAHs) were targeted, thereby providing only a limited understanding of PFE’s efficiency for the wide range of polar PAH oxidation products. PFE has been shown to be efficient in the extraction of oxy-PAHs from urban PM; however, the influence of the extraction solvent was not reported \[31\]. Hydroxy-PAHs (which are considered highly polar in comparison to PAH) and carboxy-PAHs (even more polar) were not investigated in these studies and, to our knowledge, have not been considered in any other studies utilising PFE for PM.

In optimising PFE, the main parameters that affect the amounts of analyte extracted are the extraction temperature, pressure and solvent(s) selection. It has previously been shown that the extraction pressure employed does not play a significant role in extracted yields for PAHs and oxy-PAHs from PM \[23,28,30,31\]. With a large number of analytes spanning a wide range of polarity, the extraction solvent selection becomes more challenging. While a relatively non-polar solvent, such as toluene or cyclohexane, would be a logical choice for extracting relatively non-polar PAHs, studies have shown that higher amounts of PAHs can be extracted with a mildly polar solvent such as dichloromethane (DCM) or a toluene/methanol (MeOH) mixture \[24,29,30\]. For mildly polar nitro-PAHs, both DCM and toluene/MeOH (1:1–9:1) have been shown to be efficient in extractions from various PM matrices \[18–20,22\]. The use of PFE for the extraction of oxy-PAHs from PM and quartz fibre matrices has previously been evaluated for ethyl acetate as the extraction solvent \[31\]; however, optimisation using other solvent systems and other PM matrices has not been addressed. In addition, PFE has not been optimised to efficiently extract PAHs and the main classes of PAH derivatives simultaneously, which is highly valuable given the increased interest in detecting these species during air monitoring campaigns.

In this work we investigated the use of PFE for the fast extraction of both PAHs and their polar oxidation products from wood smoke PM (WS PM; a relatively polar PM matrix) and diesel exhaust PM (SRM 2975; a relatively non-polar matrix). DCM and MeOH were compared as extraction solvents in terms of their efficiency in extracting PAHs and polar derivatives simultaneously. DCM was chosen based on its ability to be effective for PAHs due to its similar polarity. It may also be a good extraction medium for mildly polar oxidation products such as oxy-and nitro-PAHs due to their similar polarity. Conversely, MeOH was evaluated due to the likelihood of it providing higher extraction amounts for the highly polar PAH derivatives (namely, hydroxyl- and carboxy-PAHs). The impact of additional PFE parameters, such as the extraction temperature and solvent volume, were investigated. Mass fractions obtained with PFE for WS PM and SRM 2975 were compared to those obtained with the well-established Soxhlet extraction.
2. Experimental

2.1. Materials and reagents

Method development was first performed using standards spiked to sand (standard Ottawa; EMD Millipore, Darmstadt, Germany) to determine the essential extraction volumes. All remaining experiments evaluating the impact of temperature on mass fractions extracted were performed using WS PM (WS PM) that was generated from softwood and hardwood combustion [32], and diesel engine exhaust standard reference material (SRM 2975; NIST, Gaithersburg, MD, USA) [33]. WS PM and SRM 2975 were chosen due to the differences in their matrices, with WS PM being relatively polar and SRM 2975 being relatively non-polar, thus allowing to evaluate extraction efficiencies of target analytes within a broad range of different matrix interactions. Detailed information on the collection and storage methods for the WS PM can be found elsewhere [32]. Briefly, the WS PM was collected from 22 different residential wood stoves, 14 burning hardwoods and 8 burning softwoods. The hardwood stoves were located in Grand Forks, ND and the softwood stoves in Salt Lake City, UT and Boulder, CO. During sample collection, the stoves were continuously operated in similar manners. Particulate samples were collected from the inside walls of the chimney at a distance of ~0.5 m up the smoke plume.

All reagents were of analytical-reagent grade with a purity of ≥98% unless stated otherwise. Gas chromatography (GC)-grade DCM and LC-MS optima grade MeOH were obtained from Fisher Scientific (Chicago, IL, USA). n-Hexane (HPLC grade, 95%) was obtained from Sigma-Aldrich (St. Louis, MO, USA). Information on all individual standards, recovery standards (RSs), internal standard (IS) and tentatively identified species are provided in Table 1. PAH standards (15 PAHs in total) were obtained as a mixture from Sigma-Aldrich (QTM PAH Mix). For derivatisation, 99% N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% of trimethylchlorosilane (TMCS) (Sigma-Aldrich) was used.

2.2. Extraction

All extraction methods and parameters used in this study are listed in Table 2. The PFE extractions were performed using a home-built apparatus (previously described in detail) used for hot pressurised water extraction [34]. The system consisted of an HP 5890 GC oven, Waters 1100 LC pump and an extraction vessel. Needle valves (VICI, Houston, TX, USA) were placed at the inlet and outlet of the PFE extraction vessel outside the oven. The PFE extraction vessel was comprised of an empty 50 mm × 4.6 mm ID (0.83 mL internal volume) stainless steel liquid chromatography column capped with 0.5 µm pore size stainless steel frits (Chromtech, Apple Valley, MN, USA). Extractions were performed in triplicate using either DCM or MeOH, which were chosen due to their polarities being similar to the polarity range for the majority of the targeted analytes. In terms of extraction efficiency, DCM has been shown to be comparable to other relatively non-polar solvent systems in extracting lower molecular weight (2–4 ring) PAHs from SRM 2975 [28]. However, it has been shown that using DCM results in poorer recovery yields for higher molecular weight (5+ ring) PAHs than when using non-polar solvent systems (i.e., toluene) [28,29,35]. DCM has also been previously used for the extraction of nitro-PAHs from SRM 2975 [19]. For oxy-PAHs, ethyl acetate has been shown to be efficient for their extraction from urban PM and quartz fibre filters [31]; however, other solvent systems have not, to our knowledge, been investigated for other PM matrices. Currently, PFE has not been reported for the extraction of highly polar PAH derivatives, such as hydroxy- and carboxy-PAHs, from PM. These species may require a more polar solvent.
Table 1. Compound information and quantitation parameters for all targeted analyte species and RS evaluated in this study.

