

Determination of atmospheric particulate-phase polycyclic aromatic hydrocarbons from low volume air samples

Delgado Saborit, Juana; Aquilina, Noel; Baker, Stephen; Harrad, Stuart; Meddings, Claire; Harrison, Roy

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3 **DETERMINATION OF ATMOSPHERIC**
4 **PARTICULATE-PHASE POLYCYCLIC**
5 **AROMATIC HYDROCARBONS FROM LOW**
6 **VOLUME AIR SAMPLES**
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8
9 Juana Mari Delgado-Saborit, Noel Aquilina, Stephen Baker, Stuart Harrad,
10 Claire Meddings and Roy M. Harrison *

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12
13 Division of Environmental Health & Risk Management
14 School of Geography, Earth & Environmental Sciences
15 University of Birmingham
16 Edgbaston, Birmingham B15 2TT
17 United Kingdom

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* **To whom correspondence should be addressed**

Division of Environmental Health & Risk Management, School of Geography, Earth & Environmental
Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom
Tel: +44 (0)121 41 43494; Fax: +44 (0)121 41 43709; email: r.m.harrison@bham.ac.uk

1 **Summary**

2
3 This study has tested and optimized different filter media and pre-conditioning methods,
4 extraction methodologies, cleaning techniques and solvents, concentration procedures and
5 GC-MS parameters in order to establish the best methodology to sample and analyze particle-
6 bound PAH collected in low volume samples (1.4 m³). The procedure developed combines
7 the use of quartz fiber filters pre-conditioned at 400°C for 48 hours with a simple extraction
8 procedure and optimized GC-MS parameters. The average method detection limits ranged 4
9 to 15 pg m⁻³ for the 4-7 ring PAHs, precision (RSD) ranged from 0.3-9.7% and accuracy
10 ranged from -6 to 25%. This method was validated with the extraction and analysis of the
11 Standard Reference Material 1649a. and was tested successfully on samples collected in
12 outdoor microenvironments proving suitable for determination of particle-bound PAH
13 concentrations without interferences in low volume samples.

14 **KEYWORDS**

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17 Polycyclic aromatic hydrocarbons, benzo[*a*]pyrene, low volume sample, method
18 development, method validation, standard reference material, gas chromatograph-mass
19 spectrometry, airborne particulate, ambient air.

20

1 **ABBREVIATIONS**

2	Ac	Acenaphthylene
3	Ace	Acenaphthene
4	AM	Arithmetic mean
5	An	Anthracene
6	B[<i>a</i>]A	Benz[<i>a</i>]anthracene
7	B[<i>a</i>]P	Benzo[<i>a</i>]pyrene
8	B[<i>b</i>]F	Benzo[<i>b</i>]fluoranthene
9	B[<i>ghi</i>]P	Benzo[<i>ghi</i>]perylene
10	B[<i>k</i>]F	Benzo[<i>k</i>]fluoranthene
11	Chry	Chrysene
12	Cor	Coronene
13	D[<i>a,h</i>]A	Dibenz[<i>a,h</i>]anthracene
14	DCM	Dichloromethane
15	Fl	Fluorene
16	Fluo	Fluoranthene
17	GC–MS	Gas chromatography mass spectra
18	HPLC	High performance liquid chromatography
19	I[<i>1,2,3-cd</i>]P	Indeno[<i>1,2,3-cd</i>]pyrene
20	IDL	Instrument detection limit
21	MDL	Method detection limit
22	PAH	Polycyclic aromatic hydrocarbons
23	Ph	Phenanthrene
24	Pyr	Pyrene
25	RDS	Recovery determination standard
26	SDL	Sample detection limit

1	SIM	Single ion monitoring
2	SRM	Standard reference material
3	STD	Standard deviation
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1 **1. Introduction**

2 Polycyclic aromatic hydrocarbons (PAH) are a group of widespread environmental
3 pollutants containing two or more fused benzene rings. PAHs are considered the most
4 commonly distributed class of potent carcinogens present in the human environment, and
5 many of them are listed as proven or possible carcinogens ¹. Consequently, PAHs are widely
6 studied with focus on their health-related impacts ².

7 Atmospheric particle-bound PAHs are commonly sampled onto filter media by high-
8 volume samplers collecting around 1000-2000 m³ ³⁻⁵, while some authors have also used
9 medium-volume samplers collecting between 7 and 30 m³ ^{6, 7}. On the other hand, a few
10 authors have used low volume samplers (<2 m³), with the analysis of these samples being
11 performed with high performance liquid chromatography (HPLC) ^{8, 9} or in-line thermal
12 desorption gas chromatography / mass spectrometry (GC-MS) ¹⁰.

13 Using low volume samples to analyse airborne PAH is vital for applications such as
14 personal exposure assessment, where low sampling flowrates (e.g. 3 L min⁻¹) are maintained
15 for e.g. 24 hours ¹¹; for the study of diurnal variations, where snapshots of 1-2 hours are
16 required; or even for microenvironment characterization, where the lack of power supply
17 requires the use of battery-operated equipment which can only maintain certain flowrates for
18 short periods of time (e.g. 12 L min⁻¹ for 2 hours) ¹².

