Optimized simultaneous pressurized fluid extraction and in-cell clean-up, and analysis of polycyclic aromatic hydrocarbons (PAHs), and nitro-, carbonyl-, hydroxy -PAHs in solid particles

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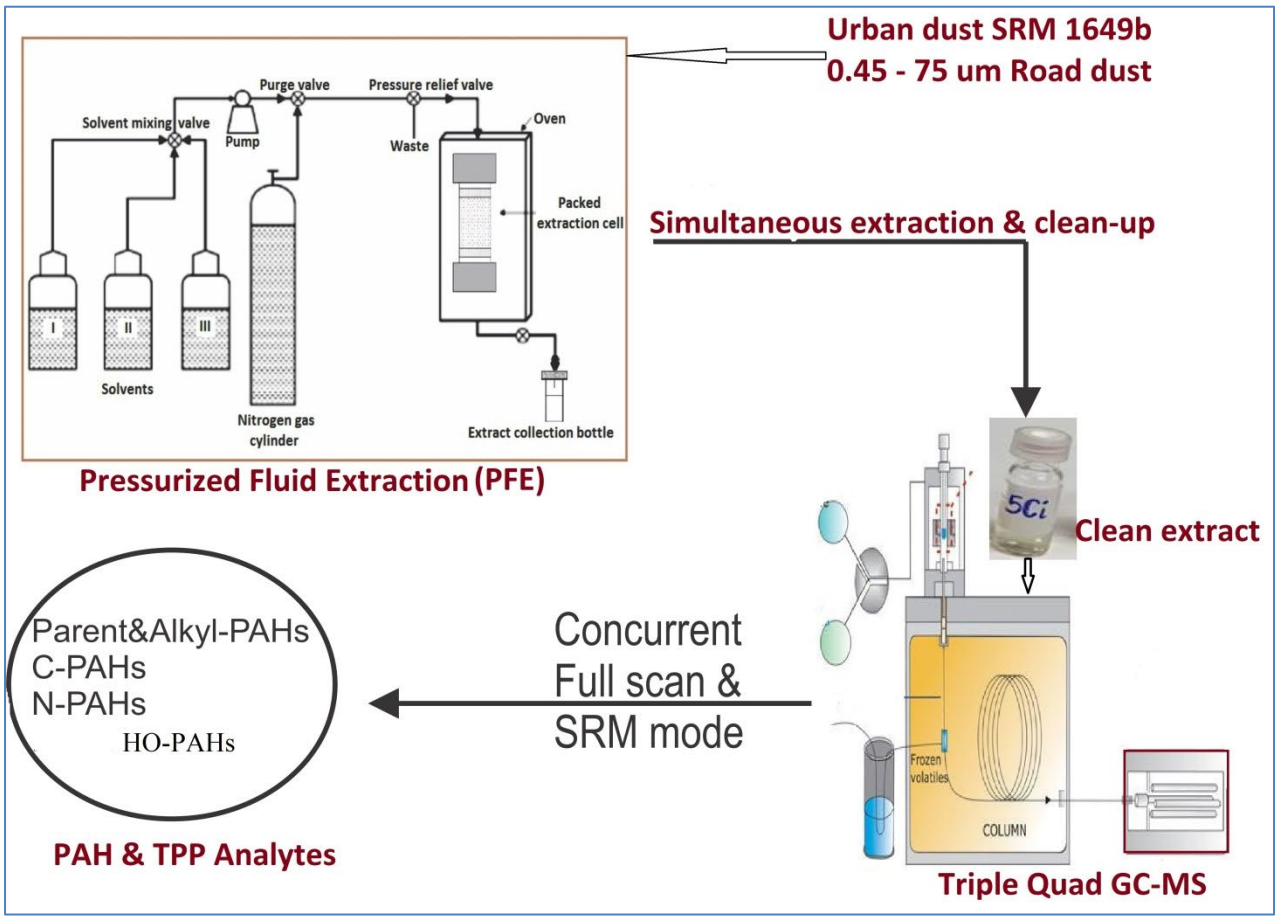
ABSTRACT

The development, modification and optimization of analytical methods capable of simultaneous extraction and in-cell clean-up of extracts for subsequent determination of parent PAHs and their associated transformed nitro-PAHs (NPAH), carbonyl-PAHs (CPAH) and hydroxy-PAHs (HO-PAH) products (TPPs) is essential for reducing the time and cost of analysis. The aim of this study was to modify and optimize pressurized fluid extraction (PFE) technique capable of simultaneous extraction and in-cell clean-up of PAHs and TPPs in urban dust standard reference material and road dust for GC-MS analyses. In this study, multivariate data analysis such as factor analysis (FA), and preference ranking organisation method for enrichment evaluation (PROMETHEE) and geometrical analysis for interactive aid (GAIA) were used to assess the performance of methods. As the key outcome of the study, an optimized selective reaction monitoring (SRM) Triple Quadrupole (TQ) electron ionization (EI)-GC/MS for measuring PAHs and TPPs without derivatization of polar HO-PAHs was developed. The limits of detection (LOD) for parent PAHs, CPAHs, NPAHs and HO-PAHs using Shimadzu TQ were 1.0-5.0 pg, 1.0-5.0 pg, 1.0-50.0 pg, and 1.0-25.0 pg, respectively. The PROMETHEE-GAIA analysis of the results showed that a combination of 3% deactivated silica gel and activated alumina (2:1) as in-cell clean-up material, and sequential PFE extraction (200 ^{o}C ASE temperature, 9 min preheat time and 3 times extraction cycle) using 100% hexane followed by hexane/DCM (1:1) is the best condition for analytes extraction from road dust. An optimized, fast and reliable GC/MS method operated solely in electron ionization (EI) mode was developed for measuring all analytes. The outcomes of this study will contribute significantly to future research on PAHs and TPPs thereby promoting safe and sustainable environment.

Keywords

Pressurized fluid extraction; Optimization; Transformed PAH products; Electron ionization; Multivariate data analysis

GRAPHICAL ABSTRACT



1. Introduction

The growing recognition of the significant health and environmental hazards associated with transformed PAH products (TPPs) such as nitro-PAH (NPAH), carbonyl-PAH (CPAH) and hydroxy-PAHs (HO-PAH) have stimulated interest in assessing these micro-organic pollutants in the environment [1, 2]. Further interest in these TPPs arises because of their enhanced polarity, solubility and mobility due to the incorporation of new functional groups into the molecular structure of the parent PAHs [3-5]. As a result, some TPPs may have greater estrogenic, mutagenic and carcinogenic toxicity, bioavailability and bioaccumulation properties compared to their parent PAHs [2, 6, 7]. Additionally, many of these compounds are listed as potential human carcinogens and priority pollutants by the International Agency for Research on Cancer (IARC) and various National Regulatory Authorities such as the USEPA [7, 8]. In this regard, a reduction in the environmental concentration of parent PAHs is not an absolute guarantee of diminished toxicity and exposure to these pollutants. Therefore, a holistic determination of both PAHs and their associated TPPs in the environment, including road dust sample, a major accumulation matrix for these analytes in the urban environment is warranted since most previous studies have focussed primarily on parent PAHs [2, 9, 10].

Numerous challenges have been identified by Gbeddy, Goonetilleke [2] as impediments in the widespread assessment of PAHs and their TPPs incorporated in road dust. Notably, the lack of comprehensive analytical methods that are rapid, less solvent consuming, cost-effective and

capable of measuring trace quantities of these critical pollutants simultaneously in small quantities of sample is a major challenge. The integrity of the data underpinning any research finding is highly dependent on the selection of robust analytical method during sample processing and analysis. In this context, sample preparation, extraction, extract clean-up and concentration, and analysis constitute critical steps in the effective assessment of these pollutants. Numerous techniques including Soxhlet extraction (SE), mechanical agitation (MA), ultrasonic/sonication agitation (UA), subcritical water extraction (SWE) and supercritical fluid extraction (SFE) have been used to extract PAH analytes from solid samples. Other extraction methods include solid-phase extraction (SPE), solid-phase micro-extraction (SPME), microwave-assisted extraction (MAE), fluidised-bed extraction (FBE), micro-extraction, flash pyrolysis /high temperature distillation (HTD), thermal desorption (TD), quick easy cheap effective rugged and safe (QuEChERS) like extraction, and pressurised fluid extraction (PFE). The advantages and disadvantages associated with these methods are shown in Table S1. Additional information on these methods can also be found in Albinet, Tomaz [11], Barcelo [12] and Lau, Gan [13]. The choice of a particular method is largely dependent on the method's potential for optimization so as to enhance its efficiency and suitability for the sample matrix [14]. In this context, PFE using the accelerated solvent extractor (ASE) has proven to be highly versatile with great modification and optimization potential for the simultaneous extraction of analytes and in-cell clean-up of extracts.

PFE is a state-of-the-art automated and streamlined sample preparation technique that utilizes elevated pressure and temperature simultaneously with liquid solvents, thereby elevating the extraction kinetics in order to attain efficient and rapid abstraction of analytes from various solid matrices such as soil and road dust. In comparison with other solvent intensive techniques such as sonication and SE, PFE is faster, has comparable or higher analyte recoveries with excellent reproducibility and low solvent consumption. Moreover, PFE meets the requirements of USEPA Method 3545 for extracting PAH analytes [15-17].

Performance of PFE can generally be enhanced by considering a combination of actions and operational parameters of the ASE. These include drying and grinding of samples to increase surface area, thereby ensuring enough contact of solvent with analytes, and dispersing the samples by adding clean inert material such as diatomaceous earth to prevent sample aggregation during extraction. Additionally, the selection of appropriate cell size which can be packed very well with the sample to minimize void space is also vital. Furthermore, using effective volatile solvent or mixture of solvents with suitable polarity for the analytes, and the application of appropriate temperature are essential for the effective extraction of analytes. The application of these conditions facilitates the attainment of the correct solvent viscosity necessary for sample wetting thereby expediting analyte solubility. Moreover, the use of precise pressure capable of sustaining the solvent in the liquid phase above their atmospheric boiling point is highly relevant for the rapid movement of fluid through the packed ASE cell system. Finally, the choice of appropriate number of static cycles especially for highly concentrated or difficult to penetrate samples, and the application of correct static time to allow analyte diffusion into extraction solvent are key factors in enhancing PFE efficiency [15].

The resultant extracts from the PFE process are typically complex with interference. Therefore, the extracts require clean-up or fractionation via SPE and open column chromatography prior to the determination of analytes [11, 18-20]. Ahmed, Bergvall [20] noted that coupling of the clean-up step to the extraction process could drastically reduce the labour intensity, time, cost and the risk of errors. In this regard, Lundstedt, Haglund [18], developed a selective PFE method with in-built simultaneous extraction and fractionation of parent PAHs and their oxygenated carbonyl TPPs (CPAHs) in contaminated soils. Although this method is an enhanced PFE method; it was only used to extract a limited number of TPPs in large quantities

of soil samples. Therefore, the PFE process requires further modification in order to deal with a wider range of TPPs in minute quantities of solid particles.
Among the TPP analytes, HO-PAHs usually require chemical derivatization into their more volatile trimethylsilyl (TMS) ether derivatives [21] prior to gas chromatography – mass spectrometry (GC-MS) analysis [22]. The derivatization process enhances the sensitivity, thermal stability and chromatographic performance of HO-PAHs [4]. However, the derivatization process often extends the duration of the GC-MS analysis significantly. As a result, most previous studies exclude HO-PAHs during analysis. It is, therefore, prudent to explore the applicability of PFE in extracting HO-PAHs devoid of the derivatization process, thereby reducing the time and cost of analysis. Past literature shows that PFE has only been applied to simultaneously extract and fractionate parent PAHs and some TPPs in soil samples weighing more than one gram [23]. In this regard, this study was aimed at modifying and optimizing an easy, cost effective, and efficient PFE and GC-MS analytical program to test simultaneously parent PAHs, NPAHs, CPAHs and HO-PAHs in SRM 1649b urban dust and road dust samples. The specific objectives entailed (i) developing a PFE method capable of simultaneous extraction and clean-up of analytes from minute quantities of road dust samples; (ii) evaluating the effectiveness of the developed method by applying it to urban dust standard reference material (SRM) 1649b and collected road dust samples; and (iii) developing an optimized GC-MS method capable of measuring all analytes without derivatization of HO-PAHs. This study constitutes the foundation for the application of PFE in the simultaneous extraction and in-cell clean-up of parent PAHs, NPAHs, CPAHs and HO-PAHs laden in aerosol urban dust SRM and road dust samples. It is anticipated that the outcomes of this study will be beneficial in the environmental monitoring of these analytes in varied solid samples.

2. Materials and methods

2.1 Materials and reagents

PFE method development and optimization was carried out using the following three different types of samples: (1) Pro analysis Sea sand (100-315 µm particle size) obtained from Merck KGaA, Germany as a pseudo dust sample for initial assessment of various extraction conditions; (2) Urban dust Standard Reference Material (SRM) 1649b (<63 µm particle size) procured from the National Institute of Standards and Technology (NIST), USA to evaluate the precision and accuracy of the method; and (3) 0.45-75 µm road dust collected on the eleventh antecedent dry day (as described in Gbeddy, Jayarathne [24]) to optimize the developed method for a real-world sample. The chemical standards for 26 parent PAHs, 14 potential TPPs (6 NPAHs, 4 CPAHs, 4 HO-PAHs) and deuterated surrogates and internal standard as indicated in Table S2 of the Supplementary material were acquired from Novachem Superior Standards, Australia and Sigma-Aldrich group Australia. These ubiquitous TPPs were selected based on a careful comparison of previous studies on road dust and soil samples (see Gbeddy, Goonetilleke [2]). HPLC grade organic solvents including acetone, dichloromethane (DCM), toluene, cyclohexane, hexane, and methanol were obtained from Sigma-Aldrich group Australia. Diatomaceous earth, silica gel 60 (70–230 mesh), alumina and Na_2SO_4 (pro-analysis quality, water free) were purchased from Novachem Superior Standards, Australia. Na_2SO_4, silica gel and alumina were heated at 300 °C for 12 hours whilst diatomaceous earth was baked at 460 ºC for 12 hours before use. Deactivated silica gel (2 % and 3 %) was prepared from the activated silica gel cooled to room temperature.