| Compound name | \( t_R \) (min) | Quant. mode | Quant. ion (m/z) | Confirm. ion (m/z)\( ^b \) | Calibration based on | RS | Manufacturer |
|---------------|----------------|-------------|----------------|----------------------------|----------------------|----|-------------|
| **PAHs**      |                |             |                |                            |                      |    |             |
| naphthalene   | 4.570          | SIM         | 128            | 102 (10)                   | Standard             | naph-d8 | Supelco     |
| acenaphthylene| 6.657          | SIM         | 152            | 126 (7)                    | Standard             | phen-d10 | Supelco     |
| acenaphthene  | 6.943          | SIM         | 154            | 126 (10)                   | Standard             | phen-d10 | Supelco     |
| fluorene      | 7.857          | SIM         | 166            | 82 (15)                    | Standard             | phen-d10 | Supelco     |
| phenanthrene  | 9.728          | SIM, TIC    | 178            | 152 (10)                   | Standard             | phen-d10 | Supelco     |
| anthracene    | 9.835          | SIM, TIC    | 178            | 152 (10)                   | Standard             | phen-d10 | Supelco     |
| 2-methylanthracene | 11.029 | SIM      | 192            | 165 (15)                   | Standard             | phen-d10 | Supelco     |
| phen/anth-C~1~ A T | 10.818 | SIM         | 192            | 165 (15)                   | 2-methylanthracene   | phen-d10 | Nac         |
| phen/anth-C~1~ B T | 10.868 | SIM         | 192            | 165 (15)                   | 2-methylanthracene   | phen-d10 | NA          |
| phen/anth-C~1~ C T | 10.969 | SIM         | 192            | 165 (15)                   | 2-methylanthracene   | phen-d10 | NA          |
| phen/anth-C~1~ D T | 11.033 | SIM         | 192            | 165 (15)                   | 2-methylanthracene   | phen-d10 | NA          |
| phen/anth-C~1~ E T | 11.085 | SIM         | 192            | 165 (15)                   | 2-methylanthracene   | phen-d10 | NA          |
| phen/anth-C~2~ A T | 11.923 | TIC         | 206            | 191 (50)                   | phenanthrene         | phen-d10 | NA          |
| phen/anth-C~2~ B T | 12.074 | TIC         | 206            | 191 (50)                   | phenanthrene         | phen-d10 | NA          |
| phen/anth-C~2~ C T | 12.136 | TIC         | 206            | 191 (50)                   | phenanthrene         | phen-d10 | NA          |
| phen/anth-C~2~ D T | 12.184 | TIC         | 206            | 191 (50)                   | phenanthrene         | phen-d10 | NA          |
| phen/anth-C~2~ E T | 12.251 | TIC         | 206            | 191 (50)                   | phenanthrene         | phen-d10 | NA          |
| fluoranthene  | 12.337         | SIM, TIC    | 202            | 101 (10)                   | Standard             | py-d10   | Supelco     |
| pyrene        | 12.812         | SIM, TIC    | 202            | 101 (10)                   | Standard             | py-d10   | Supelco     |
| 1-methylpyrene| 13.620         | SIM         | 216            | 189 (20)                   | 1-methylpyrene       | py-d10   | NA          |
| flu/pyr-C~1~ A T | 13.822 | SIM         | 216            | 189 (20)                   | 1-methylpyrene       | py-d10   | NA          |
| flu/pyr-C~1~ B + C T | 13.867 | SIM         | 216            | 189 (20)                   | 1-methylpyrene       | py-d10   | NA          |
| flu/pyr-C~1~ D T | 14.062 | SIM         | 216            | 189 (20)                   | 1-methylpyrene       | py-d10   | NA          |
| flu/pyr-C~1~ E T | 14.130 | SIM         | 216            | 189 (20)                   | 1-methylpyrene       | py-d10   | NA          |
| flu/pyr-C~1~ F T | 15.630 | SIM         | 228            | 114 (10)                   | Standard             | py-d10   | Supelco     |
| flu/pyr-C~1~ G T | 15.703 | SIM         | 228            | 114 (10)                   | Standard             | py-d10   | Supelco     |
| benzo[e]pyrene| 17.975         | SIM         | 252            | 126 (15)                   | Standard             | py-d10   | Supelco     |
| benzo[a]anthracene | 18.067 | SIM         | 252            | 126 (15)                   | Standard             | py-d10   | Supelco     |
| chrysene      | 18.234         | SIM         | 252            | 126 (15)                   | Standard             | py-d10   | Supelco     |
| benzo[e]acephenanthrylene | 18.599 | SIM         | 252            | 126 (15)                   | Standard             | py-d10   | Supelco     |
| benzo[k]fluoranthene | 18.672 | SIM         | 252            | 126 (15)                   | Standard             | py-d10   | Supelco     |
| benzo[j]fluoranthene | 18.841 | SIM         | 252            | 126 (15)                   | Standard             | py-d10   | Supelco     |

(continued)
| Compound name<sup>a</sup> | \( t_R \) (min) | Quant. mode | Quant. ion (m/z) | Confirm. ion (m/z)<sup>b</sup> | Calibration based on | RS | Manufacturer               |
|--------------------------|----------------|-------------|-----------------|-------------------------------|---------------------|----|---------------------------|
| benzo[\textit{b}]fluoranthene | 20.636 | SIM | 276 | 138 (20) | Standard | py-d10 | Supelco                   |
| benzo[\textit{a}]pyrene | 20.707 | SIM | 278 | 139 (20) | Standard | py-d10 | Supelco                   |
| indeno[1,2,3-\textit{cd}]pyrene | 21.014 | SIM | 276 | 138 (20) | Standard | py-d10 | Supelco                   |
| benzo[\textit{ghi}]perylene | 9.302 | SIM | 180 | 152 (40) | Standard | py-d10 | Sigma-Aldrich             |
| benzo[\textit{ghi}]perylene | 11.507 | SIM | 208 | 152 (40) | Standard | py-d10 | Sigma-Aldrich             |
| dibenz[\textit{a,h}]anthracene | 10.467 | SIM | 196 | 168 (50) | Standard | py-d10 | Sigma-Aldrich             |
| **Oxy-PAHs**              |               |             |                 |                               |                     |    |                           |
| benzo[\textit{b}]naptho\[2,3-d\]furan T | 14.124 | SIM | 216 | 189 (20) | 9-fluorenone | 2-caq | Supelco                   |
| benzo[\textit{b}]naptho\[2,1-d\]furan T | 13.419 | SIM | 216 | 189 (20) | 9-fluorenone | 2-caq | NA                        |
| 9-fluorenone              | 12.999 | TIC | 218 | 189 (30) | Standard | 2-caq | NA                        |
| xanthone                 | 13.170 | TIC | 218 | 189 (30) | Standard | 2-caq | NA                        |
| 9,10-anthraquinone       | 13.342 | TIC | 218 | 189 (30) | Standard | 2-caq | NA                        |
| benzo[\textit{b}]fluoren-11-one T | 14.815 | SIM | 230 | 202 (30) | 9-fluorenone | 2-caq | NA                        |
| benzo[\textit{a}]fluoren-11-one T | 15.072 | SIM | 230 | 203 (30) | 9-fluorenone | 2-caq | NA                        |
| benzo[\textit{c}]fluoren-7-one T | 15.318 | SIM | 230 | 202 (30) | 9-fluorenone | 2-caq | NA                        |
| benzo[\textit{de}]anthracen-7-one T | 15.971 | SIM | 230 | 203 (30) | 9-fluorenone | 2-caq | NA                        |
| benzo[\textit{a}]anthracene-7,12-dione | 16.701 | SIM | 258 | 230 (30) | Standard | 2-caq | Sigma-Aldrich             |
| **Nitro-PAHs**            |               |             |                 |                               |                     |    |                           |
| 9-nitrophenanthrene      | 15.791 | SIM | 223 | 193 (140) | Standard | 2-caq | Sigma-Aldrich             |
| 3-nitrofluoranthrene     | 19.269 | SIM | 247 | 217 (60) | Standard | 2-caq | Sigma-Aldrich             |
| 1-nitropyrene            | 19.719 | SIM | 247 | 217 (120) | Standard | 2-caq | Sigma-Aldrich             |
| 6-nitrochrysene          | 21.822 | SIM | 273 | 243 (25) | Standard | 2-caq | Sigma-Aldrich             |
| **Hydroxy- and carboxy-PAHs<sup>d</sup>** | | | | | | | |
| 2-hydroxybiphenyl        | 7.843 | SIM | 211 | 227 (80) | Standard | 2-CHM<sup>e</sup> | Alfa Aesar |
| hydroxybiphenyl T        | 9.171 | SIM | 227 | 242 (80) | 4-hydroxybipheny | 2-CHM | NA                       |
| 4-hydroxybiphenyl        | 9.570 | SIM | 242 | 227 (90) | Standard | 2-CHM | Alfa Aesar                |
| 7-hydroxycadalene        | 11.399 | SIM | 271 | 286 (75) | Standard | 2-CHM | Sigma-Aldrich             |
| 9-phenanthrol            | 12.653 | SIM | 266 | 251 (65) | Standard | 2-CHM | Sigma-Aldrich             |
| 3-phenanthrol T          | 12.923 | SIM | 266 | 251 (65) | 9-phenanthrol | 2-CHM | NA                       |
| 2-hydroxy-9-fluorenone   | 12.760 | SIM | 253 | 268 (80) | Standard | 2-CHM | Sigma-Aldrich             |
| 4-phenanthrenemethanol   | 13.231 | SIM | 191 | 280 (50) | Standard | 1-OH-py-d9 | Sigma-Aldrich             |
| hydroxypyrene A T        | 15.496 | SIM | 290 | 275 (75) | Standard | 1-OH-py-d9 | Sigma-Aldrich             |
| hydroxypyrene B T        | 15.733 | SIM | 290 | 275 (25) | 1-hydroxypyrene | 1-OH-py-d9 | NA                       |
| Compound                        | Retention Time (min) | SIM   | Confirmation Ion | Quantification Ion | Mass (Da) | Standards          |
|--------------------------------|----------------------|-------|------------------|--------------------|-----------|--------------------|
| hydroxypyrene C T              | 15.128               | SIM   | 290              | 275 (50)           | 1-hydroxypyrene | 1-OH-py-d9    |
| 1-hydroxypyrene                 | 15.170               | SIM   | 290              | 275 (40)           | 1-hydroxypyrene | 1-OH-py-d9    |
| hydroxypyrene D T               | 15.823               | SIM   | 290              | 275 (75)           | 1-hydroxypyrene | 1-OH-py-d9    |
| 1,8-dihydroxyanthraquinone     | 16.166               | SIM   | 369              | 370 (35)           | Standard       | 1-OH-py-d9    |
| 4-phenanthrene-COOH             | 13.824               | SIM   | 205              | 294 (70)           | Standard       | 1-OH-py-d9    |
| 9-anthracene-COOH               | 14.201               | SIM   | 205              | 294 (60)           | Standard       | 1-OH-py-d9    |
| 9-phenanthrene-COOH             | 14.695               | SIM   | 205              | 279 (95)           | Standard       | 1-OH-py-d9    |
| n-phen/anth-COOH                | 14.725               | SIM   | 205              | 294 (60)           | 9-phenanthrene-COOH | 1-OH-py-d9 |
| RS                             |                      |       |                  |                    |            | Sigma-Aldrich    |
| naphthalene-d₈                  | 4.552                | SIM   | 136              | –                  | –           | –                  |
| phenantheone-d₁₀                | 9.701                | SIM   | 188              | –                  | –           | –                  |
| anthracene-d₁₀                  | 9.812                | SIM   | 188              | –                  | –           | –                  |
| pyrene-d₁₀                      | 12.795               | SIM   | 212              | –                  | –           | –                  |
| 2-chloroantraquinone            | 13.452               | SIM   | 242              | –                  | –           | –                  |
| 2-CHM                          | 14.512               | SIM   | 303              | –                  | –           | –                  |
| 1-hydroxypyrene-d₉              | 15.120               | SIM   | 299              | –                  | –           | –                  |
| IS                             |                      |       |                  |                    |            | Sigma-Aldrich    |
| fluoranthene-d₁₀                | 15.138               | SIM   | 212              | –                  | –           | –                  |