19 Sensitive, rapid and accurate methods have been developed to determine PAHs in
20 atmospheric particles. As highly efficient separation tools, GC and HPLC have been used for
21 analysing all kinds of samples containing complex components ¹³. While sensitive HPLC
22 methods have been published for the determination of PAHs ^{14, 15}, GC-MS is more commonly
23 used due to greater separation efficiency of complex non-polar analytes ¹⁶. There are
24 numerous standard procedures to determinate PAHs in ambient air using GC-MS, such as the
25 EPA compendium method TO-13A ¹⁷, the Integrated Atmospheric Deposition Network to
26 analyze PCBs, pesticides and PAHs in air and precipitation samples ¹⁸ or the California

1 Environmental Protection Agency method to determine PAHs in ambient air¹⁹ among others.
2 However, all these methodologies collect PAHs in high volume samples and are not directly
3 applicable to airborne particulate samples collected at low volume conditions. Low volume
4 samples pose a challenge to analytical sensitivity. All atmospheric samples, i.e. high and low
5 volume samples, are complex mixtures that contain a diverse range of substances. Hence,
6 prior to analysis in a GC-MS, sample pretreatment is necessary to simplify the interpretation
7 of chromatograms and mass spectra by preventing interfering compounds in the
8 chromatograms. Typically, sample pretreatment for GC-MS involves three steps: extraction
9 of the analytes, fractionation of the extracts by solid-liquid or liquid-liquid extraction, and
10 since injection volumes of conventional GC-MS are small, evaporation of excess solvent to
11 concentrate the analytes²⁰ Extraction methods for PAHs from atmospheric samples include
12 traditional Soxhlet^{4, 21}, ultrasonic²², microwave assisted²³, accelerated solvent²⁴,
13 supercritical fluid²⁵ and solid-phase microextraction²⁶. Whilst super fluid extraction and
14 accelerated solvent extraction have high extraction efficiency, good selectivity and require
15 low time for extraction, they require dedicated and more expensive equipment, which may
16 sometimes preclude their application. On the other hand, traditional Soxhlet extraction is
17 cheaper, but generates large amounts of solvents¹³.

18 Since low volume samples generally will contain small amounts of analyte, it is essential
19 not only to reduce as much as possible the number of pre-treatment steps to reduce the level
20 of blank contamination, but also to avoid the use of large solvent volumes which require
21 subsequent concentration, hence increasing the risk of losing analytes by evaporation in the
22 concentration steps.

23 This study has tested and optimized different GC-MS operational conditions, extraction
24 procedures, cleaning techniques and solvents, different concentration methodologies, filter
25 media and pre-conditioning methods in order to develop the best method able to sample and
26 analyze particle-bound PAH collected in low volume air samples (1.4 m³) using low-cost

1 extraction equipment and reducing as much as possible solvent use and sample handling. The
2 optimized methodology for extraction and analysis was later validated with the Standard
3 Reference Material 1649a. This method was used to measure snapshots of 2-h atmospheric
4 samples in streets and other outdoor environments (i.e. parks).

5

6 **2. Experimental**

7 **2.1. Atmospheric Sampling**

8 The particle-phase PAH measured and analysed were acenaphthylene (Ac), acenaphthene
9 (Ace), fluorene (Fl), phenanthrene (Ph), anthracene (An), fluoranthene (Fluo), pyrene (Pyr),
10 benz[*a*]anthracene (B[*a*]A), benzo[*b*]fluoranthene (B[*b*]F), benzo[*k*]fluoranthene (B[*k*]F),
11 benzo[*a*]pyrene (B[*a*]P), indeno[*1,2,3-cd*]pyrene (I[*1,2,3-cd*]P), benzo[*ghi*]perylene
12 (B[*ghi*]P), dibenz[*a,h*]anthracene (D[*a,h*]A) and coronene (Cor).

13 Particle phase PAH were collected onto Membrane AQFA reinforced quartz fiber 47 mm
14 filters (Millipore, Watford, UK), held in a polycarbonate filter holder, drawing air with a
15 pump at a flow rate of 12 L min⁻¹ for 2 hours, collecting a final volume of 1.44 m³. Quartz
16 fiber filters were pre-baked for 48 hours at 400°C. Samples were collected in different street
17 microenvironments referred as trafficked roadsides, background streets, pedestrian streets
18 and parks.

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21 **2.2. Reagents and Standards**

22 Dichloromethane (HPLC grade) was purchased from Fischer Scientific (Loughborough,
23 UK) and nonane purum 99% was supplied by Sigma-Aldrich (Dorset, UK). Certified
24 standard 16 EPA Priority PAH pollutant mixture CERTAN 100 µg/mL of each analyte in
25 toluene was purchased from LGC Promochem (Teddington, UK). Coronene standard solution
26 100 µg mL⁻¹ in toluene, acenaphthylene-*d*₈ 200 µg mL⁻¹ in isooctane, pyrene-*d*₁₀ 500 µg mL⁻¹
27 in acetone, chrysene-*d*₁₂ 2000 µg mL⁻¹ in dichloromethane, benzo[*a*]pyrene-*d*₁₂ 200 µg mL⁻¹

1 in isooctane, indeno[1,2,3-*cd*]pyrene-*d*₁₂ 200 µg mL⁻¹ in isooctane, benzo[*ghi*]perylene-*d*₁₂
2 200 µg mL⁻¹ in toluene were supplied by Greyhound ChemService (Birkenhead, UK),
3 benz[*a*]anthracene-*d*₁₂ and phenanthrene-*d*₁₀ 1000 µg mL⁻¹ in dichloromethane were
4 purchased from UltraScientific (North Kingstown, RI, USA) whilst anthracene-*d*₁₀ and p-
5 terphenyl-*d*₁₄ 2000 µg mL⁻¹ in dichloromethane were purchased from Greyhound
6 ChemService and UltraScientific. Standard Reference Material SRM 1649a was supplied by
7 Greyhound ChemService.