2.2 Assessing the optimum simultaneous PAH analytes extraction and clean-up method

A combination of three different sets of conditions and parameters were used for assessing the optimum scenario for the simultaneous extraction and in-cell clean-up of parent PAHs and TPPs in this study. This entailed varying cell packing materials, solvent mixtures and ASE operating conditions.

2.2.1 Cell packing

Five different categories of cell packing consisting of varied in-cell clean-up materials were used based on the findings of previous research by Lundstedt [23] and Lundstedt, Haglund [18]:

1) Approximately 3 g of deactivated (2 %) silica gel was placed on top of the outlet filter paper.
2) Approximately 2 g of deactivated (2%) silica gel and 1 g of activated alumina (2:1 silica gel and alumina) mixture was placed on top of the outlet filter paper.
3) Approximately 2 g of activated silica gel and 1 g of activated alumina (2:1 silica gel and alumina) mixture was placed on top of the outlet filter paper.
4) Approximately 3 g of deactivated (3 %) silica gel was placed on top of the outlet filter paper.
5) Approximately 2 g of deactivated (3 %) silica gel and 1 g of activated alumina (2:1 deactivated (3 %) silica gel and alumina) mixture was placed on top of the outlet filter paper.

A glass fibre filter paper was fitted to the outlet of all the 5 mL and 33 mL cells to prevent clogging of the metal frit. A second glass fibre filter paper was placed on top of the packed in-cell clean-up material and then about 0.150 g of sample, 0.075 g diatomaceous earth and 1 g anhydrous Na_2SO_4 homogenate mixture were added to each of the cells. 100 µL of PAH and TPP analytes, and surrogate standard solution (1 ng μL^{-1}) was spiked on top of the packed cell. Excess space in the cell was filled with anhydrous Na_2SO_4 and diatomaceous earth followed by a third filter paper was placed on top. The packed cell was then closed and allowed to equilibrate in a desiccator at room temperature for 24 hours prior to the PFE process.

2.2.2 Extraction solvent mixtures

The significant variability in polarities of the analytes requires appropriate solvent mixtures to facilitate optimum sequential and simultaneous extraction of parent PAHs and their TPPs. It is believed that a mixture of solvents of varying polarities (polar and nonpolar) may be more efficient in extracting analytes than individual solvents [15, 25]. In this regard, four different solvent mixtures each consisting of three solvent ratios of increasing polarities was used during the extraction process of loaded cells in the ASE. These solvents were selected based on previous studies, capacity to solubilize analytes without destroying the sample matrix and their cost-effectiveness [15, 18, 26].

A. Cyclohexane/dichloromethane (5:1 v/v); cyclohexane/dichloromethane (1:3 v/v); and cyclohexane/acetone (1:1 v/v).
B. Dichloromethane/acetone (1:1 v/v); dichloromethane/acetone (3:1 v/v); and dichloromethane/acetone (1:3 v/v).
C. 100% hexane; hexane/dichloromethane (1:1 v/v); and 100% methanol.
D. 100% dichloromethane; dichloromethane/methanol/acetone (1:1:1 v/v); and dichloromethane/methanol/acetone (1:2:1 v/v).

2.2.3 Accelerated solvent extractor (ASE) operating conditions

Two different sets of DIONEX ASE 350 operating conditions were employed during the PFE process starting with the default method conditions by DIONEX [15] and USEPA method 3545A [26] as follows:

i. ASE was pressurized to 17 MPa and heated to 100°C within 5min. Pressure and heat were held for 5 min (static extraction), with a flush volume of 100% followed by rinsing with more solvent (60% of cell volume) and purging with N_2 for 90 seconds.
ii. ASE was pressurized to 17 MPa and heated to 120°C within 6min. Pressure and heat were held for 5 min (static extraction), with a flush volume of 100% followed by rinsing with more solvent (60% of cell volume) and purging with N_2 for 90 seconds.

Using a permutation of the five cell packings, four extraction solvent mixtures and two ASE operating conditions as described in Section 2.2, a series of forty cells were prepared for subsequent PFE. Each of the cells was labelled appropriately by combining the three components above. For example, 1Aii referred to 1st cell packing, using Ath solvent mixture and iith ASE operating condition, respectively. The capped cells were loaded into the ASE and sequentially extracted using each of the solvent mixtures in order to obtain three extract fractions per cell. Each fractional extract per solvent mixture was collected into separate 60 mL glass vials and labelled accordingly. A total of 120 fractional extracts were obtained from the 40 packed cells during the method screening phase. Collected extracts were evaporated to dryness using a gentle stream of nitrogen gas. The solvent phase was then changed by adding 0.9 mL of DCM and then transferred to a 2 mL glass vial. 100 µL of Fluoranthene-D_{10} and Chrysene-D_{12} internal standard solution was added to obtain 1 mL solution for GC-MS analyses.

2.2.4 Choice of screening methods and application to standard reference material (SRM 1649b)

The results generated from the screening test were analysed using two approaches. First, the analyte concentrations were converted to absolute deviation from the spiked concentration and then subjected to Preference Ranking Organisation Method for Enrichment Evaluation (PROMETHEE) in order to rank the methods according to their accuracy and performance. The full details of the complete ranking method used (PROMETHEE-II) can be found in Ayoko, Bonire [29], Behzadian, Kazemzadeh [30] and Doyi, Essumang [31]. Equal weight was allocated to all criteria and the V-shape preference function was used. Ranking was done based on preference for minimal absolute deviation. The top seven (7) methods were selected for subsequent validation using SRM 1649b sample. Secondly, the analyte concentrations were converted to percentage recovery and further subjected to PROMETHEE-II. All criteria were maximised (that is methods with the highest value of each criterion was ranked higher) and was assigned equal weights in order to identify the method with the highest analyte recovery. The V-shape preference function was used during the process. Further details on the data analysis methods are presented in Section 2.3. The four (4) highest ranking methods were selected and applied to SRM 1649b due to the limited quantities of SRM and the need to use a minimum of 150 mg sample during each extraction process as stipulated by NIST [32]. The average precision of the methods was estimated as 1.6% standard error, thus indicating high reproducibility.

The size of the ASE cell was changed from 5 mL to 33 mL due to the need to increase the quantity of the clean-up material to 15 g. The ratio of the clean-up mix was however, maintained at 2:1 for silica gel and alumina, respectively, where applicable. This adjustment was necessary to facilitate the cleanliness of the extracts since the application of the same quantum of initial screening ASE cell materials could not yield clean extracts. This underscores

the need to always evaluate new analytical protocols using actual sample matrices since spiked proxy matrices may not be truly representative [25, 33]. Unclean extract may cause contamination of the GC inlet liner, column and bleeding, cross contamination, loss of detector sensitivity and longevity. In this regard, the purity of the final extract was highly critical for this study.

2.2.5 Application of the selected methods to road dust samples

The best performing method from the SRM 1649b analysis as stipulated in Section 2.2.5 was applied to actual road dust samples in order to assess its applicability and efficacy in extracting parent PAHs and TPP analytes. The best performing method was also modified in line with existing literature and then applied to the road dust sample. This enabled the evaluation of the usefulness of the best performing and modified methods for the simultaneous extraction and in-cell clean-up of the analytes, thereby affirming whether the research objectives were met.

2.3 Triple-quadrupole GC-MS analysis of extracts

2.3.1 Screening test extract analysis

The cleaned screening test extracts were then analysed using Thermo Scientific Triple Quadrupole (TSQ) 8000 Evo GC-MS System containing Rxi-5Sil MS column (30 m x 0.25 mm ID x 0.25 µm thickness) with ultra-helium (He) carrier gas at constant column flows of 1.2 mL min^{-1}. Extracts were analysed using splitless injection, full scan (50-650 amu) and selective reaction monitoring (SRM) modes simultaneously. Compared to previous GC-MS analysis of PAHs and TPPs by Wei, Bandowe [10], Cochran, Dongari [22], Bandowe, Bigalke [27] as discussed in Section 3.1, the mass spectrometer in this study was operated solely in the electron ionization (EI) mode for all analytes thereby saving time and cost of analysis. The SRM and EI energies used for all analytes are shown in Table S3. High purity argon (Ar) gas was used as the collision gas. The GC oven temperature program used includes an initial temperature of 60 ºC held for 1 min, increased to 200 ºC at a rate of 5.0 ºC per min, held for 1 min, and finally increased to 320 ºC at a rate of 8.0 ºC per min and held for 10 min. The data acquisition, reprocessing and report generation was done using Thermo Scientific TraceFinder 4.1 General Quan data system.

2.3.2 SRM 1649b and road dust extract analysis

The GC-MS analysis was changed to Shimadzu Triple Quadrupole (TQ) 8040 due to its lower limits of detection (LOD) for most analytes compared to the TSQ 8000 as evident in Tables S3 and S4. Final extracts for SRM 1649b and road dust were analysed using the Shimadzu TQ 8040 GC-MS System containing Rxi-5Sil MS column (30 m x 0.25 mm ID x 0.25 µm thickness) with ultra-helium (He) carrier gas at constant column flow of 1.2 mL min^{-1}. Extracts were analysed using splitless injection and selective reaction monitoring (SRM) mode. The mass spectrometer was operated solely in the electron ionization (EI) mode for all analytes, thereby saving time during analysis (22.83 min). The SRM and EI energies used for analytes are shown in Table S4, whilst the chromatogram is shown in Fig. S1 in the Supplementary material. High purity argon (Ar) gas was used as the collision gas. The GC oven temperature program used included an initial temperature of 50 ºC held for 1 min, increased to 260 ºC at a rate of 20.0 ºC per min, elevated to 280 ºC at a rate of 5.0 ºC per min and finally increased to 340 ºC at a rate of 18.0 ºC per min and held for 4 min. The data acquisition, reprocessing and report generation were done using GC-MS real time analysis and LabSolutions GC-MS. The regression coefficient for the calibration curves of the analytes ranged from 0.995-1.0 for the Shimadzu TQ instrument.

2.3.3 QC/QA

Quality control (QC) and quality assurance (QA) protocols were employed to ensure the accuracy and precision of analytical results. Blank analysis, duplicate analysis of extracts and re-analysis of samples exceeding ±20% relative percent difference, re-calibration of standard curves daily using reference standards and checking of calibration levels after every ten extract analysis were carried out [28]. The concentrations of analytes in the blank samples were negligible, that is below LOD. The regression coefficient for the calibration curves of analytes ranged from 0.975 – 0.997 for the TSQ instrument. The average percentage recoveries for most surrogate standards differ according to the extraction method used. The results of each ASE method were highly precise with relative error between 0.1% – 5.0%.

2.4 Data analysis

The data acquired from the analysis were interpreted using multicriteria decision-making and multivariate analytical methods such as preference ranking organisation method for enrichment evaluation (PROMETHEE) and geometrical analysis for interactive aid (GAIA), and factor analysis (FA) using Visual PROMETHEE Academic Edition Version 1.4.0.0 and StatistiXL Version 1.8. This was done in accordance with the stated research objectives by maximising the latent information in the generated data.

PROMETHEE essentially computes the extent of preference of one object to another for each criterion based on various modelling scenarios including the choice of appropriate preference function and whether low (minimized) or high (maximized) criteria values are preferred. In this regard, PROMETHEE is highly relevant in ranking the performance of various analytical methods. FA is a pattern recognition method whereby the dimensionality of the data is reduced by minimizing the multi-collinearity of variables with minimum loss of information. The original variables are transformed into new sets of variables called factors. Factors are estimated from the eigenvalues and the corresponding eigenvectors [34]. FA is of value in assessing the relationships between various analytical methods and the analytes.

3. Results and discussion

3.1 Analysis of extracts without derivatization

Most previous studies on the analysis of PAHs and TPPs have shown that varying ionization modes are often used for different categories of PAH analytes. Electron ionization (EI) is often used for parent PAHs, alkyl-PAHs, CPAHs and HO-PAHs whilst negative ion chemical ionization (NICI) is mostly used for NPAHs [22, 35, 36]. This often extends the duration of analysis as these two ionization processes cannot be deployed simultaneously. In this regard, this study employed only EI during the qualitative and quantitative GC-MS analyses. This method is highly relevant in the assessment of TPPs during transformation and degradation investigation of PAHs thereby enabling targeted quantitation of relevant TPPs. SRM mode is suitable if the analytes and the relevant standards are well-known. However, if the purpose of an analysis involves identifying both known and unknown TPPs then simultaneous full scan and SRM mode runs may be relevant although the duration of analysis may be affected. For instance, the simultaneous mode spent 49 min whilst the SRM mode expended approximately 22 min as shown in Table S3 and S4, respectively.

SRM mode utilizes the triple quadrupole mass spectrometer (MS) to selectively quantify analytes embedded in complex mixtures by initially targeting the corresponding ion of the analyte (parent ion) and the resultant fragments of the target ion (daughter ions). As a result, specific parent ion and particular daughter ions corresponding to the mass of the analyte are isolated within the MS, thereby enhancing the sensitivity and accuracy of the analysis [37]. From Table S4, the limits of detection (LOD) for Shimadzu TQ based on the analysis of serially diluted standard solutions were 1.0-5.0 pg, 1.0-5.0 pg, 1.0-50.0 pg, and 1.0-25.0 pg, whilst that

for TSQ were 2.5-25.0 pg, 5.0-25.0 pg, 5.0-100.0 pg, and 10.0-250.0 pg compared to 6.0-34.0 pg, 5.0-36.0 pg, 1.0-10.0 pg and 1.0-21.0 pg obtained by Cochran, Dongari [22] for parent PAHs, CPAHs, NPAHs and HO-PAHs, respectively. The LOD for Shimadzu TQ was lower compared to TSQ using the same GC column in both instruments. In this regard, Shimadzu TQ was the preferred instrument for all post-screening test extracts analysis. Even though the LOD for NPAHs and HO-PAHs are relatively higher in the study conducted by Cochran, Dongari [22], the GC-MS method used was time consuming due to the application of NICI and EI modes, respectively during their analysis.

This study constitutes an important contribution for further exploration into the simultaneous analysis of HO-PAH with other TPPs in overcoming the column trailing of these polar analytes in the GC column. The SRM mode for Shimadzu TQ was ten times more sensitive for HO-PAHs based on the estimated LOD compared to TSQ. However, it must be noted that due to the lack of certified values for HO-PAHs and CPAHs in the SRM analysed, the results of the analysis could not be evaluated further.