Notes:

- Compounds that were identified without available standards are indicated with a ‘T’ next to the compound name.
- Values in parenthesis are the relative response of the confirmation ions to that of the quantification ion listed.
- ‘NA’ denotes that standards for that particular compound were not available during the time of the study.
- All hydroxy- and carboxy-PAHs are shown as trimethylsilyl derivatives after derivatisation with BSTFA.
- 2-CHM is an acronym for 2-chloro-2-hydroxy-4-methylbenzophenone.

Sigma-Aldrich, Supelco, Isotec.
(i.e., MeOH) for the efficient extraction from a polar matrix. However, such a polar solvent (when used either alone or as a modifier) has been shown to be less efficient at extracting PAHs from the PM matrix [29].

The PFE extraction method consisted of several cycles, each including a static extraction step (5 min) followed by a dynamic extraction step at a flow rate of 0.6 mL min\(^{-1}\) for 5 min (i.e., a flushing volume of 3.0 mL, more than three internal cell volumes). To determine the total volume of DCM and the number of extraction cycles sufficient to achieve a complete extraction of wood smoke PM, initial experiments were performed with three cycles (each collecting 3 mL into a single vial), followed by three additional dynamic extraction steps, collecting each 3.0 mL fractions in separate vials (Method 1 in Table 2).

For extractions of PM, the extraction cell was first filled to approximately half volume with sand followed by ~10 mg of the PM. RS mixtures were then spiked to the PM and let sit for 2 min to allow for their complete adsorption onto the PM matrix. The remaining volume of the extraction cell was then filled with sand. The amount of each RS spiked to PM was 0.2 µg (20 µL of 10 µg mL\(^{-1}\) stock mixture) for the majority of analytes with the exception of hydroxy-PAHs, which was spiked at 1.0 µg (10 µL of 100 µg mL\(^{-1}\) stock mixture). Extraction temperatures were evaluated in the range of 130–200°C. For these experiments three extraction cycles (giving a total volume of 9.0 mL) were employed. The mass fractions obtained with the final PFE method at 100°C and 2000 psi (13.8 MPa) from WS PM were compared to those obtained using Soxhlet extraction. The extraction pressure was not evaluated since it was previously shown to have no significant role in the amounts of PAHs and oxy-PAHs extracted from PM matrices [23,28,30,31].

All components of the Soxhlet apparatus (i.e., the extractor, condenser, thimble and flask) were obtained from Chemglass (Vineland, NJ, USA). For all Soxhlet extractions, glass thimbles (coarse frit; 25 mm O.D. by 85 mm height) were used to avoid contamination observed for cellulose thimbles in preliminary experiments. The Soxhlet extractions were carried out with either 90 mL of DCM or 90 mL of MeOH, each for 18 h. After the extraction, the DCM and MeOH extracts were cooled to room temperature and evaporated under a stream of nitrogen while on ice to limit the loss of more volatile compounds, in addition to the losses that may have occurred during extraction.

All PM extracts were evaporated to 100 µL using a six-port evaporator (Sigma-Aldrich, St. Louis, MO, USA) and then diluted to 1.0 mL with \(n\)-hexane and submitted to the solid phase extraction (SPE) fractionation/purification protocol.