8 The GC-MS system was calibrated with an eight calibration point curve. The
9 concentrations level of the standards, which span the monitoring range of interest, were 0, 20,
10 50, 200, 500, 1000, 5000 and 10000 pg µL⁻¹. All the standards contained the internal
11 standards at a concentration of 1000 pg µL⁻¹. The recovery standard p-terphenyl-*d*₁₄ was
12 prepared at a concentration of 2000 pg µL⁻¹.

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2.3. Extraction, cleaning and concentration

16 PAH filters were spiked with a mixture of deuterated internal standards with concentration
17 1000 pg µL⁻¹ dissolved in dichloromethane (DCM). Filters were placed in conical flasks
18 with 15 mL of dichloromethane (HPLC grade) and shaken for 15 minutes at 1400 rpm using
19 a reciprocating shaker. The extract was pre-concentrated to around 0.5 mL by blowing down
20 with nitrogen and subsequently dried and cleaned by removing the remaining filter fibers
21 with a chromatography column filled with 0.5 g of anhydrous sodium sulphate. The cleaned
22 extract was then further concentrated by blowing down with nitrogen to 25 µL. The solvent
23 was exchanged from DCM to nonane purum 99% with a final volume of 25 µL. Extracted
24 samples were stored in GC vials in a freezer at -20°C.

25 Prior to analysis, every sample was spiked with 25 µL of the recovery determination
26 standard (RDS), p-terphenyl-*d*₁₄ to give a final extract volume of 50 µL. Samples were stirred
27 to allow homogeneous mixing of the recovery standard with the sample using a vortexer.

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2.4. Analysis of PAH samples

An Agilent Technologies 6890 Gas Chromatograph (GC) equipped with an Agilent HP-5MS, non-polar capillary column (30 m, 0.25 mm ID, 0.25 μm film thickness - 5% phenylpolysiloxane), in tandem with a 5973N Mass Spectrometer (MS) was used for the PAH analysis.

1 μL of sample was injected using an Agilent 7683 auto- liquid sampler, in a split-less and non-pulsed injection mode at 300 $^{\circ}\text{C}$. The initial temperature was held at 120 $^{\circ}\text{C}$ for 2 minute and then ramped at 4 $^{\circ}\text{C min}^{-1}$ to a final temperature of 300 $^{\circ}\text{C}$ held for 10 minutes. The carrier gas was helium with a constant flowrate of 1mL min^{-1} . Solvent delay was set to 3.8 minutes.

The detector was set to quantify the analytes in single ion monitoring (SIM) mode covering specific masses ranging from 122 to 300 atomic mass units with a dwell time of 50 to 100 milliseconds per ion (Table 1). The selection of one target and one qualifier ion per compound proved enough to its identification, maximizing the time that the detector scanned each ion and hence improving the sensitivity of the SIM method. The mass spectrometer quad and source temperatures were 150 $^{\circ}\text{C}$ and 230 $^{\circ}\text{C}$ respectively. The analysis time per sample was 57 minutes.

Each chromatogram was checked using MSDS Chemstation software. The samples were analyzed and quantified using a six-point calibration graph of the concentration ratio of analyte to internal standard against the corresponding peak area ratios using linear regression.

3. Results and Discussion

3.1. Optimization of GC-MS conditions

Several GC columns, ramp rates, injection and initial temperatures as described in detail in Table 2 have been tested in order to establish the best conditions for which the internal and natural standards peaks were separated and identified.

1 The starting conditions (Program 1) were those described by Lim et al (1999). In brief, the
2 program consists of an initial temperature of 40°C, a ramping rate of 8°C min⁻¹ up to 300°C
3 using a 60 m Varian CP7950 DB5 (60 m, 0.2 mm id, 0.2 µm df) column. The injector mode
4 was splitless non-pulsed, the injection and detector temperatures were both 300°C, the carrier
5 gas was helium at 1 mL/min and the GC-MS was set up in splitless mode.

6 The separation and resolution between peaks for some of the standards was poor (e.g.
7 pyrene-*d*₁₀ and pyrene, Figure 1a), the peaks had low response and some of the peaks
8 appeared with a shoulder (e.g. fluoranthene, Figure 2a) and in some cases there was
9 overlapping between consecutive peaks (e.g. indeno(1,2,3-cd)pyrene and
10 dibenz[*a,h*]anthracene, Figure 3a). A second program using the same column was tested
11 which included raising the initial temperature from 40°C to 120°C. This second program had
12 a run time shorter than the first, but the problem with close peaks, overlapping and
13 shouldering of some peaks still persisted. The existence of two peaks instead of a shoulder of
14 the same peak was rejected as all the standard solutions were prepared with certified
15 standards and therefore the compounds present in the mixture and the approximate retention
16 times were known.

17 A new set of GC-MS programs were then tested after changing the GC column to DP-
18 5MS (30 m, 0.25 mm id, 0.25 µm df) and lowering the ramping rate to 5°C min⁻¹ (Program 3)
19 and 4°C min⁻¹ (Program 4). The rest of the program parameters were maintained (i.e. injector
20 mode, injector temperature, carrier flow rate and MS mode) In the new GC-MS program a
21 considerable improvement was observed in peak separation with better resolution between
22 peaks increasing the difference in the retention times of standard peaks by up to a factor of
23 two (Figure 1b), the resolution factor improved (Table 1), the peaks appeared well defined,
24 the peak intensity was around ten-fold higher (Figure 2b) and the problem of overlapping of
25 peaks was solved (Figure 3b).