Any drifts in the retention time (RT) of analytes were regularly corrected during the re-calibration of standard curves. Co-eluting isomers as shown in Table S3 and S4 were analysed together. However, this challenge could probably be overcome by using a more specific GC column designed for PAH and TPPs with greater analyte separation properties than the generic Rxi-5Sil MS column used in this study.

3.2 Ranking of screening methods via multi-criteria decision making

The performance of the 40 proposed analyte screening methods were ranked using PROMETHEE-II by considering a data matrix of 40 actions and 45 criteria. The actions represented the different PFE methods whilst the criteria denoted the PAH and TPP analytes. As noted in Section 2.2.5, the absolute deviations of measured concentration of analytes from the spiked concentration were used to rank the performance of the methods and the PROMETHEE result is shown in Table 1.

From Table 1, the increasing trend of the top seven (7) PFE methods based on the absolute deviation is 1Dii < 4Bi < 2Bii < 2Dii < 2Bi < 3Dii < 5Di. This indicates that method 5Di consisting of 3% deactivated silica gel and activated alumina (2:1) clean-up material, and DCM, DCM/acetone/methanol (1:1:1) and DCM/acetone/methanol (1:1:2) sequential solvent mixtures was appropriate for the analytes extraction. The associated ASE operating condition entailed 17 MPa pressurized ASE cell heated to 100 °C within 6 minutes held for 5 min static extraction. The cell was flushed with 100% solvent volume followed by 60% for rinsing and then purged with N_2 for 90 seconds. The ranking further indicates that alteration of the ASE temperature between 100 °C and 120 °C does not have any significant influence on the extraction efficiency of analytes whilst with solvent mixture '**D**' being potentially more suitable for the extraction of analytes. In addition to clean-up material '**5**', material '**2**' also plays an important role during the in-situ clean-up of extract. It can be inferred that the polarities of the solvent mixture and clean-up material exert significant influence on the simultaneous extraction and in-cell clean-up of extracts. However, there is the need to further examine the performance of these methods on actual samples which are often more complex.

Table 1: PROMETHEE-II of PFE screening methods using absolute deviation

Rank	Action	Phi	Phi+	Phi –
1	5Di	0.4152	0.4871	0.0720
2	3Dii	0.2864	0.3983	0.1095
3	2Bi	0.2372	0.3783	0.1411
4	2Dii	0.2330	0.3669	0.1340
5	2Bii	0.2282	0.3633	0.1351
6	4Bi	0.2059	0.3553	0.1494
7	1Dii	0.1973	0.3451	0.1478
8	3Di	0.1900	0.3499	0.1599
9	1Bii	0.1841	0.3338	0.1497
10	4Di	0.1628	0.3204	0.1576
11	4Bii	0.1436	0.3027	0.1591
12	1Di	0.1243	0.2869	0.1627
13	2Di	0.1191	0.3249	0.2058
14	3Bi	0.0974	0.3382	0.2407
15	3Bii	0.0947	0.3309	0.2363
16	4Ci	0.0936	0.2792	0.1856
17	1Cii	0.0877	0.2572	0.1695
18	2Aii	0.0835	0.2669	0.1833
19	4Cii	0.0822	0.2597	0.1774
20	5Bi	0.0502	0.2513	0.2012
21	1Ci	0.0017	0.2230	0.2212
22	2Cii	0.0015	0.2220	0.2205
23	4Dii	-0.0451	0.1924	0.2375
24	2Ai	-0.0795	0.1605	0.2400
25	5Ai	-0.0994	0.1586	0.2580
26	3Aii	-0.1204	0.1588	0.2792
27	4Ai	-0.1367	0.1349	0.2717
28	1Aii	-137E7	135E7	273E7
29	5Dii	-138E7	148E7	285E7
30	1Ai	-149E7	137E7	286E7
31	5Aii	-158E7	123E7	281E7
32	3Ai	-159E7	125E7	284E7
33	2Ci	-169E7	191E7	360E7
34	5Bii	-179E7	248E7	427E7
35	3Cii	-194E7	175E7	369E7
36	4Aii	-210E7	104E7	314E7
37	1Bi	-250E7	975E7	347E7
38	5Cii	-319E7	140E7	459E7
39	3Ci	-381E7	129E7	510E7
40	5Ci	-397E7	163E7	561E7

Secondly, the performance of the methods was also assessed based on the maximum percentage recoveries of analytes. The results of PROMETHEE-II as indicated in Table 2 show the decreasing trend of the seven ranked methods as 5Bii > 5Ci > 3Ci > 3Bi > 3Bii > 2Di > 5Cii. In this regard, PFE method 5Bii is the highest ranked method. It entails in-cell clean-up material made up of 3% deactivated silica gel and activated alumina (2:1), and sequential extraction solvent mixture of DCM/acetone (1:1), DCM/acetone (3:1) and DCM/acetone (1:3). The ASE operating condition entailed 17 MPa pressurized cell heated to 120°C within 6 minutes held for 5 minutes for static extraction, flushed with solvent volume of 100% followed by rinsing with more solvent (60% of cell volume). The cell was finally purged with N_2 for 90 seconds.

Table 2: PROMETHEE-II of PFE screening methods using percentage recovery

Rank	Action	Phi	Phi+	Phi –
1	5Bii	0.7803	0.8846	0.1043
2	5Ci	0.7524	0.8570	0.1046
3	3Ci	0.6687	0.8188	0.1501
4	3Bii	0.6231	0.8037	0.1806
5	3Bi	0.6154	0.7991	0.1838
6	2Di	0.5883	0.7886	0.2003
7	5Cii	0.5325	0.7370	0.2046
8	3Di	0.3801	0.6778	0.2977
9	3Cii	0.3741	0.6570	0.2829
10	2Bii	0.3698	0.6769	0.3071
11	2Ci	0.3644	0.6399	0.2755
12	4Bi	0.3182	0.6479	0.3296
13	4Di	0.2536	0.6037	0.3501
14	4Ci	0.2484	0.6006	0.3521
15	5Di	0.1883	0.5835	0.3952
16	1Ci	0.1675	0.5553	0.3877
17	1Bi	0.0675	0.5108	0.4433
18	5Bi	0.0621	0.5017	0.4396
19	2Cii	0.0353	0.4781	0.4427
20	4Bii	0.0322	0.5066	0.4744
21	1Di	0.0296	0.4835	0.4538
22	3Di	-0.0570	0.4601	0.5171
23	1Cii	-0.0684	0.4299	0.4983
24	4Cii	-0.0991	0.4214	0.5205
25	1Dii	-0.0994	0.4373	0.5368
26	2Dii	-0.1046	0.4328	0.5373
27	2Bi	-0.1160	0.4308	0.5467
28	2Aii	-0.2345	0.3621	0.5966
29	4Dii	-0.3704	0.2957	0.6661
30	2Ai	-0.4624	0.2293	0.6917
31	5Dii	-0.4860	0.2262	0.7123
32	5Ai	-0.5048	0.2114	0.7162
33	3Aii	-0.5288	0.2068	0.7356
34	4Ai	-0.5610	0.1786	0.7396
35	1Aii	-0.5675	0.1795	0.7470
36	3Ai	-0.5940	0.1644	0.7584
37	1Ai	-0.6154	0.1575	0.7729
38	5Aii	-0.6157	0.1501	0.7658
39	4Aii	-0.6561	0.1365	0.7926
40	1Bi	-0.7108	0.1179	0.8288

The average recovery for method 5Bii is 162% with 2HBP and BaFN as least and highest recovered analytes. Relatively low recoveries of 2-70% were reported for HO-PAHs in soil using PFE method by Bandowe and Wilcke [4] even though silylation derivatization was incorporated. It must be noted that the third fraction of extracts obtained from 5Bii was not clean thereby requiring further clean-up in order to protect the GC column from contamination and bleeding. Fortunately, the third fraction contained an insignificant concentration of analytes and was thus discarded.

Furthermore, method 5Ci was the second ranked PFE method consisting of cells packed with 3% deactivated silica gel and activated alumina (2:1) clean-up material and extracted sequentially with 100% hexane, hexane/DCM (1:1), and 100% methanol solvent mixtures. The

ASE operating condition entailed cells pressurized to 17 MPa and heated to 100 °C within 5 min held for 5 min static extraction, with a flush volume of 100% followed by rinsing with more solvent (60% of cell volume) and purged with N_2 for 90 seconds. In this study, eleven methods consisting of seven and four methods from the absolute deviation and percentage recovery approaches respectively were selected for subsequent evaluation using SRM 1649b.

3.3 Application of the selected methods to standard reference material

The eleven selected top ranked screening methods were evaluated for their efficiency using SRM 1649b sample. The results of the analysis together with their corresponding NIST certified or reference values are shown Table S5, whilst analytes with no NIST estimated or only informational values are presented in Table S6. Multivariate data analysis and PROMETHEE-II were applied to the results. The correlation between the NIST values (NIST_SRM) and the results of PFE extract analysis were assessed. The resultant correlation matrix is shown in Table 3.

Table 3: Correlation matrix for NIST reference values and different extraction methods result for analytes

	NIST_SRM	**5Di**	**3Dii**	**2Bi**	**2Dii**	**2Bii**	**4Bi**	**1Dii**	**5Bii**	**5Ci**	**3Ci**	**3Bii**
NIST_SRM	1.000											
5Di	0.674	1.000										
3Dii	0.648	0.987	1.000									
2Bi	0.631	0.984	0.998	1.000								
2Dii	0.692	0.996	0.984	0.981	1.000							
2Bii	**0.725**	0.992	0.977	0.968	0.990	1.000						
4Bi	**0.749**	0.967	0.931	0.918	0.966	0.987	1.000					
1Dii	0.603	0.973	0.989	0.993	0.973	0.955	0.905	1.000				
5Bii	**0.725**	0.987	0.966	0.956	0.988	0.996	0.987	0.943	1.000			
5Ci	**0.730**	0.975	0.940	0.928	0.970	0.990	0.997	0.913	0.991	1.000		
3Ci	**0.722**	0.809	0.722	0.699	0.808	0.850	0.918	0.681	0.864	0.906	1.000	
3Bii	**0.718**	0.802	0.714	0.692	0.806	0.844	0.912	0.675	0.867	0.903	0.993	1.000

Significant positive correlation at 95% level of significance exists between NIST_SRM, and methods 4Bi, 5Ci, 2Bii, 5Bii and 3Ci (in decreasing order) as shown in Table 3. Similarly, from factor analysis (FA), only one factor was found to be significant (eigenvalue > 1) and methods 2Bii, 5Bii, 5Ci and 4Bi have significant factor loadings that are greater than 0.99 as depicted in Table S7. Therefore, these methods are capable of simultaneously extracting the analytes. As shown in Fig.1, most of the final extracts are not clean and thus unsuitable for direct GC/MS analysis. It is therefore prudent to consider the cleanliness status of the extracts in the choice of most suitable method.

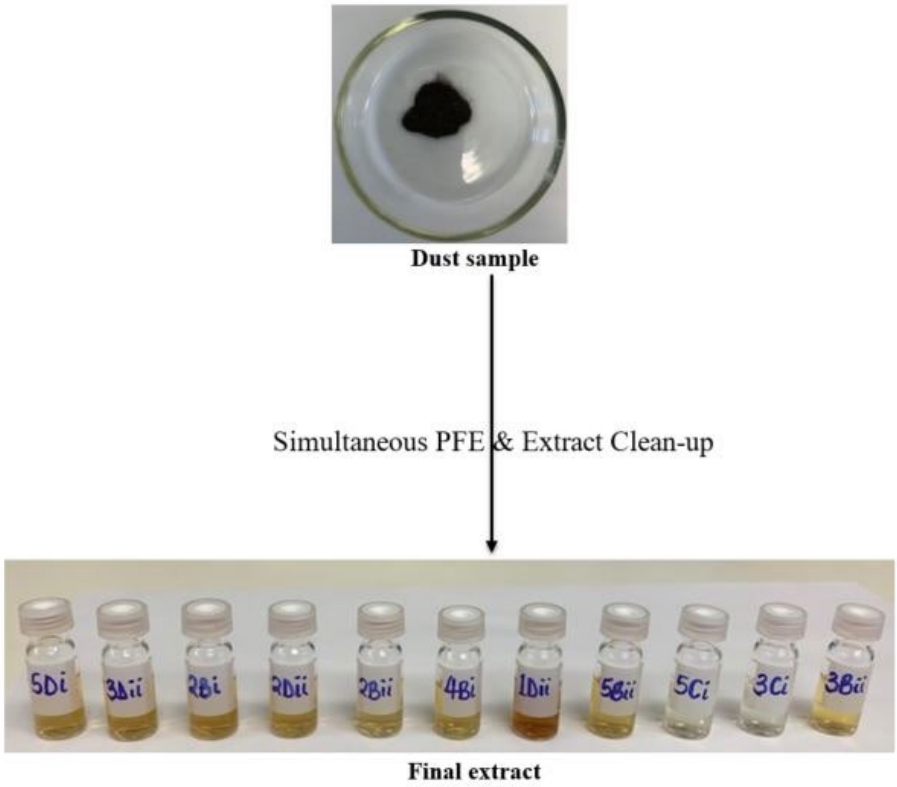


Fig. 1: Cleanliness of SRM 1649b extracts using selected PFE methods

Table 4: PROMETHEE-II ranking of PFE methods using extract cleanliness and absolute deviation of results from the NIST_SRM values

Rank	Action	Phi	Phi+	Phi−
1	5Ci	0.0556	0.1057	0.0501
2	3Dii	0.0316	0.0662	0.0346
3	2Bi	0.0281	0.0714	0.0433
4	5Bii	0.0236	0.0615	0.0379
5	5Di	0.0207	0.0660	0.0453
6	2Dii	0.0147	0.0595	0.0447
7	2Bii	0.0028	0.0494	0.0466
8	3Ci	0.0010	0.0928	0.0918
9	1Dii	-0.0006	0.0552	0.0559
10	3Bii	-0.0454	0.0389	0.0843
11	4Bi	-0.1321	0.0141	0.1461

The cleanliness of the extracts as shown in Table S5 was incorporated into the PROMETHEE analysis as a qualitative property. It was assigned 'Level' preference function and weighting of three (3) due its relevance to the protection and longevity of the GC column and MS detector. The resultant PROMETHEE-II ranking of the PFE Methods is presented in Table 4. Method 5Ci is the highest ranked PFE in terms of simultaneous extraction of analytes and efficient in-cell clean-up of extracts. It comprises of 3% deactivated silica gel and activated alumina (2:1)

clean-up material, and sequential solvent mixtures of 100% hexane and hexane/DCM (1:1). The ASE operating condition involved cells pressurized to 17 MPa and heated to 100°C within 5 min held for 5 min static extraction, with a flush volume of 100% followed by rinsing with more solvent (60% of cell volume) and purged with N_2 for 90 seconds. The fractional extracts from 5Ci were clean compared to the extracts from other high-ranking methods. Lundstedt [23] also found that using hexane and hexane/DCM (1:1) to sequentially extract PAHs and oxygenated PAHs (OPAHs) laden in soil via PFE in-cell clean-up approach using 2% deactivated silica gel yielded cleaned extracts for direct GC-MS analysis. Therefore, method 5Ci can be considered as highly suitable for simultaneous extraction and in-cell clean-up of extracts.