### Table 2. Extraction parameters and information for the various PFE and Soxhlet methods evaluated in this work.

| Method Number | Extraction method | Solvent | Temperature (°C) | Pressure (psi) | Number of static cycles | Total volume of extract (mL) | Additional dynamic extraction (mL) |
|---------------|-------------------|---------|-----------------|---------------|------------------------|-----------------------------|----------------------------------|
| 1             | PFE               | DCM     | 100             | 2000          | 3                      | 9                           | 9                                |
| 2             | PFE               | DCM     | 100             | 2000          | 3                      | 9                           | –                                |
| 3             | PFE               | DCM     | 130             | 2000          | 3                      | 9                           | –                                |
| 4             | PFE               | DCM     | 160             | 2000          | 3                      | 9                           | –                                |
| 5             | PFE               | DCM     | 200             | 2000          | 3                      | 9                           | –                                |
| 6             | PFE               | MeOH    | 100             | 2000          | 3                      | 9                           | –                                |
| 7             | Soxhlet            | DCM     | –               | –             | –                      | 90                          | –                                |
| 8             | Soxhlet            | MeOH    | –               | –             | –                      | 90                          | –                                |

Note: aCollection of additional extract in a separate vial from the 9 mL collected during the 3 cycle extractions.
2.3. SPE fractionation and preparation for GC analysis

We have previously demonstrated an SPE fractionation protocol applied to the PM extracts that is essential for the determination of trace concentrations of PAH derivatives [36]. Briefly, an aminopropyl SPE cartridge with 500 mg of sorbent, 55–105 µm particle size and a 125 Å pore size was used (Sep-Pak, Waters, Milford, MA). All SPE were performed using an SPE vacuum manifold with a 10-port top (Alltech/Grace, Columbia, Maryland, USA). Prior to the fractionation, the SPE sorbent was conditioned sequentially with DCM and n-hexane (6 mL each). The elution solvents employed sequentially were 5.0 mL of 100% n-hexane, 20% DCM in n-hexane and 100% MeOH. All collected SPE fractions were concentrated to 200 µL under a gentle nitrogen stream, and then divided into two 100 µL aliquots. One aliquot was used to determine PAHs and oxy-PAHs whereas the other was evaporated and derivatised with 100 µL of BSTFA + TMCS at 70°C for 6 h for the determination of hydroxy-PAHs.

2.4. GC-MS analysis

Determination of PAHs, oxy-PAHs and hydroxy-PAHs was performed using an Agilent 6890 N GC coupled to a 5975C MS with an electron ionisation (EI) source. The analyses were accomplished on a 25 m long DB-5MS column with a 0.25 mm I.D., and 0.25 µm film thickness (J&W Scientific, Inc., Folsom, CA). Ultra-pure helium (99.999%) was used as the carrier gas with a constant flow rate of 1.0 mL min⁻¹. Injection conditions were 1 min splitless time with a pressure pulse of 25 psi for 0.95 min and the injection volume of 1.0 µL using a splitless liner with deactivated glass wool (Restek, Bellefonte, PA). The temperatures of the injector and transfer line were 250°C and 280°C, respectively. The GC oven temperature programme started at 40°C for 1 min, increased at a rate of 20°C min⁻¹ to 140°C, followed by a gradient of 10°C min⁻¹ to 290°C, and an increase at the rate of 15°C min⁻¹ to 310°C, and held for 12 min.

The GC-MS data were acquired using a combination of total ion current (TIC) and selected ion monitoring (SIM) modes, i.e., selected-ion-total-ion (SITI). SITI combines the advantages of improved sensitivity, resulting from the use of SIM monitoring single ions, with simultaneous compound identification using TIC. A dwell time of 25 ms was used for all ions listed in Table 1 for the SIM mode. A range of 50–500 m/z was used for TIC.

2.5. Quantification

Quantification was based on the IS method, using fluoranthene-d₁₀ as the IS. Calibration solutions were prepared by serial dilutions of a stock mixture to obtain final analyte concentrations in the range of 9–9000 ng mL⁻¹. Volumes of each solution were the same as for the final prepared extracts, i.e., 100 µL, and spiked with the same amount of IS as the extracts.

Satisfactory interday precisions of calculated slopes of multiple calibration curves for selected species over different days are shown in Table 3. Prior to the extraction of PM, RS compounds were spiked to the PM. The RS compounds (listed in Table 1) were used to correct for analyte loss during extraction and fractionation. For each RS compound, a recovery yield (RY) was calculated (See Equation (1)).

\[
RY(\%) = \frac{m_{RS \text{ in PM extract}}}{m_{RS \text{ spiked to PM}}} \cdot 100\%
\]
For the extractions from both WS PM and SRM 2975, the calculated mass fractions (mass of analyte per mass of PM subjected to extraction) in each SPE fraction were summed to give a total mass concentration. The summed mass concentrations were then corrected by the RY (70–110%) of the RS compounds that were added prior to extraction (See Table 1 for each analyte’s assigned RS).

To ensure cleanliness of the extraction systems, blank extractions were routinely performed to evaluate any levels of background contamination, which served as a basis for determining the limits of detection (previously reported by Cochran et al. [36]).

3. Results and discussion

3.1. Optimisation of PFE

PFE conditions were optimised in order to achieve an efficient extraction of both PAHs and their oxidation products observed in WS PM and diesel exhaust PM (SRM 2975). For PAHs, it was previously reported that extraction pressures above 2000 psi (13.8 MPa) had no significant impact on the mass fractions extracted [28,35]. Thus, a pressure of 2000 psi was selected and maintained throughout all the experiments performed. To determine the

| Calibration standard | Interday precision | RSD |
|----------------------|--------------------|-----|
|                      | Average slope a (n = 3) |     |
| PAHs                 |                    |     |
| naphthalene          | 1.148 ± 0.112      | 10  |
| phenanthrene         | 1.201 ± 0.039      | 3   |
| anthracene           | 1.020 ± 0.140      | 14  |
| fluoranthene         | 1.257 ± 0.135      | 11  |
| pyrene               | 1.245 ± 0.150      | 12  |
| chrysene             | 1.256 ± 0.086      | 7   |
| benzo[a]pyrene       | 0.634 ± 0.066      | 10  |
| indeno[1,2,3-cd]pyrene| 0.490 ± 0.087      | 18  |
| benzo[ghi]perylene   | 0.724 ± 0.063      | 9   |
| Oxy-PAHs             |                    |     |
| 9-fluorenone         | 0.379 ± 0.012      | 3   |
| anthrone             | 0.100 ± 0.013      | 13  |
| 9,10-anthraquinone   | 0.544 ± 0.088      | 16  |
| 9,10-phenanthrenequinone| 0.047 ± 0.008 | 17  |
| Hydroxy-PAHs         |                    |     |
| 2-hydroxyphenyl-TMS  | 0.502 ± 0.080      | 16  |
| 4-hydroxyphenyl-TMS  | 0.557 ± 0.076      | 14  |
| 9-phenanthrol-TMS    | 0.335 ± 0.054      | 16  |
| 2-hydroxy-9-fluorenone-TMS| 0.597 ± 0.069 | 11  |
| 4-phenanthreneMeOH-TMS| 1.224 ± 0.181    | 15  |
| 1-hydroxyamine-TMS   | 0.507 ± 0.067      | 13  |
| 1,8-dihydroxyanthraquinone-TMS| 0.735 ± 0.078 | 11  |
| Carboxy-PAHs         |                    |     |
| 9-phenanthreneCOOH-TMS| 0.311 ± 0.031     | 10  |

Note: a Slope = (Area Analyte/Area IS)/Conc Analyte.
sufficient number of static/dynamic extraction cycles for WS PM, three 3 mL dynamic extraction steps were added to the previously used three extraction cycles. No PAH species were recovered in either of the additional dynamic extraction steps, showing that the use of three extraction cycles (giving a total extraction volume of 9.0 mL) was sufficient. Extraction temperatures were evaluated in the range of 100–200°C for PM extractions. Varying the extraction temperature did not appear to have a significant impact on the extracted mass concentrations of PAHs, oxy-PAHs or hydroxy-PAHs (shown in Figure 1 for representative species; see Figure S1 for data of all tested compounds). Therefore, the extraction temperature of 100°C was selected for all subsequent PFE experiments.