1 Further optimization of the GC-MS program was performed checking the injection
2 conditions by comparing the results of the splitless non-pulsed mode (Figure 4a) with the
3 splitless pulsed mode (Figure 4b). Better chromatography results were obtained in the
4 splitless non-pulsed mode program, with higher intensity of peaks and a better separation
5 compared with the splitless pulsed mode program.

6 The conditions set in Program 4 with splitless non-pulsed injection were selected as the
7 most appropriate considering the better separation and resolution between peaks with respect
8 to Program 3 (See Table 1).

9 The selected GC-MS program was used to develop and validate the method of extraction
10 as well as to perform a blank contamination study in different filter media to see the best
11 condition to sample and extract PAH from ambient air.

12

13 **3.2. Optimization of extraction method**

14 To test the recovery of the extraction method, blank filters were spiked with 50 μL of
15 internal and natural standards at a concentration $1000 \text{ pg } \mu\text{L}^{-1}$ and were subsequently
16 extracted using different extraction methods. Extracting filters spiked with standards was
17 preferred over extracting certified materials for two reasons. The first was to homogenize the
18 matrix as samples are collected onto filters and certified materials are normally powder.
19 Secondly, the certified material 1649a was more expensive than the PAH standards solution.
20 Therefore, the employment of the standards for method development and the use of the
21 certified materials for method validation as shown in Section 3.5 was preferred, considering
22 the large number of tests performed to optimize the extraction method.

23 Originally, samples were extracted with Accelerated Solvent Extraction (Dionex ASE-
24 200), pre-concentrated with the TurboVap (Zymark) ^{27, 28}, cleaned with 10 mL of DCM
25 through 0.5 g of Florisil inactivated, and were further concentrated to 25 μL blowing a gentle
26 stream of N_2 , to be finally solvent exchanged to nonane, following established procedures

1 within our analytical group ²⁹. However, the recovery efficiency of this methodology was
2 around 70%. Therefore, different combinations of purification solvents (hexane,
3 hexane/toluene (9.5/5.4 v/v), dichloromethane, hexane/DCM (6/4 v/v) at different volumes
4 (10 mL to 150 mL) were tested in order to increase the recovery factor, giving results ranging
5 from 25% to 76%. However, the more volatile standards (e.g. acenaphylene-*d*₈) had
6 recoveries ranging from 3 to 72% (Detailed information on extraction conditions tested and
7 recovery factors can be found in Supporting Information). Accelerated solvent extraction has
8 normally high efficiency recoveries ³⁰. Therefore the poor performance of this proposed
9 sequence of procedures to extract the PAHs (i.e. ASE followed by clean-up with Florisil)
10 might be due to the large quantities of solvent used in the combination of extraction and
11 clean-up steps that need to be evaporated, which implies a risk of losing analytes by
12 evaporation as otherwise suggested by the low recoveries of the more volatile PAHs (see
13 Supporting Information).

14 To improve the recovery, especially for the more volatile standards, a simpler extraction
15 method was tested. The proposed method consisted of the extraction of the PAH from the
16 filters by shaking them in conical flasks with DCM, concentration of the sample by blowing
17 N₂ gently, cleaning the extract of fibres with a column of sodium sulphate anhydrous and
18 further concentration of the extracts with an N₂ stream before exchanging the solvent to
19 nonane (See specific details in the Experimental section).

20 With this method, the recovery efficiency of both the internal and natural standards was
21 much improved, with average recovery values of $106 \pm 4\%$. This method was adopted as the
22 extraction procedure not only because it was the one which had the highest recovery factors
23 but also because this method involved less sample handling, less solvent use and therefore
24 shorter extraction times, less risk of losing analytes by evaporation and less risk of high blank
25 levels due to simplicity of the pre-treatment steps.

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3.3. Optimization of filter media

As reported by many authors, glass fibre filters and quartz fibre filters have been used commonly to collect particle-bound PAHs¹³. Considering that the methodology developed is aimed at analysing low volume samples with reduced amounts of analyte, reducing the blank introduced by the filter media is paramount. Some researchers have solvent-extracted^{31, 32} or baked the³³⁻³⁵ filter media as a measure to lower the filter blank contamination. In this study different filter media (i.e. glass and quartz fibre filters) and different pre-conditioning methods have been tested in order to assess the best combination to reduce blank levels in the filter media.

Glass (GFF) and Quartz (QFF) fibre filter media were tested as received (RAW-treatment), after baking for 48 hours in a Carbolite oven at 400°C (48H-treatment) and for a set of glass fibre filters, thermal conditioning followed by extraction with DCM by Accelerated Solvent Extraction (Dionex ASE-200) (48H-ASE-treatment). Results of each pre-conditioning treatment performed on 5 replicate filters spiked with 50 µL of internal standard 1000 pg µL⁻¹ solution and subsequently extracted as described in the Experimental Section are presented in Table 3.

Glass fibre filters showed higher blank levels for the more volatile PAH compounds (i.e. acenaphthylene to phenanthrene) compared with the quartz fibre filters (t-test for comparison of means, p<0.05), although for the rest of the compounds (i.e. high molecular weight PAH), the levels were comparable. In addition, those results from the thermal followed by the extraction treatment (48H-ASE-treatment) showed the highest blank levels throughout all the PAH compounds (p<0.05). Hence, quartz fibre filters were preferred as a filter medium. As regards the comparison between different pre-conditioning techniques for quartz fibre filters, baking the filters at 400°C for 48 hours lowered the blank levels for the more volatile PAHs (p<0.05), whilst the levels for the remaining PAH compounds were very similar between the

1 RAW- and the 48H-treatments. In view of the data, quartz fibre filters thermally pre-
2 conditioned at 400°C for 48 hours were selected as the appropriate filter media to sample
3 particle-bound PAH in low volume samples.