Titaley, Chlebowski [38] have also reported the effectiveness of hexane and DCM in extracting PAHs and TPPs from pavement related samples. The polarity index of hexane and DCM is 0.0 and 3.1, respectively. Thus, the 1:1 ratio addition of these solvents would have resulted in the right polarity for the sequential extraction of all analytes. However, a further evaluation of the results for method 5Ci in Table S5 shows that the recovery of most surrogate standards is low ranging from 12% to 120%, although there is significant correlation and good cleanliness of the extracts. Therefore, there is the need to improve the analyte recovery status of this PFE method. In this regard, Schantz, McGaw [25] in their study on evaluating the effects of pressure, temperature, number of static cycles and times on the extraction of PAHs and NPAHs from various SRM's including 1649b concluded that elevating the temperature from 100 ºC to 200 ºC had the highest positive effect on analytes extraction efficiency. Secondly, the application of three extraction cycles, and 5 min extraction time may also contribute to the extraction efficiency whilst alterations in pressure and solvent had minor effects on the efficiency. Due to the shortage of SRM 1649b sample during the analytical process, the effect of 200 ºC could not be confirmed. It was however, assessed using actual road dust samples.

3.4 Assessment of the selected 5Ci method to road dust

The selected 5Ci method and related modified methods, as shown in Table 5, based on the findings of Lundstedt [23] and Schantz, McGaw [25] study, were applied to actual road dust samples in order to assess their efficiency on the simultaneous extraction and in-cell clean-up of extracts. The temperature, number of extraction cycles and preheat time were altered accordingly to assess their influence on the PFE process. The pressure was, however, maintained at 17 MPa in all modification instances.

Table 5: Modification of selected 5Ci PFE method

PFE method	Temperature (ºC)	Preheat time (min)	No. of extraction cycles
5Cia	100	5	1
5Cib	200	9	1
5Cic	200	9	2
5Cid	200	9	3
5Cie	150	7	3

The results of analysis using each of these methods are shown in Table S8. The results show varying analyte concentrations in road dust using different modified PFE methods as represented in Fig. 2. Noticeably, methods employing 200 ºC extraction temperatures have higher analytes extraction potential compared to 100 ºC and 150 ºC. This observation concurs with that of Schantz, McGaw [25]. In this regard, 1-nitronaphthalene (NNAP), naphthalene (NAP), acenaphthene (ACE) and 1-hydroxypyrene (HPY) were the dominantly determined

analytes. However, in order to assess the comparative performance of each method, the results were subjected to PROMETHEE-GAIA analysis.

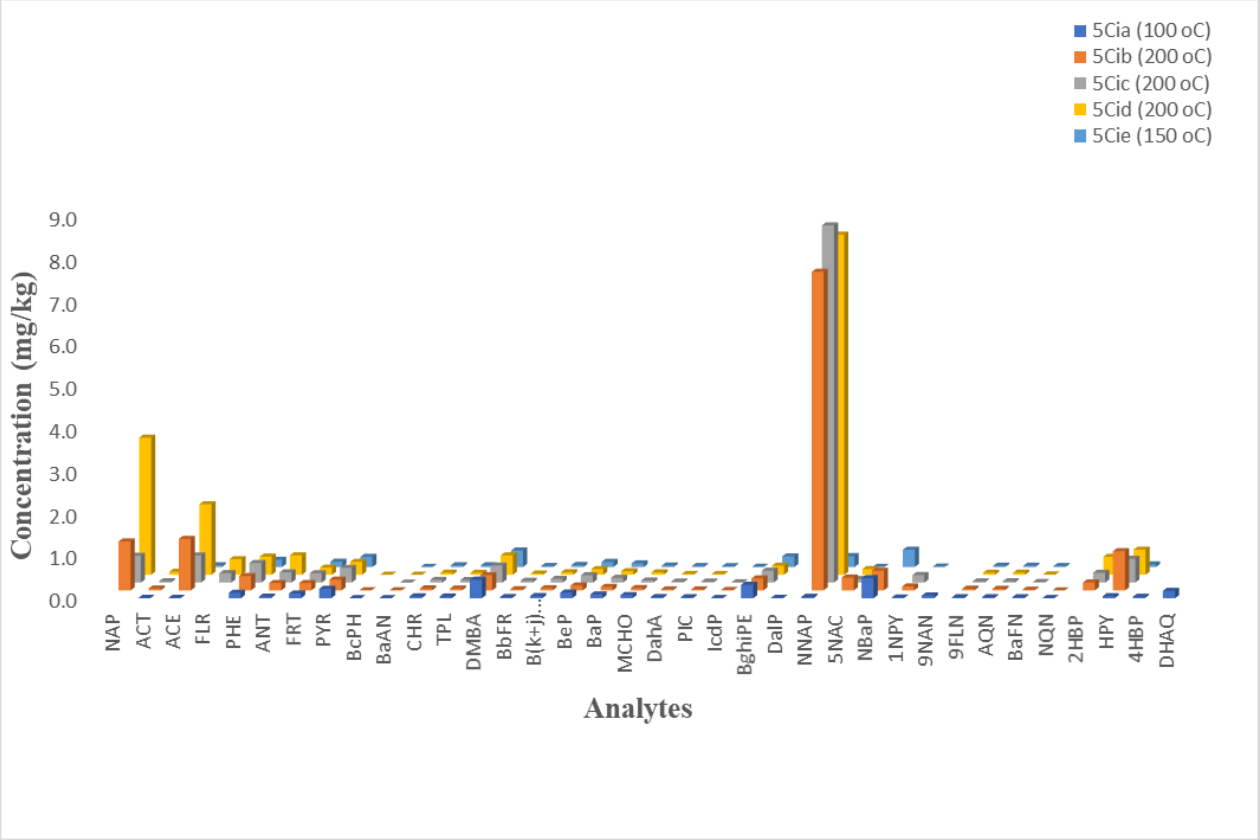


Fig. 2: Comparison of analytes concentration by different modified PFE methods

All criteria were allocated equal weights and maximized using V-shape preference function for the PROMETHEE analysis. The PROMETHEE-II ranking results are presented in Table 6 whilst the GAIA biplot is shown by Fig. 3. All the modified methods involving 200 ºC extraction temperatures ranked among the top three performing method whilst 100 ºC and 150 ºC were the least ranking methods. This is further collaborated by the close proximity of methods 5Cib, 5Cid and 5Cic to the pi-decision axis in Fig. 3. Methods 5Cia and 5Cie were highly correlated but are directly opposite to the pi-decision axis in Fig. 3. This indicates the significant effect of ASE temperature during the extraction process with 200 ºC as the optimum condition. The higher temperature increases the extraction kinetics so as to attain efficient and rapid abstraction of analytes. The ranking further shows that the preheat time and number of extraction cycles have minimal influence on the analyte extraction process thus agreeing with Schantz, McGaw [25] observation. In this context, modified PFE method 5Cid entailing 200 ºC extraction temperature, 9 min preheat time and 3 times extraction cycles as indicated in Table 5 and 6 can be inferred as the optimized method for the simultaneous extraction and in-cell clean-up of extracts for road dust and other related samples. Most surrogate standards were recovered between 80 to 111% using method 5Cid.

Table 6: Complete ranking of modified 5Ci PFE methods

Rank	Action	Phi	Phi+	Phi-
1	5Cid (200°C)	0.0721	0.0843	0.0122
2	5Cib (200°C)	0.0334	0.0558	0.0224
3	5Cic (200°C)	0.0220	0.0473	0.0253
4	5Cia (100°C)	-0.0604	0.0099	0.0704
5	5Cie (150°C)	-0.0670	0.0045	0.0715

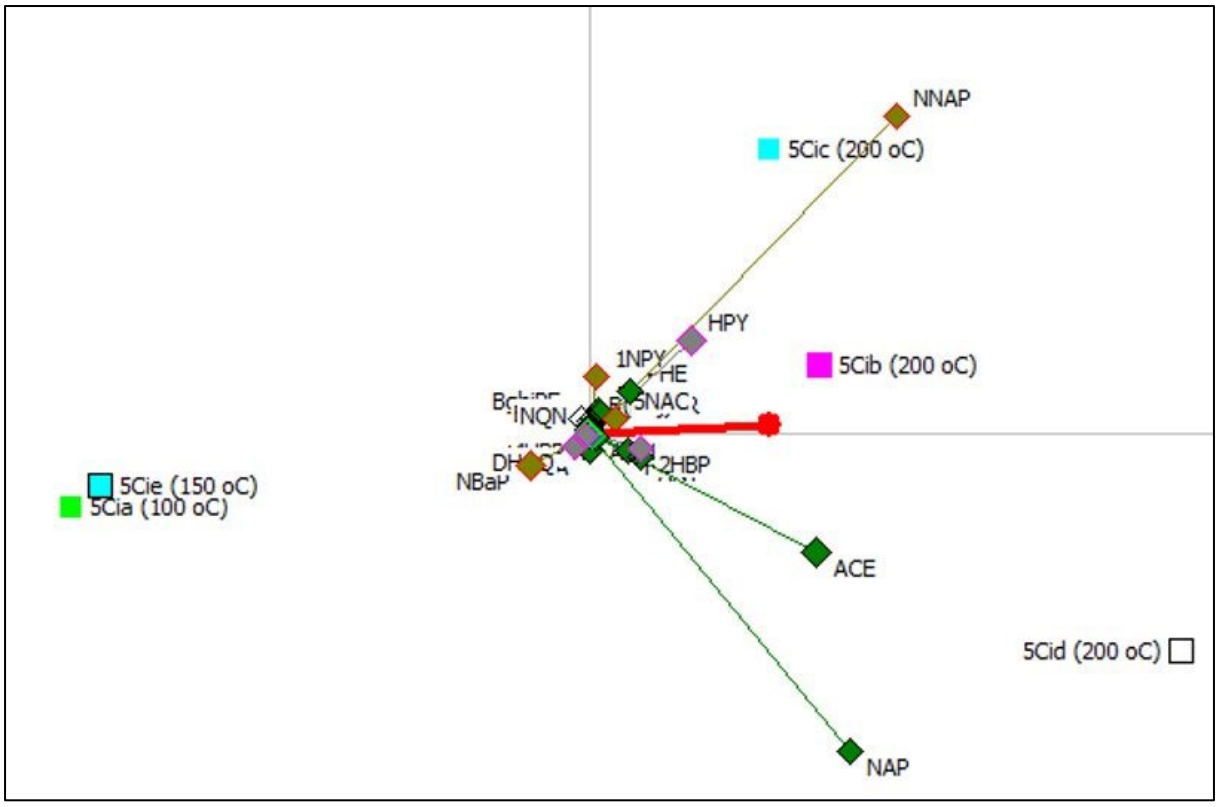


Fig. 3: GAIA biplot of modified selected PFE methods

4. Conclusions

This study has developed an optimized pressurized fluid extraction (PFE) method capable of simultaneous extraction and in-cell clean-up of parent PAHs, CPAHs, NPAHs and HO-PAHs from minute quantities of road dust samples. The potential of forty (40) different PFE methods involving a combination of cell packing materials for clean-up, solvent mixtures and accelerated solvent extractor (ASE) conditions to successfully extract these PAH analytes spiked into pro-analysis sea sand were evaluated. Multivariate statistical analysis and Preference Ranking Organisation Method for Enrichment Evaluation (PROMETHEE) - Geometrical Analysis for Interactive Aid (GAIA) were highly relevant in the choice of the most suitable PFE method. The best performing eleven (11) PROMETHEE-II ranked PFE methods from pro-analysis process were applied to SRM 1649b dust sample in order to evaluate their

efficiency. The results from the SRM analysis indicated that ASE cells packed with 3% deactivated silica gel and activated alumina (2:1) and then extracting sequentially with 100% hexane followed by hexane/DCM (1:1) under 100 ^{o}C ASE temperature is suitable for the simultaneous extraction and in-cell clean-up of PAH and TPP analytes. The modified selected PFE methods further showed that the application of 200 ^{o}C ASE extraction temperatures is the optimum condition for most analytes. The selection of appropriate clean-up material, solvent media and ASE condition is critical for achieving the desired objectives of this study. Finally, an optimized GC-MS method was developed for determining the concentrations of analytes concurrently using only electron ionization mode, thereby reducing the time and cost of analysis. Although this study reported higher limits of detection (LOD) for some nitro- and hydroxy- PAH analytes compared to other existing methods, on the whole the outcome of this study is highly relevant to the future of environmental and analytical chemistry in terms of micro-organic pollutants measurement in road dust, dust particles, soil and other related matrices.

Conflict of interest statement

The authors can affirm that there is no real or perceived conflict of interest such as personal, financial and connection to person(s) or institution(s) that may have impacted negatively on the outcome of this research.

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Appendix A: Supplementary material

References

1. Andersson, J.T. and C. Achten, *Time to Say Goodbye to the 16 EPA PAHs? Toward an Up-to-Date Use of PACs for Environmental Purposes.* Polycycl Aromat Compd, 2015. **35**(2-4): p. 330-354.
2. Gbeddy, G., et al., *Transformation and degradation of polycyclic aromatic hydrocarbons (PAHs) in urban road surfaces: Influential factors, implications and recommendations.* Environmental Pollution, 2019.
3. Majumdar, D., et al., *PAHs in Road Dust: Ubiquity, Fate, and Summary of Available Data.* Critical Reviews in Environmental Science and Technology, 2012. **42**(12): p. 1191-1232.
4. Bandowe, B.A.M. and W. Wilcke, *Analysis of Polycyclic Aromatic Hydrocarbons and Their Oxygen-Containing Derivatives and Metabolites in Soils.* Journal of Environment Quality, 2010. **39**(4): p. 1349.