3.2. Comparison of PFE and Soxhlet

The efficiency of the optimised PFE method was determined by comparing mass concentrations extracted from WS PM and SRM 2975 to those obtained with Soxhlet extractions using DCM or MeOH for 18 h (Table 4). The GC-MS TIC chromatograms of SPE fractions for PFE extracts of wood smoke PM are shown in Figure S2.

To evaluate the efficiency of both methods to extract the target compounds from both PM matrices, RS solutions were spiked prior to the extraction. Calculated RY values for the RS compounds spiked to WS PM and SRM 2975 are shown in Figure 2a and 2b, respectively. For WS PM, recoveries for all of the RS compounds were higher when using PFE (90–100%) than those obtained with Soxhlet (60–80%). In comparing the extraction solvents, greater recoveries were obtained with DCM than with MeOH, with the exception of 2-chloroanthraquinone (2-caq in Figure 2). For SRM 2975, PAH RS

Figure 1. PFE recoveries of representative PAHs, oxy-PAHs and hydroxy-PAHs obtained from the extraction of WS PM at different extraction temperatures. For all temperatures the extraction pressure was held constant at 2000 psi (13.8 MPa) and three extraction cycles were performed. All data are based on the mean value of multiple extractions (n = 3) ± one standard deviation.
Table 4. Mass fractions of PAHs and polar derivatives (oxy-, hydroxy- and carboxy-PAHs) obtained by the extraction of WS PM using PFE and Soxhlet. PFE was performed at 100°C and 2000 psi using either DCM or MeOH (Methods 2 and 6, respectively). All data are based on the mean value of multiple extractions \((n = 3) \pm \) one standard deviation.

| Compound | PFE DCM (µg g\(^{-1}\))\(^{a}\) mean ± SD | PFE MeOH (µg g\(^{-1}\))\(^{a}\) mean ± SD | Soxhlet DCM (µg g\(^{-1}\))\(^{a}\) mean ± SD | Soxhlet MeOH (µg g\(^{-1}\))\(^{a}\) mean ± SD |
|----------|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|
| PAHs     |                                          |                                          |                                          |                                          |
| naphthalene | 5.90 ± 0.79 | 6.36 ± 0.71 | 7.88 ± 0.53 | 8.00 ± 0.41 |
| acenaphthylene | 2.32 ± 0.27 | 2.75 ± 0.33 | 2.67 ± 0.25 | 2.70 ± 0.33 |
| acenaphthene | 0.75 ± 0.10 | 1.16 ± 0.09 | 0.96 ± 0.03 | 1.35 ± 0.13 |
| fluorene | 9.68 ± 1.18 | 10.46 ± 0.62 | 9.31 ± 0.81 | 10.25 ± 0.60 |
| phenanthrene | 196.37 ± 6.91 | 187.42 ± 1.75 | 166.49 ± 14.57 | 170.42 ± 10.95 |
| anthracene | 23.82 ± 2.40 | 23.57 ± 0.24 | 31.14 ± 2.98 | 31.82 ± 3.45 |
| 2-methylanthracene | 13.06 ± 2.17 | 11.48 ± 0.48 | 15.43 ± 0.05 | 17.39 ± 1.19 |
| phen/anth-C\(_1\) A T | 27.34 ± 0.17 | 28.31 ± 0.84 | 31.34 ± 5.03 | 30.11 ± 3.48 |
| phen/anth-C\(_1\) B T | 31.72 ± 1.42 | 34.65 ± 0.76 | 38.97 ± 6.04 | 42.40 ± 3.12 |
| phen/anth-C\(_1\) C T | 9.70 ± 1.10 | 10.81 ± 0.81 | 12.30 ± 1.42 | 13.71 ± 1.16 |
| phen/anth-C\(_1\) D T | 23.49 ± 2.21 | 23.53 ± 1.67 | 27.16 ± 0.55 | 26.65 ± 3.78 |
| phen/anth-C\(_1\) E T | 1.83 ± 0.06 | 2.00 ± 0.20 | 2.28 ± 0.20 | 2.42 ± 0.23 |
| phen/anth-C\(_2\) A T | 5.03 ± 0.79 | 5.70 ± 0.46 | 5.53 ± 0.33 | 5.32 ± 0.48 |
| phen/anth-C\(_2\) B T | 3.74 ± 0.29 | 5.67 ± 0.52 | 4.14 ± 0.43 | 4.04 ± 0.38 |
| phen/anth-C\(_2\) C T | 3.63 ± 0.52 | 5.87 ± 0.62 | 4.68 ± 0.27 | 4.89 ± 0.52 |
| phen/anth-C\(_2\) D T | 2.54 ± 0.40 | 2.75 ± 0.30 | 3.31 ± 0.08 | 3.19 ± 0.35 |
| fluoranthene | 165.46 ± 6.49 | 169.29 ± 4.93 | 134.08 ± 8.22 | 139.03 ± 4.15 |
| pyrene | 160.22 ± 4.28 | 167.07 ± 7.00 | 136.45 ± 12.34 | 140.90 ± 6.18 |
| 1-methylpyrene | 14.00 ± 2.46 | 14.15 ± 0.44 | 14.35 ± 2.31 | 14.69 ± 1.04 |
| flu/pyr-C\(_1\) A T | 16.42 ± 0.75 | 15.12 ± 1.24 | 14.60 ± 2.02 | 15.36 ± 1.32 |
| flu/pyr-C\(_1\) B + C T | 27.97 ± 1.28 | 29.92 ± 1.13 | 25.09 ± 4.50 | 23.93 ± 2.93 |
| flu/pyr-C\(_1\) D T | 8.00 ± 1.08 | 11.09 ± 1.18 | 10.18 ± 1.53 | 12.28 ± 0.47 |
| flu/pyr-C\(_1\) E T | 13.40 ± 1.78 | 11.52 ± 0.89 | 13.48 ± 2.38 | 12.58 ± 1.22 |
| flu/pyr-C\(_1\) F T | 14.06 ± 1.73 | 12.81 ± 1.67 | 14.35 ± 2.31 | 13.43 ± 1.48 |
| flu/pyr-C\(_1\) G T | 10.99 ± 1.31 | 11.48 ± 1.45 | 13.47 ± 0.88 | 14.02 ± 1.54 |
| benzo[e]pyrene | 31.30 ± 4.25 | 39.66 ± 4.17 | 40.79 ± 2.38 | 38.50 ± 3.41 |
| benzo[a]anthracene | 52.56 ± 4.10 | 55.44 ± 2.43 | 52.47 ± 7.93 | 47.11 ± 2.61 |
| chrysene | 53.23 ± 5.36 | 52.89 ± 2.90 | 55.38 ± 4.86 | 51.15 ± 4.39 |
| benzo[e]acephenanthrylene | 4.57 ± 0.49 | 5.90 ± 0.56 | 5.17 ± 0.27 | 5.12 ± 0.27 |
| benzo[k]fluoranthene | 18.44 ± 1.64 | 19.87 ± 3.24 | 19.96 ± 1.27 | 18.98 ± 1.34 |
| benzo[j]fluoranthene | 9.59 ± 1.01 | 9.60 ± 0.73 | 9.56 ± 1.18 | 9.84 ± 0.92 |
| benzo[b]fluoranthene | 38.53 ± 3.23 | 43.27 ± 1.77 | 38.46 ± 6.27 | 38.86 ± 4.31 |
| benzo[a]pyrene | 31.47 ± 3.08 | 34.77 ± 1.54 | 37.74 ± 2.36 | 40.70 ± 1.90 |
| indeno[1,2,3-cd]pyrene | 20.40 ± 3.56 | 24.70 ± 4.27 | 26.19 ± 1.83 | 26.45 ± 2.50 |
| benzo[ghi]perylen | 17.72 ± 1.33 | 16.99 ± 1.71 | 16.38 ± 2.57 | 16.90 ± 2.00 |
| Total PAHs | 1097 ± 16 | 1134 ± 13 | 1075 ± 27 | 1089 ± 18 |
| Oxy-PAHs | 444 | 444 | R.E. Cochran and A. Kubáňová |