4

5 **3.4. Recovery levels, limits of detection and precision of the method proposed**

6 **3.4.1. Recovery levels**

7 To further assess the recovery efficiency of the selected extraction method, 5 replicate
8 filters were spiked with 50µL of standard solution with concentrations ranging 20 to 1000 pg
9 µL⁻¹ and were subsequently extracted as described in the Experimental Section.

10 The average recovery of the spiked standards across the whole range of tested
11 concentrations (Table 4) was 89±8% for the internal standards and up to 104±15% for the
12 natural standards. Looking into the different standards, the lowest recoveries were recorded
13 for the more volatile compounds i.e. acenaphthylene-*d*₈, phenanthrene-*d*₁₀, anthracene-*d*₁₀ and
14 acenaphthylene with recovery percentages ranging 70-80%. Despite this, the efficiency of the
15 proposed method is considered suitable and is in the same range as those reported elsewhere
16 ^{2, 35-37} for GC-MS analysis of airborne PAH collected in high- and medium-volume samples.

17

18 **3.4.2. Limits of detection**

19 To characterize the limits of detection of the proposed method for extraction of PAH
20 from thermally preconditioned quartz fiber filters and its subsequent analysis in the GC-MS,
21 the instrument, sample and method detection limits were calculated.

22 The instrument detection limit (IDL), defined as the amount of pollutant that gives a signal
23 to noise ratio of 3:1, was determined by calculating the signal to noise ratio for the pollutant
24 in the lowest calibration standard (in our case 20pg µL⁻¹). The sample detection limit (SDL)
25 was calculated considering the final extract volume (50µL), the sample size (1.44 m³) and the
26 percentage recovery of internal standard (Table 4) used to quantify the target pollutant in a

1 particular sample ³⁸. The method detection limit (MDL) was calculated as three times the
2 standard deviation of the blank determination (i.e. quartz fiber filter pre-baked at 400°C for
3 48h).

4 Table 5 shows the instrument, sample and method detection limits obtained with the
5 proposed methodology. The instrument detection limits are better than those reported by
6 some other workers ^{16, 39} and similar to those reported by other ^{2, 40}. As regards the sample
7 and method detection limits, these are considerably lower than the respective limits of
8 detection reported previously for PAHs in ambient air ^{37, 41} which may be attributed to the
9 combination of better instrument sensitivity, lower filter blank levels due to the
10 preconditioning of the filter and lower contamination levels throughout the extraction,
11 cleaning and concentration of the sample prior to GC-MS analysis.

12 The limits of detection of the proposed method were also compared with those reported by
13 Gil-Molto et al (2009) ¹⁰, who collected low-volume samples but analyzed them with in-port
14 thermal desorption instead. The instrument limits of detection for the particle-bound PAHs
15 (i.e. B[a]A to Ind) obtained with the present procedure were two-fold lower than the
16 methodology developed by Gil-Molto et al (2009). As regards the method and sample
17 detection limits, these were 2 to 3-fold lower in the proposed methodology compared with
18 the quantification detection limits of these authors (Gil-Molto et al 2009). Other authors that
19 have used in-port thermal desorption with high-volume samples reported considerably higher
20 limits of detection than those obtained with the proposed methodology ^{42, 43}.

21

22 **3.4.3. Precision and accuracy**

23 To assess the accuracy and precision of the method, 5 replicate filters were spiked
24 with 50µL of standard solution with concentrations ranging 20 to 1000 pg µL⁻¹ and were
25 subsequently extracted as described in the Experimental Section.

1 Precision was calculated as the relative standard deviation (*i.e.* $100 \times \sigma_{n-1}/\text{average}$) of
2 concentrations obtained from the 5 replicate analyses of the same sample at each
3 concentration ranges (*i.e.* $20 \text{ pg } \mu\text{L}^{-1}$ to $1000 \text{ pg } \mu\text{L}^{-1}$) and the overall average values are
4 presented in Table 5. The average precision of the method is $3.2 \pm 1.9\%$ (arithmetic mean
5 (AM) \pm standard deviation (STD)) which is comparable with values reported in the literature
6 ¹⁶.

7 The accuracy of the method was calculated as the difference between the true value of the
8 quantity being measured (concentration spiked) and the result of the measurement
9 (concentration analysed), normalized by the true value times 100. The present method has an
10 average accuracy of $13.4 \pm 17.3\%$ (AM \pm STD), ranging between -6% and 25%. The highest
11 values (*i.e.* poorer accuracy) corresponded with compounds that did not have their own
12 internal standard, as in the cases of Ace, Fl and B[k]F with average accuracy values ranging
13 14-25%. Phenanthrene had also high values of accuracy ($16.1 \pm 17.5\%$), which could be a
14 consequence of the proximity of the peak of anthracene, which makes correct separation of
15 both peaks difficult on some occasions and hence increases the accuracy value. However,
16 experimental concentration means of the spiked filters extracted were compared with the
17 nominal standard concentration values using the ANOVA test (SPSS 15.0). None of the
18 compounds had statistically significant differences between the nominal and analyzed values
19 ($p > 0.1$). Similarly, the precision of extracted spiked filters was compared with the precision
20 of the analysis of the standard solutions and no statistically significant differences were found
21 ($p > 0.10$).