5. Lundstedt, S., et al., *Sources, fate, and toxic hazards of oxygenated polycyclic aromatic hydrocarbons (PAHs) at PAH-contaminated sites.* AMBIO: A Journal of the Human Environment, 2007. **36**(6): p. 475-485.
6. Mallakin, A., D.G. Dixon, and B.M. Greenberg, *Pathway of anthracene modification under simulated solar radiation.* Chemosphere, 2000. **40**: p. 1435-1441.
7. Bandowe, B.A. and M.A. Nkansah, *Occurrence, distribution and health risk from polycyclic aromatic compounds (PAHs, oxygenated-PAHs and azaarenes) in street dust from a major West African Metropolis.* Sci Total Environ, 2016. **553**: p. 439-49.
8. IARC, *Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures*. IARC monographs on the evaluation of carcinogenic risks to humans. Vol. 92. 2010, Lyon, France: WHO.
9. Achten, C. and J.T. Andersson, *Overview of Polycyclic Aromatic Compounds (PAC).* Polycycl Aromat Compd, 2015. **35**(2-4): p. 177-186.
10. Wei, C., et al., *Polycyclic aromatic hydrocarbons (PAHs) and their derivatives (alkyl-PAHs, oxygenated-PAHs, nitrated-PAHs and azaarenes) in urban road dusts from Xi'an, Central China.* Chemosphere, 2015. **134**: p. 512-20.
11. Albinet, A., S. Tomaz, and F. Lestremau, *A really quick easy cheap effective rugged and safe (QuEChERS) extraction procedure for the analysis of particle-bound PAHs in ambient air and emission samples.* Sci Total Environ, 2013. **450-451**: p. 31-8.
12. Barcelo, D., *Wilson & Wilson's Comprehensive Analytical Chemistry.* Elsevier, 2015. **67**.
13. Lau, E.V., S. Gan, and H.K. Ng, *Extraction techniques for polycyclic aromatic hydrocarbons in soils.* Int J Anal Chem, 2010. **2010**: p. 398381.
14. Gfrerer, M., M. Serschen, and E. Lankmayr, *Optimized extraction of polycyclic aromatic hydrocarbons from contaminated soil samples.* J. Biochem. Biophys. Methods, 2002. **53**: p. 203–216.
15. DIONEX, *Methods Optimization in Accelerated Solvent Extraction (ASE).* Thermo Fischer Scientific Inc., 2013. **Technical Note 208**.
16. Jinshui, C., et al., *Accelerated Solvent Extraction — GC-MS Analysis and Detection of Polycyclic Aromatic Hydrocarbons in Soil.* Thermo Fischer Scientific Inc., 2013. **Application Updates 313**.
17. Lopez, L. and A. Kettle, *Simultaneous Extraction of PAHs and PCBs from Environmental Samples Using Accelerated Solvent Extraction.* Thermo Fischer Scientific Inc., 2013.
18. Lundstedt, S., P. Haglund, and L. Oberg, *Simultaneous extraction and fractionation of polycyclic aromatic hydrocarbons and their oxygenated derivatives in soil using selective pressurized liquid extraction.* Anal Chem, 2006. **78**(9): p. 2993-3000.
19. Albinet, A., et al., *A simple QuEChERS-like extraction approach for molecular chemical characterization of organic aerosols: application to nitrated and oxygenated PAH derivatives (NPAH and OPAH) quantified by GC-NICIMS.* Anal Bioanal Chem, 2014. **406**(13): p. 3131-48.
20. Ahmed, T.M., et al., *Determination of oxygenated and native polycyclic aromatic hydrocarbons in urban dust and diesel particulate matter standard reference materials using pressurized liquid extraction and LC-GC/MS.* Anal Bioanal Chem, 2015. **407**(2): p. 427-38.
21. Orata, F., *Derivatization Reactions and Reagents for Gas Chromatography Analysis, Advanced Gas Chromatography - Progress in Agricultural, Biomedical and Industrial Applications, Dr. Mustafa Ali Mohd(Ed.), ISBN: 978-953-51-0298-4.* InTech, 2012.
22. Cochran, R.E., et al., *Determination of polycyclic aromatic hydrocarbons and their oxy-, nitro-, and hydroxy-oxidation products.* Anal Chim Acta, 2012. **740**: p. 93-103.
23. Lundstedt, S., *Analysis of PAHs and their transformation products in contaminated soil and remedial processes.* PhD Thesis Umeå University, 2003.
24. Gbeddy, G., et al., *Variability and uncertainty of particle build-up on urban road surfaces.* Science of The Total Environment, 2018. **640-641**: p. 1432-1437.

25. Schantz, M.M., E. McGaw, and S.A. Wise, *Pressurized liquid extraction of diesel and air particulate standard reference materials: effect of extraction temperature and pressure.* Anal Chem, 2012. **84**(19): p. 8222-31.
26. USEPA, *USEPA method 3545A Pressurized fluid extraction (PFE)*. 2007: Washington DC.
27. Bandowe, B.A., et al., *Polycyclic aromatic compounds (PAHs and oxygenated PAHs) and trace metals in fish species from Ghana (West Africa): bioaccumulation and health risk assessment.* Environ Int, 2014. **65**: p. 135-46.
28. Peng, C., et al., *Polycyclic aromatic hydrocarbons in urban soils of Beijing: status, sources, distribution and potential risk.* Environmental Pollution, 2011. **159**(3): p. 802-808.
29. Ayoko, G.A., et al., *A multicriteria ranking of organotin(IV) compounds with fungicidal properties.* Applied Organometallic Chemistry, 2003. **17**(10): p. 749-758.
30. Behzadian, M., et al., *PROMETHEE: A comprehensive literature review on methodologies and applications.* European Journal of Operational Research, 2010. **200**(1): p. 198-215.
31. Doyi, I., et al., *Spatial distribution, accumulation and human health risk assessment of heavy metals in soil and groundwater of the Tano Basin, Ghana.* Ecotoxicol Environ Saf, 2018. **165**: p. 540-546.
32. NIST, *Certficate of analysis Standard Reference Material (SRM) 1649b Urban Dust*. 2016.
33. Schantz, M.M., *Pressurized liquid extraction in environmental analysis.* Anal Bioanal Chem, 2006. **386**(4): p. 1043-7.
34. Miller, J.N. and J.C. Miller, *Statistics and chemometrics for analytical chemistry Sixth edition.* Pearson Education Limited, England, 2010.
35. Bandowe, B.A., et al., *PM(2).(5)-bound oxygenated PAHs, nitro-PAHs and parent-PAHs from the atmosphere of a Chinese megacity: seasonal variation, sources and cancer risk assessment.* Sci Total Environ, 2014. **473-474**: p. 77-87.
36. Lundstedt, S., et al., *First intercomparison study on the analysis of oxygenated polycyclic aromatic hydrocarbons (oxy-PAHs) and nitrogen heterocyclic polycyclic aromatic compounds (N-PACs) in contaminated soil.* TrAC Trends in Analytical Chemistry, 2014. **57**: p. 83-92.
37. PILL, *Targeted mass spectrometry (MRM/SRM).* Proteomics International Laboratories Ltd., 2018.
38. Titaley, I.A., et al., *Identification and Toxicological Evaluation of Unsubstituted PAHs and Novel PAH Derivatives in Pavement Sealcoat Products.* Environmental Science & Technology Letters, 2016. **3**(6): p. 234-242.

Supplementary Material

Optimized simultaneous pressurized fluid extraction and in-cell clean-up, and analysis of polycyclic aromatic hydrocarbons (PAHs), and nitro-, carbonyl-, hydroxy -PAHs in solid particles

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Table S1: Merits and demerits of PAH extraction techniques

Technique	Attributes	Merits	Demerits
Mechanical Agitation (MA) [1]	Uses a shake-flask positioned on a rotary shaker or magnetic stirrer immersed into a flask to agitate and extract the analytes	Very easy and simple Low cost Minimal solvent required	Poor efficiency of extraction Time consuming
Sonication or Ultrasonic Agitation (UA) [2-4]	Employs ultrasonic waves' acoustic energy in fluid to facilitate cavitation (recurring formation and collapse of microbubbles)	Relatively good extraction efficiency compared to SE	Low recovery of low molecular weight (LMW) PAHs Extreme care required to prevent degradation of analytes as a result of excessive exposure to irradiation Requires further processes such as filtration and centrifugation
Soxhlet Extraction (SE) [5-8]	Solid sample in an extraction thimble placed into the Soxhlet apparatus is subjected to reflux cycle until desired extraction efficiency is attained Automated SE ensures simultaneous boiling, rapid condensation of evaporated solvent and rinsing of sample thereby reducing overall extraction time and solvent requirement.	Widespread application due to its availability and comparative extraction efficiency Higher extraction efficiency for higher molecular weight (HMW) PAHs	Large volume of solvent Time consuming Labour intensive Poor selectivity for analytes; extracts bulk organic matter and therefore, requires thorough clean-up High probability of cross contamination of sample Difficult to incorporate in-situ clean-up step
Subcritical Water Extraction (SWE) and Supercritical Fluid Extraction (SFE) [9]	In SWE water is transformed into organic-like hydrophobic substance by elevating the temperature of water from 100ºC to 274ºC under pressure thereby enhancing its miscibility with light hydrocarbons. The high diffusivity, low viscosity, liquid-like density and zero surface tension of supercritical fluids facilitate fluids penetration and capacity to dissolve samples into their constituents during SFE.	SWE is more efficient for more polar analytes whilst non polar organic analytes are more inclined to SFE SWE coupled with oxidation is believed to promote higher extraction efficiency SFE produces cleaner extract and better selectivity Integrated SFE facilitates simultaneous clean-up of concentrated extracts thereby saving time and manual clean-up	SFE and SWE techniques are relatively expensive SFE is relatively difficult to optimise SFE technique is highly complex and may result in lack of consistency in results
Solid Phase Extraction (SPE) /Solid Phase Micro-extraction (SPME) [10-12]	Generally deployed as a pre-fractionation / clean-up technique in order to obtain enriched fractions of desired analytes. Suitable solvent is used to clean-up contaminants from sample in SPE column prior to the extraction of the analytes. SPME, a special variant of SPE employs a syringe-like apparatus containing a small diameter	SPE is good for contaminant removal from samples SPME is solvent free technique and requires minimum volume of sample SPME is simple, fast and good for on-site extraction Well stored fibres can be analysed later	Efficient SPME requires homogenous fibre SPME may be suitable for only LMW analytes

	fused-silica fibre covered with the extracting phase. The fibre adsorbs the analyte which is then moved directly into the injection port of an analytical instrument		
Microwave-Assisted Extraction (MAE) [10]	Sample and solvent mixture is exposed to heat energy generated by microwave electromagnetic radiation of frequencies ranging from 300MHz to 300GHz, and wavelength between 1m and 1mm	Minimum solvent required Time effective Microwave radiation is reproducible with minimal energy loss Lower cost compared to SPE Ensures selective interaction with polar analytes	Physical removal of solvent extract from the sample matrix is required before further analysis Prone to extract contamination and loss of analytes
Fluidised-Bed Extraction (FBE) [13]	FBE is similar to SE where the sample is placed in an extraction tube secured with a filter on a Teflon plate at the base whilst the solvent is located in the basic vessel beneath the soil sample. The continuous penetrating stream of solvent vapour through the filter heats up and mixes the sample causing fluidizing agitation. The system is scheduled to turn off heating and concurrently cool down the basic heating-cooling block and the solvent.	Reduced solvent usage compared to SE Reduced extraction time compared to SE	Poor selectivity for analytes; extract bulk organic matter and may therefore require clean-up
Flash Pyrolysis (FP) / High Temperature Distillation (HTD) [14]	Thermal cracking of macromolecules into simpler monomers occurs during FP as a result of rapid heating of sample using either Ohmic heating or inductive heating using platinum foil or ferromagnetic foil respectively HTD also utilizes high rate of temperature ramping	Does not require solvent or high-pressure extraction tool; reduces cost Does not require concentration of extracts and clean-up Reduces the risk of contamination Offers fast and direct analysis of samples for analytes Offers greater temperature control than TD Significant quantum of samples can be analysed due to the high rate of extraction	The minute sample size required demands absolute homogeneity in samples The temperature program requires careful optimization to forestall cellulose filter breakdown and the subsequent formation of unwanted by-products
Thermal Desorption (TD) [15-20]	Solid sample is directly injected into the cold injector of a GC, heated quickly to appropriate temperature whilst the carrier gas is temporary stopped to cause volatilisation of analyte. Extracted analytes are subsequently transferred	Solvent free Simple and rapid Reduced cost Concentration of extracts and clean-up not required Reduces the risk of contamination	May not be suitable for thermally unstable and highly volatile analytes Comes with attendant technical challenges such as re-calibration of equipment to facilitate nonlinear response to

	by the reconnected carrier gas onto the GC column	On-line coupling capability to GC Offers greater specificity and sensitivity	analyte concentration and sample size
Accelerated Solvent Extraction (ASE) /Pressurised Fluid Extraction (PFE) [11, 21-26]	The temperature of the extraction solvent is elevated above its boiling point but due to increase pressure the solvent remains in the fluid phase. The pressurized fluid is forced through the pores of the sample matrix located in the extraction cell thereby making contact with the analytes. The elevated pressure facilitates the solubilisation of air bubbles in order to expose greater portion of the sample to the solvent. The elevated temperature interrupts the strong solute-matrix interactions; minimizes solvent viscosity for greater penetration into sample and also ensures higher diffusion and solubility of analytes in the solvent. Nitrogen gas is deployed to purge residual solvents from the samples at the end of the extraction.	Commercially available for extracting organic analytes from myriad of solid samples Several extraction cells can be loaded onto the loading tray of the accelerated solvent extractor Rapid and less time consuming Minimum solvent usage Can be optimized for simultaneous extraction of wide array of analytes using different solvents or solvent mixture Automated online purification of extract can be carried out Relatively high precision, accuracy and recovery of analytes; minimizes loss of volatile analytes	Extraction cell components are very delicate and require maximum care and attention The cells are relatively expensive compared to SE apparatus