(continued)
recoveries were significantly lower for both extraction methods and solvents compared to WS PM. This trend is likely due to the relatively non-polar matrix of the DE PM matrix, which is further supported by DCM (less polar than MeOH) providing greater recoveries for all RS compounds. For the more polar RS compounds (2-CHM and 1-OH-py-d9), both methods and extraction solvents provided similar recoveries (85–98%).

3.3. Application of PFE and Soxhlet to WS PM

The efficiency of the PFE method for extracting WS PM was determined using DCM and MeOH as the extraction solvents. For DCM, the total mass fractions of PAHs and all polar derivatives were similar for PFE and Soxhlet (1849 and 1727 µg g⁻¹ in WS PM, respectively; more detailed values are shown in Table 4). For PAHs, the total mass fractions extracted were similar between both extraction methods (1097 µg g⁻¹ for PFE and 1075 µg g⁻¹ for Soxhlet). All individual PAH mass fractions followed this pattern (Table 4). PFE consistently provided higher mass fractions of most oxy-PAHs, 381 ± 12 µg g⁻¹ compared to 272 ± 13 µg g⁻¹.

| Compound                                      | PFE               | Soxhlet            |
|-----------------------------------------------|-------------------|--------------------|
|                                               | DCM (µg g⁻¹)      | MeOH (µg g⁻¹)     |
|                                               | mean ± SD (n = 4) | mean ± SD (n = 4) |
| benzo[c]fluoren-7-one T                       | 18.95 ± 2.71      | 33.93 ± 3.05       |
| benz[de]anthracen-7-one T                    | 31.54 ± 1.22      | 45.78 ± 5.95       |
| benz[a]anthracene-7,12-dione                 | 7.47 ± 0.48       | 13.42 ± 0.97       |
| **Total Oxy-PAHs**                           | **381 ± 12**      | **317 ± 10**       |
| **Hydroxy- & Carboxy-PAHs**                  |                   |                    |
| 2-hydroxybiphenyl                            | 13.35 ± 1.03      | 14.17 ± 0.36       |
| hydroxybiphenyl T                            | 28.27 ± 1.12      | 29.43 ± 1.70       |
| 4-hydroxybiphenyl                            | 25.17 ± 0.51      | 27.63 ± 1.67       |
| 7-hydroxycadalene                            | 108.14 ± 2.03     | 101.19 ± 5.76      |
| 9-phenanthrol                                | 6.99 ± 0.48       | 7.53 ± 0.71        |
| 3-phenanthrol T                              | 47.91 ± 0.71      | 64.50 ± 7.70       |
| 2-hydroxy-9-fluorenone                       | 28.70 ± 1.39      | 28.55 ± 1.15       |
| 4-phenanthrenemethanol                       | 1.87 ± 0.28       | 1.98 ± 0.17        |
| hydroxypyrone A T                            | 15.82 ± 1.59      | 17.25 ± 1.45       |
| hydroxypyrone B T                            | 24.74 ± 1.43      | 30.16 ± 2.53       |
| hydroxypyrone C T                            | 14.47 ± 1.47      | 19.04 ± 1.97       |
| 1-hydroxypyrine                              | 24.86 ± 1.63      | 33.56 ± 14.75      |
| hydroxypyrone D T                            | 10.46 ± 1.71      | 14.81 ± 0.95       |
| 1,8-dihydroxyanthraquinone                   | 1.17 ± 0.52       | 0.00 ± 0.00        |
| 4-penthenethrene-COOH                        | 10.40 ± 1.75      | 11.27 ± 0.68       |
| 9-anthracene-COOH                            | 1.94 ± 0.14       | 3.33 ± 0.42        |
| 9-phenanthrene-COOH                          | 6.34 ± 0.72       | 7.93 ± 0.85        |
| **Total Hydroxy- and Carboxy-PAHs**          | **371 ± 5**       | **412 ± 18**       |

Notes: a Recoveries are corrected by the response of RS.
b ‘NA’ denotes that standards for that particular compound were not available during the time of the study.
c ‘ND’ denotes that response was zero or below the limit of quantitation (determined from lowest three points of calibration curve).
d All hydroxy- and carboxy-PAHs are shown as trimethylsilyl derivatives after derivatisation with BSTFA.
e 2-CHM is an acronym for 2-chloro-2-hydroxy-4-methylbenzophenone.
obtained with Soxhlet. Specifically, 9-fluorenone had a twofold increase in the mass fraction extracted when using PFE compared to Soxhlet (both using DCM) (Table 4). Previously it has been observed that 9,10-phenanthrenedione can be degraded in the GC inlet during injection, leading to the formation of 9-fluorenone [37]. However, this would not account for differences in extraction amounts, which even after correction with their respective RSs still exhibited greater extraction amounts. PFE also enabled the detection of benz[a]anthracene-7,12-dione, which was not detected in the Soxhlet extracts (using either DCM or MeOH). While increases may be attributed to the higher temperatures used with PFE in comparison to Soxhlet, possibly

Figure 2. Recovery yields (RY; %) of RS compounds observed from PFE and Soxhlet extraction of (a) WS PM and (b) SRM 2957. RY values are shown for extractions using both DCM and MeOH as the extraction solvents. All data are based on the mean value of multiple extractions ($n = 3$) ± one standard deviation.
due to an increased disruption of the analyte–matrix interactions, it is not certain why significant differences were observed.

To evaluate possible influences of the solvent on extraction efficiencies, PFE was applied to WS PM using MeOH. Mass fractions of PAHs extracted were similar to those obtained with DCM (1134 ± 13 compared to 1097 ± 16 µg g⁻¹, respectively). The combined mass fractions of oxy-PAHs were lower than with DCM (317 ± 10 and 381 ± 12 µg g⁻¹, respectively); however, the extraction yields of 4-ring oxy-PAHs were higher with MeOH. For hydroxy- and carboxy-PAHs, the total obtained mass fractions were greater with MeOH (412 ± 18 µg g⁻¹) than those with DCM (371 ± 5 µg g⁻¹). This feature was the most prevalent for carboxy-PAHs; however, the mass fractions were still lower than those determined in extracts from Soxhlet (using either DCM or MeOH).