22 The values of accuracy and precision of this method accomplish the quality objectives for
23 air toxics stated by the EPA in the “Quality Assurance Handbook for Air Pollution Systems”
24 which should be a precision of $\pm 25\%$ and an accuracy of $\pm 20\%$ ⁴⁴. Only
25 benzo[k]fluoranthene shows values of accuracy above the limit of the requirement.
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3.5. Standard reference material analysis

Five samples (1 mg) of the Standard Reference Material NIST SRM 1649a – (Urban Dust) were analyzed in order to validate the accuracy and the precision of the method. Experimental concentrations were compared with the certified concentration using a one-sample t-test (SPSS 15.0). Most of the compounds did not present statistically significant differences between the certified and analyzed values ($p>0.10$), with the exception of An, B[k] and D[ah]A ($p<0.05$) and Chry ($p<0.01$), which had higher concentrations in the experimental dataset. Those compounds were the ones showing higher values of accuracy and precision, ranging from 32-50% and 22-38% respectively, in contrast with the low accuracy and precision values of the majority of the compounds (i.e. 0.2-8.7% and 4-18% respectively). In summary, the mean experimental concentrations obtained in this study when the SRM was treated, extracted and analyzed in the same way as the proposed extraction method were generally consistent with the certified values of concentrations (Table 6). Similar results were reported by Crimmins and Baker¹⁶ for the high molecular weight PAH, whilst better reproducibility and accuracy are reported in this study for the low molecular weight compounds (i.e. phenanthrene to fluoranthene).

3.6. Concentrations of particulate-phase PAH in ambient air

After validating the methodology with the NIST SRM 1649a standard, low volume samples collected in outdoor air in different street microenvironments were extracted and analyzed for particulate-bound PAH using the method described in this study.

The average concentration of benzo[a]pyrene measured as a marker of the carcinogenic activity of the PAH mixture, were 0.09 ng m^{-3} in parks, 0.18 ng m^{-3} in pedestrian streets, 0.16 ng m^{-3} in background streets and 0.26 ng m^{-3} on trafficked roadsides. The minimum benzo[a]pyrene value reported in outdoor air was 0.05 ng m^{-3} which is 7.5 times the Method

1 Detection Limit, showing the suitability of the proposed method to sample and analyze
2 particle-bound PAHs in low volume and low concentration samples.

3 The air quality in Birmingham seems to have improved as evidenced by the concentrations
4 of particulate-phase B(a)P, 0.48 ng/m³ measured in Birmingham urban air (1996)⁴⁵ and 0.26
5 ng/m³ in Birmingham trafficked roadside (2008). This trend is consistent with previously
6 reported studies which indicated a decrease of PAH levels in ambient air in Germany⁴⁶ and
7 USA⁴⁷. The B(a)P values in this study are comparable though generally lower than typical
8 values obtained elsewhere in Europe in the last decade, which range from 0.7-2.97 ng/m³⁴⁸⁻
9 ⁵⁰.

10 In street microenvironments, traffic is a major source of PAH, and therefore, it would be
11 expected that the magnitude of PAH concentrations would correlate with traffic volumes. A
12 t-test was performed comparing the values measured at trafficked roadside locations with
13 PAH concentrations measured away from traffic. The results of PAH concentrations for
14 compounds An-Chry, B[k]F, B[a]P and B[ghi]P (Figure 5) show that PAH concentrations
15 measured in trafficked streets were generally higher (p<0.005) compared with other street
16 types, with parks being the outdoor environment where the lowest PAH concentrations were
17 generally recorded. This is consistent with traffic loads as reported by previous studies^{51, 52}.

18

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20 **4. Conclusion**

21 This study has tested different filter media and pre-conditioning methods, extraction
22 methodologies, cleaning techniques and cleaning solvents, concentration procedures and GC-
23 MS conditions in order to establish the best methodology to sample and analyze particle
24 phase PAH collected in low volume samples.

25 The methodology developed, which combines optimized GC-MS parameters, a simple
26 extraction procedure with the use of quartz fiber filters pre-conditioned at 400°C for 48 hours

1 has not only been successfully characterized (i.e. detection limits, precision and accuracy) but
2 also has been validated with the analysis of a Standard Reference Material.

3 Moreover, the analysis of specially collected atmospheric samples has shown the
4 suitability of the proposed method to determine PAH concentrations without interference in
5 real samples. The proposed methodology has therefore been demonstrated to be suitable to
6 sample and analyze particle-bound PAHs collected in low volume samples (1.44 m³).

7

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2**Table 1. Target ions, qualifier ions, dwelling time and evolution of retention time and resolution factors with different GC-MS programs (min)**