Table S2: Summary of PAHs, TPPs and surrogate standards

Analyte/Chemicals	**Conc/Quantity**	**Manufacturer**

A. Parent PAHs		
1. Picene (H184S, CAS:213-46-7)	50µg/mL in Toluene	AccuStandard, USA
2. Triphenylene (N-13711, CAS:217-59-4)	100mg neat	Chem Service Inc, USA
H-QME-01 Quebec Ministry of Environment PAH Mix (24 PAHs):	500µg/mL in DCM:Benzene (50:50)	AccuStandard, USA
1. Acenaphthene		
2. Acenaphthylene		
3. Anthracene		
4. Benz[a]anthracene		
5. Benzo[b]fluoranthene		
6. Benzo[j]fluoranthene		
7. Benzo[k]fluoranthene		
8. Benzo[ghi]perylene		
9. Benzo[c]phenanthrene		
10. Benzo[a]pyrene		
11. Benzo[e]pyrene		
12. Chrysene		
13. Dibenz[a,h]anthracene		
14. Dibenzo[a,h]pyrene		
15. Dibenzo[a,i]pyrene		
16. Dibenzo[a,l]pyrene		
17. 7,12-Dimethylbenz[a]anthracene		
18. Fluoranthene		
19. Fuorene		
20. Indeno[1,2,3-cd]pyrene		
21. 3-Methylcholanthrene		
22. Naphthalene		
23. Phenanthrene		
24. Pyrene		
B. Carbonyl-PAHs		
1. 1,4-Naphthaquinone (C 15425000, CAS: 130-15-4)	0.25 g neat	Dr. Ehrenstorfer GmbH, Germany
2. 9-Fluorenone (C 20805000, CAS: 486-25-9)	0.25 g neat	Dr. Ehrenstorfer GmbH, Germany
3. Benzo[a]fluoren-11-one (TRC-B203590, CAS: 479-79-8)	100mg neat	Toronto Research Chemicals (trc), Canada
4. 9,10-Anthraquinone (C 10281000, CAS: 84-65-1)	0.25 g neat	Dr. Ehrenstorfer GmbH, Germany
C. Hydroxy-PAHs		
1. 2-Hydroxybiphenyl (HBP-001N, CAS: 90-43-7)	100mg neat	AccuStandard, USA
2. 4-Hydroxybiphenyl (HBP-003N, CAS: 92-69-3)	100mg neat	AccuStandard, USA
3. 1-Hydroxypyrene (R-096N, CAS: 5315-79-7)	10mg neat	AccuStandard, USA
4. 1,8-Dihydroxyanthraquinone (Danthron) (C 11961000, CAS: 117-10-2)	0.1g neat	Dr. Ehrenstorfer GmbH, Germany
D. Nitro-PAHs		
1. 5-Nitroacenaphthene (N-10899, CAS: 602-87-9)	500mg neat	Chem Service Inc, USA
2. 1-Nitronaphthalene (R-016N, CAS: 86-57-7)	100mg neat	AccuStandard, USA
3. 9-Nitroanthracene (R-003N, CAS: 602-60-8)	5mg neat	AccuStandard, USA
4. 3-Nitrofluoranthene (R-013N, CAS: 892-21-7)	5mg neat	AccuStandard, USA
5. 1-Nitropyrene (R-022N, CAS: 5522-43-0)	5mg neat	AccuStandard, USA
6. 6-Nitrobenz(a)pyrene (R-004S, CAS: 63041-90-7)	100µg/mL in Toluene	AccuStandard, USA
E. Internal & Recovery Standards		
1. Naphthalene (D8, 99%) (DLM-365-1, CAS: 1146-65-2)	1g neat	Cambridge Isotope Laboratories, Inc. (CIL), USA
2. Phenanthrene (D10, 98%) (DLM-371-0.1 (CAS: 1517-22-2)	0.1g neat 1g neat	CIL, USA CIL, USA
3. Anthracene (D10, 98%) (DLM-102-1, CAS: 1719-06-8)	0.1g neat	CIL, USA
4. Pyrene (D10, 98%) (DLM-155-0.1, CAS: 1718-52-1)	50µg/mL in Toluene-D8	CIL, USA

5. 9-Nitroanthracene (D9, 98%) (DLM-4712-1.2)	50µg/mL in Toluene-D8	CIL, USA
6. 1-Nitropyrene (D9, 98%) (DLM-1528-1.2)	1mg neat	trc, Canada
7. 1-Hydroxypyrene-d9 (TRC-H952702-1)	0.1g neat	CIL, USA
8. Fluoranthene (D10, 98%) (DLM-2140-0.1, CAS: 93951-69-0)	5g neat	CIL, USA
9. Benzophenone-D10, 98%		

Table S3: TSQ SRM and electron ionization energies for analytes

Analytes	**Analyte ID**	**Retention time (min.)**	**Precursor ion mass**	**Product ion mass**	**Collision Energy (eV)**	**Limit of detection (pg)**
naphthalene-d8	NAPd	11.46	136.1	108.1	20	2.5
naphthalene-d8	NAPd	11.46	134.0	106	15	
Naphthalene	NAP	11.54	128.1	127	15	2.5
Naphthalene	NAP	11.54	128.1	77	30	
1,4-Naphthaquinone	NQN	17.51	158	102	15	25
1,4-Naphthaquinone	NQN	17.51	158	130	5	
Acenaphthylene	ACT	18.48	152.1	151	20	2.5
Acenaphthylene	ACT	18.48	152.1	126	25	
Acenaphthene	ACE	19.31	154	153	15	2.5
Acenaphthene	ACE	19.31	154	151	40	
2-Hydroxybiphenyl	2HBP	20.04	169	141	10	25
2-Hydroxybiphenyl	2HBP	20.04	169	115	25	
Fluorene	FLR	21.72	165.1	163.1	30	10
Fluorene	FLR	21.72	165.1	139	25	
1-Nitronaphthalene	NNAP	22.13	173	115	15	25
1-Nitronaphthalene	NNAP	22.13	173	143	5	
Benzophenone-d10	BZPd	22.65	192	110	10	25
Benzophenone-d10	BZPd	22.65	192	82	30	
4-Hydroxybiphenyl	4HBP	24.64	170	141	15	50
4-Hydroxybiphenyl	4HBP	24.64	141	115	15	
9-Fluorenone	9FLN	25.16	180	152	15	25
9-Fluorenone	9FLN	25.16	180	76	45	
Phenanthrene	PHE	26.02	178.1	152.1	20	10
Phenanthrene	PHE	26.02	178.1	176.1	25	
Phenanthrene-d10	PHEd	26.02	188	160.1	25	10
Phenanthrene-d10	PHEd	26.02	184	156.1	25	
Anthracene	ANT	26.27	178.1	176	25	25
Anthracene	ANT	26.27	178	177	15	
Anthracene-d10	ANTd	26.27	188	186	25	25
Anthracene-d10	ANTd	26.27	188	187	15	
9,10-Anthraquinone	AQN	29.98	180	152	12	10
9,10-Anthraquinone	AQN	29.98	208	180	10	
9,10-Anthraquinone	AQN	29.98	208	152	22	
5-Nitroacenaphthene	5NAC	30.7	199.1	169	10	5
5-Nitroacenaphthene	5NAC	30.7	199.1	141	20	
Fluoranthene-d10	FRTd	31.7	212.1	210.1	35	2.5

Fluoranthene-d10	FRTd	31.7	212.1	186.1	30	
Fluoranthene	FRT	31.8	202.1	200.1	35	2.5
Fluoranthene	FRT	31.8	202.1	176.1	30	
Pyrene-d10	PYRd	32.65	212.1	208.1	30	2.5
Pyrene-d10	PYRd	32.65	212.1	180	35	
Pyrene-d10	PYRd	32.65	212.1	106	35	
Pyrene	PYR	32.7	202.1	200.1	35	2.5
Pyrene	PYR	32.7	202.1	176.1	30	
9-Nitroanthracene-d9	9NANd	32.9	232.2	202.2	10	25
9-Nitroanthracene-d9	9NANd	32.9	232.2	174.2	25	
9-Nitroanthracene	9NAN	33	223.2	193	10	10
9-Nitroanthracene	9NAN	33	223.2	165	25	
1,8-Dihydroxyanthraquinone (Danthron)	DHAQ	33.97	240	212	10	250
1,8-Dihydroxyanthraquinone (Danthron)	DHAQ	33.97	240	184	15	
Benzo[a]fluoren-11-one	BaFN	36.09	230	202	15	10
Benzo[a]fluoren-11-one	BaFN	36.09	230	200	40	
Benzo[c]phenanthrene	BcPH	36.62	228	227	15	2.5
Benzo[c]phenanthrene	BcPH	36.62	228	226	35	
Benzo(a)anthracene	BaAN	37.33	228.1	226.1	30	2.5
Benzo(a)anthracene	BaAN	37.33	228.1	202.1	25	
Triphenylene+ Chrysene	TPL	37.41	228	227	15	5
Triphenylene+ Chrysene	TPL	37.41	228	226	30	
Chrysene-d12	CHRd	37.43	240	236	30	5
Chrysene-d12	CHRd	37.43	240	212	25	
Chrysene-d12	CHRd	37.43	240	238	30	
Chrysene-d12	CHRd	37.43	240	214	25	
1-Hydroxypyrene-d9	HPYd	37.7	227.3	197	25	100
1-Hydroxypyrene-d9	HPYd	37.7	227.3	199	10	
1-Hydroxypyrene	HPY	37.75	218	189	50	50
1-Hydroxypyrene	HPY	37.75	218	187	25	
3-Nitrofluoranthene	3NFR	38.35	247.3	189	20	25
3-Nitrofluoranthene	3NFR	38.35	247.3	217	10	
1-Nitropyrene d9	1NPYd	38.91	256.3	226	10	25
1-Nitropyrene d9	1NPYd	38.91	256.3	198	25	
1-Nitropyrene d9	1NPYd	38.91	256.3	256.3	0	
1-Nitropyrene	1NPY	38.95	247.3	189	25	25
1-Nitropyrene	1NPY	38.95	247.3	217	10	
Benzo(b)+(j)fluoranthene	BbFR	40.61	252.1	250.1	30	5
Benzo(b)+(j)fluoranthene	BbFR	40.61	252.1	226.1	35	
Benzo(k)fluoranthene	BkFR	40.61	252.1	250.1	35	2.5
Benzo(k)fluoranthene	BkFR	40.61	252.1	226.1	30	
7,12-Dimethylbenz[a]anthracene	DMBA	40.65	256	241	10	5
7,12-Dimethylbenz[a]anthracene	DMBA	40.65	256	239	40	
Benzo(e)pyrene	BeP	41.32	252	250.1	35	2.5
Benzo(e)pyrene	BeP	41.32	252	226.1	30	
Benzo(a)pyrene	BaP	41.45	252	250.1	35	5

Benzo(a)pyrene	BaP	41.45	252	226.1	30	
3-Methylcholanthrene	MCHO	42.41	268	252	35	25
3-Methylcholanthrene	MCHO	42.41	268	253	15	
Indeno(123-cd)pyrene	IcdP	44.13	276.1	274.1	40	25
Indeno(123-cd)pyrene	IcdP	44.13	276.1	250	30	
Dibenzo(ah)anthracene	DahA	44.21	278.1	276.1	40	25
Dibenzo(ah)anthracene	DahA	44.21	278.1	274.1	50	
Picene	PIC	44.48	278	276	30	2.5
Picene	PIC	44.48	278	277	15	
6-Nitrobenz(a)pyrene	NBaP	44.49	267	239	20	100
6-Nitrobenz(a)pyrene	NBaP	44.49	297	267	10	
Benzo(ghi)perylene	BghiPE	44.67	276.1	274.1	45	10
Benzo(ghi)perylene	BghiPE	44.67	276.1	250	40	
Dibenzo[a,l]pyrene	DalP	47.31	302	300	35	2.5
Dibenzo[a,l]pyrene	DalP	47.31	302	301	10	
Dibenzo[a,h]pyrene	DahP	48.61	302	300	35	25
Dibenzo[a,h]pyrene	DahP	48.61	302	301	10	
Dibenzo[a,i]pyrene	DaiP	48.9	302	300	35	25
Dibenzo[a,i]pyrene	DaiP	48.9	302	301	10	

Table S4: Shimadzu SRM and electron ionization energies for analytes

Analytes	Analytes ID	Retention time (min)	Precursor ion mass	Product ion mass	Collision Energy (eV)	Limit of detection (pg)
Naphthalened8	NAPd	6.358	136.00	108.00	15	1.0
Naphthalene-d8	NAPd	6.358	136.00	84.00	20	
Naphthalene	NAP	6.383	128.00	102.00	15	1.0
Naphthalene	NAP	6.383	128.00	78.00	20	
1,4-Naphthaquinone	NQN	8.029	158.00	102.00	15	5.0
1,4-Naphthaquinone	NQN	8.029	158.00	130.00	5	
Acenaphthylene	ACT	8.319	152.00	151.00	20	2.5
Acenaphthylene	ACT	8.319	152.00	126.00	25	
Acenaphthene	ACE	8.534	153.00	152.00	25	2.5
Acenaphthene	ACE	8.534	153.00	127.00	25	
2-Hydroxybiphenyl	2HBP	8.695	169.00	141.00	10	5.0
2-Hydroxybiphenyl	2HBP	8.695	169.00	115.00	25	
Fluorene	FLR	9.171	166.00	165.00	20	2.5
Fluorene	FLR	9.171	166.00	164.00	30	
1-Nitronaphthalene	NNAP	9.270	173.00	115.00	15	10.0
1-Nitronaphthalene	NNAP	9.270	173.00	143.00	5	
Benzophenone-d10	BZPd	9.357	192.00	110.00	10	2.5
Benzophenone-d10	BZPd	9.357	192.00	82.00	30	
4-Hydroxybiphenyl	4HBP	9.876	170.00	141.00	15	1.0
4-Hydroxybiphenyl	4HBP	9.876	141.00	115.00	15	
9-Fluorenone	9FLN	10.091	180.00	152.00	15	1.0
9-Fluorenone	9FLN	10.091	180.00	76.00	45	
9,10-Anthraquinone	AQN	10.091	180.00	152.00	12	1.0
9,10-Anthraquinone	AQN	10.091	208.00	152.00	22	
9,10-Anthraquinone	AQN	10.091	208.00	180.00	10	
Phenanthrene-d10	PHEd	10.326	188.00	160.00	20	1.0
Phenanthrene-d10	PHEd	10.326	188.00	184.00	30	
Phenanthrene	PHE	10.355	178.00	152.00	20	1.0
Phenanthrene	PHE	10.355	178.00	176.00	25	
Anthracene-d10	ANTd	10.394	188.00	160.00	20	1.0
Anthracene-d10	ANTd	10.394	188.00	184.00	30	
Anthracene	ANT	10.418	178.00	152.00	20	1.0
Anthracene	ANT	10.418	178.00	176.00	25	
5-Nitroacenaphthene	5NAC	11.515	199.10	169.00	10	2.5
5-Nitroacenaphthene	5NAC	11.515	199.10	141.00	20	
Fluoranthene-d10	FRTd	11.807	212.10	186.10	30	1.0
Fluoranthene-d10	FRTd	11.807	212.10	210.10	35	
Fluoranthene	FRT	11.832	202.00	201.00	20	1.0
Fluoranthene	FRT	11.832	202.00	200.00	25	
Pyrene-d10	PYRd	12.109	212.10	208.10	30	1.0
Pyrene-d10	PYRd	12.109	212.10	106.00	35	
Pyrene-d10	PYRd	12.109	212.10	108.00	30	
Pyrene	PYR	12.135	202.00	201.00	20	1.0
Pyrene	PYR	12.135	202.00	200.00	25	