The hydroxy-PAH mass fractions with PFE were similar to those obtained by Soxhlet DCM extraction (75–130%) (Table 4). One of the studied carboxy PAH species (4-phenanthrene-COOH) showed similar mass fractions (82% relative to those with Soxhlet) whereas the other isomers (9-anthracene-COOH and 9-phenanthrene-COOH) yielded lower recoveries (42% and 44%, respectively, relative to those with Soxhlet) (Table 4). In comparison to Soxhlet using DCM, a small increase in the amounts extracted (up to an additional 15%) of these carboxy- and hydroxy-PAH species was observed when performing a Soxhlet extraction using MeOH (Table 4). Our temperature evaluation (Section 3.1) did not show any increase in yields for these species. When using MeOH as the extraction solvent for PFE, the extracted mass fractions increased slightly for the carboxy-PAH species (23 ± 1 compared to 19 ± 2 µg g⁻¹ for DCM); however, they were still significantly lower relative to the amounts obtained with Soxhlet (with either DCM or MeOH). Nevertheless, it is important to note that relative to the overall amounts of PAHs and their oxidation products present in WS PM, these carboxy species were only minor contributors (only ca. 1% of the total amount extracted of all species of PAHs and PAH oxidation products investigated in this study: 1849 ± 21 and 1727 ± 33 µg g⁻¹ for PFE and Soxhlet with DCM, respectively). Thus, the similar mass fractions for the majority of PAH, oxy-PAH and hydroxy-PAH species as well as the ease of use, especially during essential re-concentration steps, support the appropriateness of PFE with DCM for the extraction of PAH derivatives from PM. However, if highly polar species are targeted such as carboxy-PAHs, the use of MeOH either as a single solvent or modifier may be essential.

3.4. Application of PFE and Soxhlet to DE PM

In order to investigate the efficiency of PFE for the simultaneous extraction of PAHs and their wide range of derivatives from a relatively non-polar matrix, the PFE method was applied to diesel exhaust PM (SRM 2975). Additionally, the use of SRM allowed for the evaluation of the performance of the optimised PFE method by comparing the mass fractions extracted to those reported in previous studies (Table 5).

Similar to WS PM, the mass fractions of PAHs and oxy-PAHs extracted were similar or slightly higher for PFE than with Soxhlet. Using DCM with PFE provided increased amounts extracted for both PAHs and oxy-PAHs than when using MeOH. In contrast to WSPM, for which MeOH was more efficient for the higher molecular weight (4–6 ring) PAHs, DCM yielded greater amounts of these species from SRM 2975. For 1-nitropyrene mass fractions obtained with DCM were significantly higher than with MeOH, a trend observed for both extraction methods. We did not evaluate any other nitro-PAHs as previous studies evaluated extraction efficiencies in detail [18,19]. The only hydroxy-PAH observed (1-hydroxypyrene)
Table 5. Mass fractions of PAHs and polar derivatives (oxy-, hydroxy- and carboxy-PAHs) obtained by the extraction of SRM 2957 (diesel exhaust PM) using PFE and Soxhlet. PFE was performed at 100°C and 2000 psi using either DCM or MeOH (Methods 2 and 6, respectively). All data are based on the mean value of multiple extractions \((n = 3)\) ± one standard deviation. Reference and certified values are shown for comparison and verification of the methods accuracy.

| Compound | This study<sup>a</sup> | Ref 35 | Certified | Ref 28 |
|----------|-------------------------|--------|-----------|--------|
|          | PFE<sup>b</sup>         | PFE<sup>c</sup> | PFE<sup>c</sup> | PFE<sup>c</sup> |
|          | DCM (µg g<sup>−1</sup>)<sup>b</sup> mean ± SD | MeOH (µg g<sup>−1</sup>)<sup>b</sup> mean ± SD | DCM (µg g<sup>−1</sup>)<sup>b</sup> mean ± SD | MeOH (µg g<sup>−1</sup>)<sup>b</sup> mean ± SD | Toluene (µg g<sup>−1</sup>) mean ± SD | Toluene(MeOH) (µg g<sup>−1</sup>) mean ± SD | DCM (µg g<sup>−1</sup>) mean ± SD |
| phenanthrene | 18.39 ± 0.45 (n = 4) | 16.87 ± 1.11 (n = 4) | 18.89 ± 0.76 (n = 4) | 16.56 ± 1.65 (n = 4) | 18.30 ± 0.50 (n = 4) | 17.00 ± 2.80 (n = 4) | 17.2 ± 1.5 (n = 4) | 18.6 ± 0.9 (n = 4) |
| fluoranthene | 27.59 ± 0.73 (n = 4) | 22.74 ± 1.60 (n = 4) | 25.55 ± 1.58 (n = 4) | 23.50 ± 0.87 (n = 4) | 28.20 ± 0.60 (n = 4) | 26.60 ± 5.10 (n = 4) | 25 ± 2.4 (n = 4) | 28.9 ± 1.6 (n = 4) |
| pyrene | 1.45 ± 0.09 (n = 4) | 1.30 ± 0.14 (n = 4) | 1.24 ± 0.17 (n = 4) | 0.98 ± 0.11 (n = 4) | 1.01 ± 0.06 (n = 4) | 0.90 ± 0.24 (n = 4) | 1.04 ± 0.12 (n = 4) | 1.03 ± 0.05 (n = 4) |
| benzo[a]anthracene | 0.63 ± 0.03 (n = 4) | 0.57 ± 0.09 (n = 4) | 0.72 ± 0.10 (n = 4) | 0.36 ± 0.03 (n = 4) | 0.39 ± 0.02 (n = 4) | 0.32 ± 0.07 (n = 4) | 0.39 ± 0.02 (n = 4) | 0.34 ± 0.03 (n = 4) |
| chrysene | 4.46 ± 0.44 (n = 4) | 4.18 ± 0.22 (n = 4) | 3.70 ± 0.46 (n = 4) | 3.12 ± 0.21 (n = 4) | NR | 4.56 ± 0.16 (n = 4) | NR | NR |
| benzo[k]fluoranthene | 1.00 ± 0.05 (n = 4) | 0.78 ± 0.08 (n = 4) | ND | 0.59 ± 0.04 (n = 4) | 0.73 ± 0.03 (n = 4) | 0.68 ± 0.08 (n = 4) | 0.6 ± 0.02 (n = 4) | 0.66 ± 0.08 (n = 4) |
| benzo[e]pyrene | 1.46 ± 0.14 (n = 4) | 1.14 ± 0.10 (n = 4) | 1.40 ± 0.08 (n = 4) | 1.15 ± 0.09 (n = 4) | 1.21 ± 0.06 (n = 4) | 1.11 ± 0.10 (n = 4) | 1.07 ± 0.1 (n = 4) | 1.09 ± 0.07 (n = 4) |
| benzo[j]fluoranthene | 2.33 ± 0.18 (n = 4) | 1.88 ± 0.31 (n = 4) | 1.95 ± 0.21 (n = 4) | 1.37 ± 0.20 (n = 4) | 0.05 ± 0.00 (n = 4) | 0.05 ± 0.01 (n = 4) | 0.22 ± 0.04 (n = 4) | <0.5 |
| benzo[a]pyrene | 0.46 ± 0.10 (n = 4) | 0.22 ± 0.16 (n = 4) | 0.33 ± 0.05 (n = 4) | 0.26 ± 0.07 (n = 4) | 0.05 ± 0.00 (n = 4) | 0.05 ± 0.01 (n = 4) | 0.22 ± 0.04 (n = 4) | <0.5 |
| indeno[1,2,3-cd]pyrene | 1.41 ± 0.14 (n = 4) | 1.00 ± 0.08 (n = 4) | 0.87 ± 0.09 (n = 4) | 0.89 ± 0.09 (n = 4) | 1.45 ± 0.11 (n = 4) | 1.40 ± 0.20 (n = 4) | 0.74 ± 0.03 (n = 4) | 0.81 ± 0.03 (n = 4) |
| dibenz[a,h]anthracene | 1.18 ± 0.05 (n = 4) | 0.85 ± 0.05 (n = 4) | 0.76 ± 0.04 (n = 4) | 0.77 ± 0.06 (n = 4) | 0.37 ± 0.02 (n = 4) | 0.37 ± 0.07 (n = 4) | 1.74 ± 0.3 (n = 4) | 1.71 ± 0.12 (n = 4) |
| benzo[ghi]perylene | 1.00 ± 0.03 (n = 4) | 0.71 ± 0.09 (n = 4) | 0.84 ± 0.12 (n = 4) | 0.65 ± 0.06 (n = 4) | 0.50 ± 0.03 (n = 4) | 0.50 ± 0.04 (n = 4) | 0.47 ± 0.02 (n = 4) | 0.48 ± 0.02 (n = 4) |
| **Total of Selected PAHs** | **62 ± 1** | **53 ± 2** | **57 ± 2** | **51 ± 2** | **52 ± 1** | **54 ± 6** | **48 ± 3** | **54 ± 2** |
| Nitro-PAHs | 1-nitropyrene | 34.60 ± 1.14 (n = 4) | 26.19 ± 1.58 (n = 4) | 33.44 ± 1.39 (n = 4) | 21.14 ± 1.28 (n = 4) | 34.80 ± 4.70 (n = 4) |
| Oxy-PAHs | 9-fluorenone | 6.45 ± 0.25 (n = 4) | 4.39 ± 0.24 (n = 4) | 4.33 ± 0.35 (n = 4) | 4.26 ± 0.26 (n = 4) | NR | NR |
| 9,10-anthraquinone | 14.59 ± 1.35 (n = 4) | 8.00 ± 0.87 (n = 4) | 8.62 ± 0.74 (n = 4) | 9.21 ± 0.72 (n = 4) | NR | NR |
| benzo[b]fluoren-11-one T | 6.94 ± 0.69 (n = 4) | 4.57 ± 0.21 (n = 4) | 4.49 ± 0.22 (n = 4) | 4.62 ± 0.22 (n = 4) | NR | NR |
| benzo[a]fluoren-11-one T | 5.03 ± 0.69 (n = 4) | 3.83 ± 0.68 (n = 4) | 5.54 ± 0.38 (n = 4) | 3.78 ± 0.50 (n = 4) | NR | NR |