Compound	Target Ion (M) ⁺	Qualifier Ion (M) ⁺	Dwell Time (ms)	Retention Time (min)				Resolution Factor ²			
				Prog 1	Prog 2	Prog 3	Prog 4	Prog 1	Prog 2	Prog 3	Prog 4
Acenaphthylene- <i>d</i> ₈	160.11	158.10	75	21.05	12.23	8.11	8.56	0.7	0.4	0.5	0.5
Acenaphthylene	152.06	151.06	75	21.09	12.27	8.15	8.61	7.9	7.4	8.0	8.8
Acenaphthene	153.07	154.08	100	21.64	12.79	8.84	9.40	14.6	20.8	21.4	21.9
Fluorene	166.08	165.07	100	23.17	14.24	10.80	11.70	22.7	32.7	33.2	33.5
Phenanthrene- <i>d</i> ₁₀	188.14	184.11	75	26.01	17.02	14.72	16.39	0.6	0.7	0.8	0.8
Phenanthrene	178.08	176.06	75	26.08	17.09	14.81	16.50	0.7	0.8	1.0	1.2
Anthracene- <i>d</i> ₁₀	188.14	184.11	75	26.16	17.17	14.93	16.65	0.4	0.6	0.6	0.7
Anthracene	178.08	176.06	75	26.21	17.23	15.00	16.74	22.8	40.9	43.2	47.1
Fluoranthene	202.08	200.06	75	29.74	20.70	20.19	23.10	2.9	8.3	7.3	6.9
Pyrene- <i>d</i> ₁₀	212.14	208.11	75	30.32	21.32	21.06	24.16	0.4	0.7	0.6	0.6
Pyrene	202.08	200.06	75	30.40	21.38	21.14	24.25	18.1	39.7	10.8	11.0
p-terphenyl- <i>d</i> ₁₄	244.39	122.20	100	n.m. ¹	n.m.	22.41	25.9	n.m.	n.m.	33.8	35.1
Benzo(a)anthracene- <i>d</i> ₁₂	240.17	236.14	75	34.02	24.95	26.71	31.17	0.5	0.7	0.7	0.8
Benzo(a)anthracene	228.09	226.08	75	34.09	25.02	26.81	31.29	0.4	0.5	0.9	1.5
Chrysene- <i>d</i> ₁₂	240.17	236.14	75	34.14	25.07	26.87	31.49	0.6	0.8	2.5	3.8
Chrysene	228.09	226.08	75	34.22	25.15	26.98	31.99	32.8	32.6	35.8	39.5
Benzo(b)fluoranthene	252.09	250.08	75	37.99	28.90	31.52	37.12	0.7	0.9	0.9	1.0
Benzo(k)fluoranthene	252.09	250.08	75	38.09	28.99	31.62	37.25	4.9	6.8	8.4	10.2
Benzo(a)pyrene- <i>d</i> ₁₂	264.17	260.14	75	39.30	30.19	32.66	38.52	0.3	0.4	0.6	1.0
Benzo(a)pyrene	252.09	250.08	75	39.40	30.30	32.74	38.63	12.3	25.9	33.2	40.1
Indeno(1,2,3- <i>cd</i>)pyrene- <i>d</i> ₁₂	288.17	284.14	50	45.53	36.38	36.79	43.65	0.3	0.8	0.7	0.7
Indeno(1,2,3- <i>cd</i>)pyrene	276.09	274.08	50	45.70	36.54	36.86	43.74	0.2	0.7	1.3	1.8
Dibenz(a,h)anthracene	278.11	276.09	50	45.86	36.72	37.03	43.97	1.9	5.3	5.2	5.2
Benzo(ghi)perylene- <i>d</i> ₁₂	288.17	284.14	50	47.29	38.10	37.58	44.62	0.3	0.7	0.7	0.7
Benzo(ghi)perylene	276.09	274.08	50	47.47	38.28	37.66	44.72	14.1	28.0	31.9	36.1
Coronene	300.09	298.08	100	62.29	53.00	43.58	51.04	N/A ³	N/A	N/A	N/A

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(1) n.m., not measured

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(2) Resolution factors were calculated following the tangent method adopted by the United States

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Pharmacopeia (USP)[32]

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(3) N/A, not applicable

Table 2. Optimization of GCMS program parameters

Compound	Program 1	Program 2	Program 3	Program 4
Injection Temperature (°C)	250	250	300	300
Injection Mode	Splitless	Splitless	Splitless	Splitless
Initial GC Temperature (°C)	40	120	120	120
Initial GC Time (min)	1	2	2	2
Rate (°C min ⁻¹)	8	8	5	4
Final GC Temperature (°C)	300	300	300	300
Final GC Time (min)	35	32	10	10
Run Time (min)	69	57	48	57
GC Column	Varian CP-7950	Varian CP-7950	HP-5MS	HP-5MS
GC Column Dimensions	60 m x 0.2 mm x 0.2 µm	60 m x 0.2 mm x 0.2 µm	30 m x 0.25 mm x 0.25 µm	30 m x 0.25 mm x 0.25 µm
Flow (mL min ⁻¹)	1	1	1	1
Detector Temperature (°C)	280	280	280	280

Table 3. Optimization of filter media – Blank contamination study (pg μL^{-1})

Compound	GFF-RAW		GFF- 48H		GFF- 48H-ASE		QFF-RAW		QFF-48H	
	Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD
Acenaphthylene	93.3	57.7	32.0	27.6	74.1	74.7	2.4	0.8	1.7	0.1
Acenaphthene	523.3	207.7	455.2	522.3	396.0	283.9	7.0	1.9	9.1	0.9
Fluorene	598.5	221.1	600.4	564.1	1154.1	1231.7	11.0	5.3	9.7	1.7
Phenanthrene	19.3	2.8	20.2	7.6	22.8	5.5	10.0	2.1	11.8	1.4
Anthracene	0.3	0.1	0.5	0.1	0.8	0.6	0.9	0.3	2.8	5.3
Fluoranthene	84.1	28.8	1.1	0.2	1.4	0.6	1.5	0.7	1.1	0.3
Pyrene	15.8	32.3	0.9	0.1	1.3	0.7	1.5	0.4	0.9	0.1
Benzo(a)anthracene	0.3	0.1	0.3	0.1	0.7	0.6	0.3	0.2	0.3	0.1
Chrysene	0.8	0.1	0.7	0.1	1.0	0.7	0.4	0.2	0.6	0.2
Benzo(b)fluoranthene	0.5	0.0	0.4	0.1	0.8	0.7	0.3	0.2	0.5	0.1
Benzo(k)fluoranthene	0.6	0.1	0.5	0.0	1.0	1.1	0.4	0.2	0.5	0.1
Benzo(a)pyrene	0.6	0.1	0.7	0.1	1.4	1.2	0.8	0.2	0.6	0.1
Indeno(1,2,3-cd)pyrene	1.0	0.1	1.4	0.3	1.9	1.6	1.3	0.3	1.1	0.2
Dibenz(ah)anthracene	0.5	0.2	0.6	0.1	1.2	1.3	0.4	0.1	0.5	0.1
Benzo(ghi)perylene	1.0	0.1	1.0	0.1	2.2	2.2	1.1	0.1	1.0	0.1
Coronene	0.2	0.1	0.4	0.4	0.5	0.2	0.1	0.1	0.2	0.1