9-Nitroanthrancene-d9	9NANd	12.141	232.20	174.20	25	1.0
9-Nitroanthrancene-d9	9NANd	12.141	232.20	202.20	10	
9-Nitroanthracene	9NAN	12.166	176.00	150.10	24	1.0
9-Nitroanthracene	9NAN	12.166	193.00	165.10	21	
9-Nitroanthracene	9NAN	12.166	223.00	165.10	24	
1,8-Dihydroxyanthraquinone (Danthron)	DHAQ	12.531	240.00	212.00	10	1.0
1,8-Dihydroxyanthraquinone (Danthron)	DHAQ	12.531	240.00	184.00	15	
Benzo[a]fluoren-11-one	BaFN	13.459	230.00	202.00	15	1.0
Benzo[a]fluoren-11-one	BaFN	13.459	230.00	200.00	40	
Benzo[c]phenanthrene	BcPH	13.724	228.00	226.00	35	2.5
Benzo[c]phenanthrene	BcPH	13.724	228.00	227.00	15	
Benz(a)anthracene	BaAN	13.724	228.00	226.00	30	2.5
Benz(a)anthracene	BaAN	13.724	228.00	202.00	20	
Chrysene-d12	CHRd	14.153	240.00	236.00	30	1.0
Chrysene-d12	CHRd	14.153	240.00	212.00	20	
Chrysene	CHR	14.188	228.00	226.00	30	1.0
Chrysene	CHR	14.188	228.00	202.00	20	
Triphenylene	TPL	14.188	228.00	226.00	30	1.0
Triphenylene	TPL	14.188	228.00	227.00	15	
1-Hydroxypyrene-d9	HPYd	14.366	227.30	199.00	10	25.0
1-Hydroxypyrene-d9	HPYd	14.366	227.30	197.00	25	
1-Hydroxypyrene	HPY	14.392	218.00	189.00	25	10.0
1-Hydroxypyrene	HPY	14.392	218.00	187.00	50	
1-Nitropyrene-d9	1NPYd	15.193	256.30	226.00	10	2.5
1-Nitropyrene-d9	1NPYd	15.193	256.30	198.00	25	
1-Nitropyrene	1NPY	15.219	247.30	189.00	20	2.5
1-Nitropyrene	1NPY	15.219	247.30	217.00	10	
7,12-Dimethylbenz[a]anthracene	DMBA	16.454	256.00	241.00	10	2.5
7,12-Dimethylbenz[a]anthracene	DMBA	16.454	256.00	239.00	40	
Benzo(b)fluoranthene	BbFR	16.469	252.00	250.00	25	1.0
Benzo(b)fluoranthene	BbFR	16.469	252.00	226.00	25	
Benzo[k+j]fluoranthene	B(k+j)FR	16.480	252.10	226.10	30	1.0
Benzo[k+j]fluoranthene	B(k+j)FR	16.480	252.10	250.10	35	
Benzo[e]pyrene	BeP	16.961	252.00	226.10	30	1.0
Benzo[e]pyrene	BeP	16.961	252.00	250.10	35	
Benzo(a)pyrene	BaP	17.051	252.00	250.00	25	1.0
Benzo(a)pyrene	BaP	17.051	252.00	226.10	25	
3-Methylcholanthrene	MCHO	17.668	268.00	252.00	35	2.5
3-Methylcholanthrene	MCHO	17.668	268.00	253.00	15	
Dibenzo(a.h)anthracene	DahA	18.790	278.00	276.00	30	5.0
Dibenzo(a.h)anthracene	DahA	18.790	278.00	252.00	20	
Picene	PIC	18.791	278.00	276.00	30	5.0
Picene	PIC	18.791	278.00	277.00	15	
Indeno(1.2.3.cd)pyrene	IcdP	18.962	276.00	274.00	30	5.0

Indeno(1.2.3.cd)pyrene	IcdP	18.962	276.00	225.00	20	
6-Nitrobenz[a]pyrene	NBaP	18.958	267.00	239.00	20	50.0
6-Nitrobenz[a]pyrene	NBaP	18.958	297.00	267.00	10	
Benzo(g.h.i)perylene	BghiPE	19.096	276.00	274.00	30	2.5
Benzo(g.h.i)perylene	BghiPE	19.096	276.00	275.00	30	
Dibenzo[a.l]pyrene	DalP	20.701	302.00	300.00	35	2.5
Dibenzo[a.l]pyrene	DalP	20.701	302.00	301.00	10	
Dibenzo[a,h]pyrene	DahP	21.483	302.00	300.00	35	2.5
Dibenzo[a,h]pyrene	DahP	21.483	302.00	301.00	10	
Dibenzo[a,i]pyrene	DaiP	21.559	302.00	300.00	35	2.5
Dibenzo[a,i]pyrene	DaiP	21.559	302.00	301.00	10	

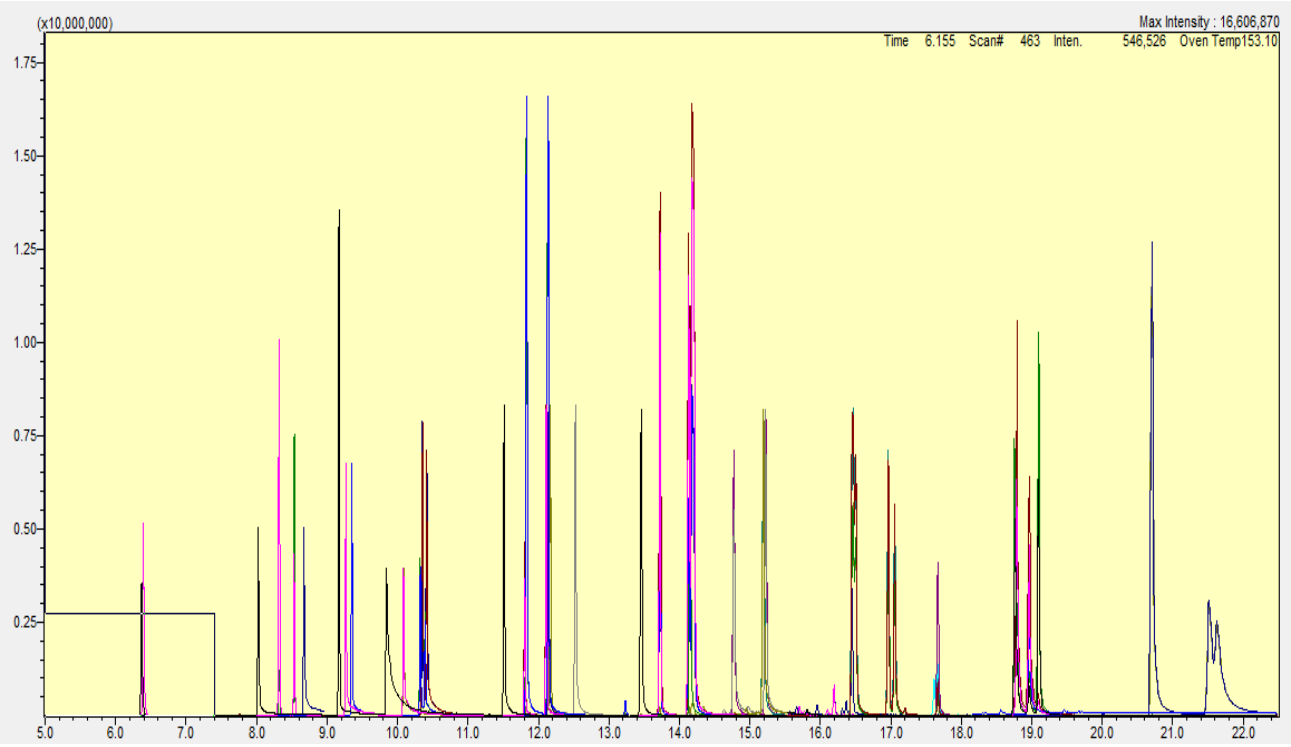

Fig. S1: Shimadzu chromatogram for analytes using SRM mode

Table S5: Comparison of NIST certified or reference values for SRM 1649b analytes with results for selected PFE methods

Compound	ID	NIST_SRM (mg/kg)	PFE extracted analyte concentration (mg/kg)										
			5Di	**3Dii**	**2Bi**	**2Dii**	**2Bii**	**4Bi**	**1Dii**	**5Bii**	**5Ci**	**3Ci**	**3Bii**
Naphthalene	NAP	0.946	0.043	0.074	0.064	0.073	0.010	0.005	0.058	0.021	0.017	0.271	0.211
Acenaphthylene	ACT	0.193	0.046	0.053	0.066	0.051	0.039	0.026	0.062	0.045	0.047	0.021	0.027
Acenapthene	ACE	0.197	0.029	0.034	0.044	0.033	0.022	0.017	0.033	0.033	0.031	0.023	0.032
Fluorene	FLR	0.223	0.052	0.054	0.067	0.054	0.038	0.032	0.055	0.047	0.049	0.031	0.042
Phenanthrene	PHE	4.03	1.523	1.602	1.798	1.505	1.374	0.932	1.584	1.480	1.379	1.078	1.382
Anthracene	ANT	0.41	0.232	0.247	0.279	0.249	0.209	0.157	0.236	0.218	0.201	0.151	0.177
Fluoranthene	FRT	6.24	2.324	2.435	2.613	2.188	2.129	1.421	2.421	2.372	2.062	2.016	2.561
Pyrene	PYR	**4.980**	1.842	1.951	2.070	1.756	1.676	1.120	1.949	1.874	1.646	1.601	2.035
Benzo[c]phenanthrene	BcPH	**0.460**	0.201	0.204	0.217	0.186	0.177	0.125	0.215	0.199	0.168	0.175	0.220
Benzo(a)anthracene	BaAN	2.110	0.000	0.208	0.224	0.186	0.176	0.136	0.217	0.000	0.000	0.175	0.000
Chrysene	CHR	**3.045**	0.770	0.859	0.906	0.763	0.705	0.485	0.937	0.756	0.668	0.620	0.754
Triphenylene	TPL	**1.324**	0.779	0.850	0.895	0.763	0.710	0.487	0.903	0.773	0.674	0.645	0.795
Benzo(b) fluoranthene	BbFR	**6.180**	0.810	1.064	1.157	0.841	0.695	0.386	1.124	0.681	0.498	0.219	0.126
Benzo(k+j)fluoranthene	B(k+j)FR	**3.427**	2.551	2.646	2.709	2.418	2.259	1.569	2.604	2.546	2.214	2.299	2.686
Benzo(e)pyrene	BeP	**2.974**	2.826	3.644	4.032	2.631	2.245	1.176	3.797	2.367	1.793	0.701	0.803
Picene	PIC	**0.399**	0.345	0.366	0.370	0.000	0.300	0.238	0.333	0.000	0.347	0.309	0.000
Indeno(123-cd)pyrene	IcdP	**2.890**	0.000	0.433	0.171	0.000	0.370	0.250	0.000	0.414	0.358	0.198	0.258
Benzo(a)pyrene	BaP	2.470	2.826	3.644	4.032	2.631	2.245	1.176	3.797	2.367	1.793	0.701	0.803
Benzo(ghi)perylene	BghiPE	3.970	1.709	1.746	1.735	1.549	1.452	0.924	1.419	1.606	1.395	1.423	1.626
Dibenzo[a,l]pyrene	DalP	0.055	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1-Nitronaphthalene	NNAP	0.00726	0.040	0.088	0.000	0.000	0.000	0.000	0.077	0.000	0.118	0.000	0.000
5-Nitroacenaphthene	5NAC	0.0031	0.024	0.108	0.097	0.107	0.000	0.002	0.000	0.000	0.011	0.000	0.001
1-Nitropyrene	1NPY	**0.075**	0.179	0.290	0.315	0.258	0.179	0.141	0.885	0.201	0.176	0.053	0.071

Surrogate standards		Spiked, mg/L	Recovered concentration (mg/L)										
naphthalene-d8	NAPd	**100.000**	6.639	11.003	12.145	7.805	3.002	0.407	4.724	3.967	14.245	2.782	1.567
phenanthrene-d10	PHEd	**100.000**	54.750	59.933	62.874	51.204	50.002	34.371	53.449	55.232	61.071	47.732	46.542
Anthracene d10	ANTd	**100.000**	53.270	55.729	58.312	47.850	51.519	34.148	51.846	56.302	63.152	51.261	48.433
Pyrene-d10	PYRd	**100.000**	58.958	64.981	66.553	55.753	57.606	40.120	60.568	61.327	66.225	62.850	58.763
Benzophenone d10	BZPd	**100.000**	58.351	62.726	67.032	56.477	51.371	10.367	58.178	61.083	68.836	43.468	52.604
9-Nitroanthracene d9	9NANd	**100.000**	64.135	74.902	78.130	65.823	56.566	48.679	116.349	60.561	57.442	46.301	41.431
1-Nitropyrene d9	1NPYd	**100.000**	124.400	157.576	164.468	145.739	110.437	82.086	192.606	114.709	120.247	80.898	81.604
1-Hydroxypyrene-d9	HPYd	**100.000**	0.000	0.000	0.000	0.000	13.991	0.000	0.000	145.697	11.837	25.843	0.521
Extract cleanliness			**bad**	**bad**	**bad**	**bad**	**bad**	**bad**	**very bad**	**bad**	**very good**	**very good**	**Bad**

NIST values in bold and not boldened refer to certified mass fraction values, and reference mass fraction values, respectively based on Soxhlet extraction or PFE at 100 oC and 150 oC [27]. The results in this study were not corrected for analyte recovery. The relative error for these results is between 0.1% – 3.0%.