<sup>a</sup> Ref 35, Certified Ref 28.
| Compound                                      | Method 1       | Method 2       | Method 3       | Method 4       |
|----------------------------------------------|----------------|----------------|----------------|----------------|
| Benzo[c]fluoren-7-one T                      | 6.56 ± 0.54    | 5.15 ± 0.22    | 5.47 ± 0.35    | 4.94 ± 0.61    |
| Benz[de]anthracen-7-one T                    | 7.20 ± 0.75    | 7.11 ± 0.56    | 7.40 ± 0.21    | 7.13 ± 0.42    |
| Benz[a]anthracene-7,12-dione                 | 5.09 ± 0.27    | 4.20 ± 0.55    | 5.13 ± 0.20    | 4.41 ± 0.30    |
| Total Oxy-PAHs                               | 52 ± 2         | 37 ± 1         | 41 ± 1         | 38 ± 1         |

**Hydroxy- & Carboxy-PAHs**

| Compound               | Method 1       | Method 2       | Method 3       | Method 4       |
|------------------------|----------------|----------------|----------------|----------------|
| 9-phenanthrene-COOH    | 24.30 ± 2.30   | 31.06 ± 2.59   | 31.69 ± 2.28   | 36.50 ± 1.80   |
| n-phen/anth-COOH A     | 25.04 ± 1.07   | 32.45 ± 1.70   | 32.51 ± 2.40   | 41.00 ± 1.94   |
| 1-hydroxypyrene        | 4.49 ± 0.44    | 3.71 ± 0.14    | 4.34 ± 0.40    | 3.63 ± 0.42    |
| Total Hydroxy- and Carboxy-PAHs | 54 ± 3   | 67 ± 3         | 69 ± 3         | 81 ± 3         |

**Notes:**

*PFE conditions: 100°C at 2000 psi; Soxhlet conditions: 90 mL solvent for 18 h.

*Mass fractions are corrected by the response of RS.

*All the reference studies shown performed PFE at 100°C and 2000 psi.

*’NR’ denotes that mass fraction were not reported. ‘ND’ denotes that the particular analyte was not observed in the extract.

*Reported as the sum of benzo[b + j]fluoranthene due to co-elution during chromatographic separation.

*Values shown are possibly due to co-elution of dibenz[a,h]anthracene+dibenz[a,c]anthracene (also reported in Reference [28]).

*All hydroxy- and carboxy-PAHs are shown as trimethylsilyl derivatives after derivatisation with BSTFA.
also followed this trend. By contrast, two carboxy-PAHs extracted from SRM 2975 were more efficiently extracted with MeOH using either PFE or Soxhlet.

Mass fractions obtained for PAHs in this study were also compared to those reported for SRM in previous studies (also using PFE with a variety of different solvent systems) (see Table 5) [19,28,33,35]. For phenanthrene and fluoranthene (the most abundant PAHs in SRM 2975), similar mass fractions extracted were observed in this study compared to previous work (95–110%). For the majority of the other higher molecular weight PAHs (4–6 rings), our optimised method provided slightly increased mass fractions. The most significant increases were observed for benzo[a]fluoranthene, benzo[a]pyrene and dibenz[a,h]anthracene, the latter of which may possibly be due to co-elution with the dibenz[a,c]anthracene isomer. While the other nitro-PAHs found in SRM 2975 can be evaluated with the use of the more sensitive negative-ion chemical ionisation (NICI), the use of 1-nitropyrene confirms both accuracy and precision of the PFE method for nitro-PAHs, showing similar results with DCM (34.6 ± 1.1 compared to 39.6 ± 1.7 µg g⁻¹ by Bamford et al. [33]).

4. Conclusions

PFE was evaluated and determined to be a suitable alternative extraction method to the commonly deployed Soxhlet extraction for the simultaneous extraction of PAHs, oxy-PAHs, hydroxy-PAHs and carboxy-PAHs from a polar PM matrix (WS PM) and a relatively non-polar matrix (DE PM; SRM 2975). PFE extraction with DCM resulted in similar mass fractions extracted in 15 min using only 9 mL of DCM, in contrast to a more solvent/time-intensive Soxhlet DCM extraction (1080 min, 90 mL). Some oxy-PAH species exhibited greater mass fractions with PFE, most likely due to the increased temperatures employed in PFE overcoming the analyte–matrix interactions within the WS PM. By contrast, highly polar carboxy-PAHs (minor components) had higher extraction yields with Soxhlet using DCM or MeOH compared to PFE with DCM. Using PFE with MeOH slightly increased the amounts extracted for these compounds. Nevertheless, the overall extraction yields of PAHs and their derivatives obtained by both methods were similar (1849 ± 21, 1727 ± 33 µg g⁻¹ for PFE and Soxhlet with DCM, respectively). The results of SRM 2975 extractions with both PFE and Soxhlet were in agreement with previous studies. For PAHs, oxy-PAHs and nitro-PAHs DCM provided higher mass fractions while MeOH yielded greater amounts for carboxy-PAHs. Finally, it is critical to note that most environmental studies focus only on PAHs. Our data on WS PM demonstrated that PAH derivatives comprised ca. 40% of all species quantified, supporting their possible contribution to environmental and health impacts.

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