Table S6: Analytes concentrations (mg/kg) without reference values in SRM 1649b

Compound	NIST [27]	Wingfors, Hägglund [28]	ID	5Di	3Dii	2Bi	2Dii	2Bii	4Bi	1Dii	5Bii	5Ci	3Ci	3Bii
3-Methylcholanthrene			**MCHO**	0.031	0.000	0.000	0.020	0.000	0.000	0.000	0.035	0.000	0.000	0.000
Dibenzo(ah)anthracene			**DahA**	0.351	0.367	0.448	0.336	0.309	0.208	0.341	0.353	0.230	0.383	0.448
Dibenzo[a,h]pyrene			**DahP**	0.000	0.000	0.144	0.000	0.101	0.000	0.076	0.105	0.000	0.000	0.000
1,4-Naphthaquinone			**NQN**	0.041	0.091	0.074	0.061	0.013	0.399	0.214	0.000	0.000	0.000	0.000
9-Fluorenone	1.4	**0.59**	**9FLN**	0.658	0.702	0.773	0.701	0.591	0.296	0.683	0.628	0.582	0.211	0.386
9,10-Anthraquinone	1.8	**1.1**	**AQN**	0.709	0.765	0.853	0.769	0.652	0.315	0.800	0.693	0.637	0.215	0.412
Benzo[a]fluoren-11-one			**BaFN**	1.566	1.680	1.764	1.546	1.417	0.692	1.728	1.501	1.373	0.999	1.488
6-Nitrobenz(a)pyrene			**NBaP**	0.000	0.000	0.000	0.000	0.000	0.892	2.159	0.000	0.000	0.000	0.392
2-Hydroxybiphenyl			**2HBP**	0.029	0.032	0.031	0.035	0.020	0.014	0.000	0.004	0.024	0.000	0.000
4-Hydroxybiphenyl			**4HBP**	0.115	0.147	0.182	0.154	0.110	0.070	0.000	0.085	0.097	0.002	0.003
1,8-Dihydroxyanthraquinone			**DHAQ**	0.057	0.000	0.000	0.000	0.000	0.001	0.021	0.000	0.000	0.001	0.000

The NIST values here are only information mass fraction values and the relative error for these results is between 0.1% – 4.0%.

Table S7: Varimax rotated factor loadings for PFE methods applied to SRM 1649b

Variable	NIST_SRM	5Di	3Dii	2Bi	2Dii	2Bii	4Bi	1Dii	5Bii	5Ci	3Ci	3Bii
Factor 1	0.752	0.987	0.963	0.954	0.988	0.997	0.993	0.941	0.997	0.994	0.877	0.872

Table S8: Analytes concentration in road dust using modified selected PFE method 5Ci

		Methods with their concentrations (mg/kg)				
Analytes	**ID**	**5Cia**	**5Cib**	**5Cic**	**5Cid**	**5Cie**
Naphthalene	NAP		1.1536	0.6327	3.2319	
Acenaphthylene	ACT	0.0072	0.0456	0.0323	0.0710	0.0128
Acenaphthene	ACE	0.0071	1.2126	0.6401	1.6621	0.0406
Fluorene	FLR			0.2219	0.3683	
Phenanthrene	PHE	0.1289	0.3380	0.4621	0.4284	0.1683
Anthracene	ANT	0.0360	0.1749	0.2401	0.4584	
Fluoranthene	FRT	0.1109	0.1753	0.2189	0.1674	0.1225
Pyrene	PYR	0.2216	0.2550	0.3455	0.3032	0.2389
Benzo[c]phenanthrene	BcPH	0.0023	0.0021		0.0014	
Benzo(a)anthracene	BaAN	0.0033	0.0032	0.0010	0.0022	0.0032
Chrysene	CHR	0.0435	0.0463	0.0633	0.0499	0.0403
Triphenylene	TPL	0.0412	0.0447	0.0606	0.0474	0.0385
7,12-Dimethylbenz[a]anthracene	DMBA	0.4362	0.3599	0.4015	0.4578	0.3875
Benzo(b) fluoranthene	BbFR	0.0275	0.0274	0.0431	0.0302	0.0233
Benzo(k+j)fluoranthene	B(k+j)FR	0.0521	0.0524	0.0860	0.0601	0.0454
Benzo(e)pyrene	BeP	0.1327	0.1143	0.1728	0.1329	0.1187
Benzo(a)pyrene	BaP	0.0898	0.0830	0.1124	0.0859	0.0863
3-Methylcholanthrene	MCHO	0.0730	0.0558	0.0496	0.0569	0.0336
Dibenzo(ah)anthracene	DahA	0.0258	0.0231	0.0260	0.0172	0.0218
Picene	PIC	0.0243	0.0236	0.0258	0.0166	0.0198

Indeno(123-cd)pyrene	IcdP	0.0059	0.0112	0.0063		0.0036
Benzo(ghi)perylene	BghiPE	0.3155	0.2809	0.2801	0.2139	0.2504
Dibenzo[a,l]pyrene	DalP	0.0104				
1-Nitronaphthalene	NNAP	0.0318	7.5089	8.4174	8.0174	0.2545
5-Nitroacenaphthene	5NAC		0.3043	0.0834	0.1348	0.0020
6-Nitrobenz(a)pyrene	NBaP	0.4720	0.4643			0.4061
1-Nitropyrene	1NPY	0.0146	0.0924	0.1765		0.0073
9-Nitroanthracene	9NAN	0.0650				
9-Fluorenone	9FLN	0.0239	0.0396	0.0290	0.0468	0.0289
9,10-Anthraquinone	AQN	0.0245	0.0381	0.0304	0.0497	0.0288
Benzo[a]fluoren-11-one	BaFN	0.0236	0.0182	0.0134	0.0082	0.0220
1,4-Naphthaquinone	NQN	0.0047	0.0000			
2-Hydroxybiphenyl	2HBP		0.1866	0.2314	0.4244	
1-Hydroxypyrene	HPY	0.0480	0.9247	0.5607	0.5921	0.0607
4-Hydroxybiphenyl	4HBP	0.0319				
1,8-Dihydroxyanthraquinone (Danthron)	DHAQ	0.1742				
naphthalene-d8	NAPd	2	69	48	111	0
Benzophenone d10	BZPd	117	97	74	80	70
phenanthrene-d10	PHEd	174	147	149	82	86
Anthracene d10	ANTd	105	124	135	103	56
Pyrene-d10	PYRd	152	132	150	90	69
9-Nitroanthracene d9	9NANd	35	6	9	27	51
1-Hydroxypyrene-d9	HPYd	145		50		84
1-Nitropyrene d9	1NPYd	130	48	14	10	81

The relative error for these results is between 0.1% – 5.0%.

Reference

1. Durán, A.C. and A. González, *Determination of lead, naphthalene, phenanthrene, anthracene and pyrene in street dust.* Int. J. Environ. Sci. Tech. , 2009. **6**(4): p. 663-670.
2. Dong, T.T. and B.K. Lee, *Characteristics, toxicity, and source apportionment of polycylic aromatic hydrocarbons (PAHs) in road dust of Ulsan, Korea.* Chemosphere, 2009. **74**(9): p. 1245-53.
3. Mostafa, A.R., et al., *Source characterization and the environmental impact of urban street dusts from Egypt based on hydrocarbon distributions.* Fuel, 2009. **88**(1): p. 95-104.
4. Han, B., et al., *Characterization of PM(10) fraction of road dust for polycyclic aromatic hydrocarbons (PAHs) from Anshan, China.* J Hazard Mater, 2009. **170**(2-3): p. 934-40.
5. Wang, D.G., et al., *Polycyclic aromatic hydrocarbons in urban street dust and surface soil: comparisons of concentration, profile, and source.* Arch Environ Contam Toxicol, 2009. **56**(2): p. 173-80.
6. Liu, M., et al., *Characterization, identification of road dust PAHs in central Shanghai areas, China.* Atmospheric Environment, 2007. **41**(38): p. 8785-8795.
7. Essumang, D.K., et al., *Analysis of polycyclic aromatic hydrocarbons in street soil dust in Kumasi Metropolis of Ghana.* Environ Monit Assess, 2006. **121**(1-3): p. 401-8.
8. Han, Y.M., et al., *Stronger association of polycyclic aromatic hydrocarbons with soot than with char in soils and sediments.* Chemosphere, 2015. **119**: p. 1335-45.
9. Ren, Y., T. Cheng, and J. Chen, *Polycyclic aromatic hydrocarbons in dust from computers: one possible indoor source of human exposure.* Atmospheric Environment, 2006. **40**(36): p. 6956-6965.
10. Christensen, A., C. Ostman, and R. Westerholm, *Ultrasound-assisted extraction and on-line LC-GC-MS for determination of polycyclic aromatic hydrocarbons (PAH) in urban dust and diesel particulate matter.* Anal Bioanal Chem, 2005. **381**(6): p. 1206-16.
11. Qiao, M., et al., *Oxygenated, nitrated, methyl and parent polycyclic aromatic hydrocarbons in rivers of Haihe River System, China: occurrence, possible formation, and source and fate in a water-shortage area.* Sci Total Environ, 2014. **481**: p. 178-85.
12. Netto, A.D.P., et al., *PAHs in SD:Polycyclic aromatic hydrocarbons levels in street dust in the central area of Niterói City, RJ, Brazil.* Water, Air, and Soil Pollution, 2006. **176**(1-4): p. 57-67.
13. Gfrerer, M., M. Serschen, and E. Lankmayr, *Optimized extraction of polycyclic aromatic hydrocarbons from contaminated soil samples.* J. Biochem. Biophys. Methods, 2002. **53**: p. 203–216.
14. Buco, S., et al., *Analysis of polycyclic aromatic hydrocarbons in contaminated soil by Curie point pyrolysis coupled to gas chromatography–mass spectrometry, an alternative to conventional methods.* Journal of Chromatography A, 2004. **1026**(1-2): p. 223-229.
15. van Drooge, B.L., I. Nikolova, and P.P. Ballesta, *Thermal desorption gas chromatography-mass spectrometry as an enhanced method for the quantification of polycyclic aromatic hydrocarbons from ambient air particulate matter.* J Chromatogr A, 2009. **1216**(18): p. 4030-9.
16. Gil-Molto, J., et al., *Application of an automatic thermal desorption-gas chromatography-mass spectrometry system for the analysis of polycyclic aromatic hydrocarbons in airborne particulate matter.* J Chromatogr A, 2009. **1216**(9): p. 1285-9.
17. Bates, M., et al., *Analysis of polycyclic aromatic hydrocarbons (PAHs) in airborne particles by direct sample introduction thermal desorption GC/MS.* Atmospheric Environment, 2008. **42**(24): p. 6144-6151.
18. Wauters, E., et al., *Improved accuracy in the determination of polycyclic aromatic hydrocarbons in air using 24 h sampling on a mixed bed followed by thermal desorption capillary gas chromatography-mass spectrometry.* J Chromatogr A, 2008. **1190**(1-2): p. 286-93.

19. Meng, H., et al., *Thermal Desorption-Gas Chromatography or Gas Chromatography-Mass Spectrometry for Analysis of Semi-Volatile Compounds on Atmospheric Particulate Matters.* Chinese Journal of Analytical Chemistry, 2014. **42**(7): p. 931-936.
20. Mercier, F., et al., *Analysis of semi-volatile organic compounds in indoor suspended particulate matter by thermal desorption coupled with gas chromatography/mass spectrometry.* J Chromatogr A, 2012. **1254**: p. 107-14.
21. Lundstedt, S., P. Haglund, and L. Oberg, *Simultaneous extraction and fractionation of polycyclic aromatic hydrocarbons and their oxygenated derivatives in soil using selective pressurized liquid extraction.* Anal Chem, 2006. **78**(9): p. 2993-3000.
22. Turrio-Baldassarri, L., C.L. Battistelli, and A.L. Iamiceli, *Evaluation of the efficiency of extraction of PAHs from diesel particulate matter with pressurized solvents.* Anal Bioanal Chem, 2003. **375**(4): p. 589-95.
23. Zhang, Y., et al., *A novel bioaccessibility prediction method for PAHs in soil: Composite extraction with hydroxypropyl-beta-cyclodextrin and extracellular polymer substances.* Sci Total Environ, 2016.
24. Zheng, X., et al., *PAH determination based on a rapid and novel gas purge-microsyringe extraction (GP-MSE) technique in road dust of Shanghai, China: Characterization, source apportionment, and health risk assessment.* Sci Total Environ, 2016. **557-558**: p. 688-96.
25. Bandowe, B.A., M.G. Lueso, and W. Wilcke, *Oxygenated polycyclic aromatic hydrocarbons and azaarenes in urban soils: a comparison of a tropical city (Bangkok) with two temperate cities (Bratislava and Gothenburg).* Chemosphere, 2014. **107**: p. 407-14.
26. Jonsson, S., et al., *Degradation of polycyclic aromatic hydrocarbons (PAHs) in contaminated soils by Fenton's reagent: a multivariate evaluation of the importance of soil characteristics and PAH properties.* J Hazard Mater, 2007. **149**(1): p. 86-96.
27. NIST, *Certficate of analysis Standard Reference Material (SRM) 1649b Urban Dust*. 2016.
28. Wingfors, H., L. Hägglund, and R. Magnusson, *Characterization of the size-distribution of aerosols and particle-bound content of oxygenated PAHs, PAHs, and n-alkanes in urban environments in Afghanistan.* Atmospheric Environment, 2011. **45**(26): p. 4360-4369.