GFF = Glass Fibre Filter

QFF = Quartz Fibre Filter

RAW = No pre-treatment

48H = Baked 48 h at 400°C

ASE = Cleaned with DCM in the ASE

STD= Standard deviation

Table 4. Recovery levels (%)

Internal Standard Recoveries	STD A 20 pg μL^{-1}		STD B 50 pg μL^{-1}		STD C 200 pg μL^{-1}		STD D 500 pg μL^{-1}		STD E 1000 pg μL^{-1}		AVERAGE	
	Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD
Acenaphthylene- <i>d</i> ₈	70	6	72	6	72	12	77	5	79	4	74	7
Phenanthrene- <i>d</i> ₁₀	77	4	80	4	79	11	85	5	85	4	81	6
Anthracene- <i>d</i> ₁₀	78	6	81	4	81	11	86	5	86	4	82	7
Pyrene- <i>d</i> ₁₀	86	5	88	4	87	11	93	4	92	4	89	7
Benzo(a)anthracene- <i>d</i> ₁₂	91	9	93	5	91	12	100	5	98	4	95	8
Chrysene- <i>d</i> ₁₂	92	7	88	4	91	13	100	11	100	11	94	10
Benzo(a)pyrene- <i>d</i> ₁₂	91	12	95	5	94	13	102	4	100	3	96	9
Indeno(1,2,3- <i>cd</i>)pyrene- <i>d</i> ₁₂	88	15	93	5	93	14	104	5	102	2	96	11
Benzo(ghi)perylene- <i>d</i> ₁₂	87	13	93	4	93	13	103	4	100	2	95	10
Natural Standard Recoveries												
Acenaphthylene	78	17	85	6	79	12	82	5	83	4	81	10
Acenaphthene	106	12	93	9	86	13	87	5	89	4	88	21
Fluorene	110	7	102	4	91	14	92	6	94	4	94	22
Phenanthrene	149	7	118	7	94	12	94	5	93	5	110	23
Anthracene	87	3	89	4	88	12	93	5	94	4	90	7
Fluoranthene	104	6	104	5	102	13	109	5	112	4	106	8
Pyrene	105	5	99	5	95	12	100	5	100	4	100	7
Benzo(a)anthracene	107	8	101	5	99	13	107	5	109	4	105	8
Chrysene	92	4	95	5	101	13	110	6	111	4	102	11
Benzo(b)fluoranthene	101	11	104	5	111	16	132	7	137	4	117	17
Benzo(k)fluoranthene	93	12	96	4	108	15	121	6	124	4	108	15
Benzo(a)pyrene	100	10	100	5	102	14	112	5	114	4	106	10
Indeno(1,2,3- <i>cd</i>)pyrene	108	9	106	5	103	15	116	5	119	2	110	10
Dibenz(ah)anthracene	100	13	99	7	112	18	138	7	149	2	116	33
Benzo(ghi)perylene	106	8	103	3	104	15	116	5	117	3	109	9
Coronene	108	14	109	6	120	19	152	8	163	2	126	36
Average Internal & Natural Standard Recoveries	97	9	95	5	95	13	104	6	106	4	99	13

Table 5. Limits of detection, accuracy and precision

Compound	Instrument Limit of Detection		Sample Detection Limit		Method Detection Limit		Accuracy (%) (a)		Precision (%) (a)	
	Average (pg μl^{-1})	STD (pg μl^{-1})	Average (pg m^{-3})	STD (pg m^{-3})	Average (pg m^{-3})	STD (pg m^{-3})	Average (%)	STD (%)	Average (%)	STD (%)
Acenaphthylene	1.0	1.0	28,1	29.0	90.2	347.6	5.4	5.5	0.7	0.4
Acenaphthene	5.0	5.9	152,8	176.3	488.4	1821.0	13.7	7.2	2.2	1.1
Fluorene	5.0	6.7	163,2	198.9	609.8	2082.0	21.8	11.7	3.9	2.7
Phenanthrene	6.7	7.2	255,9	131.5	79.0	65.1	16.1	17.5	2.6	3.3
Anthracene	1.4	2.0	43,8	38.2	281.3	379.2	2.5	1.5	0.8	0.5
Fluoranthene	0.6	0.7	22,1	11.3	15.1	16.8	3.6	1.5	0.7	0.8
Pyrene	0.5	0.5	17,4	7.5	9.9	1.6	2.5	2.0	1.2	0.7
Benzo(a)anthracene	0.2	0.2	7,3	2.1	6.8	7.1	2.7	1.2	0.4	0.1
Chrysene	0.3	0.4	10,6	5.4	13.2	11.9	7.4	2.8	7.4	1.1
Benzo(b)fluoranthene	1.0	0.8	40,6	12.1	5.7	5.2	9.4	11.2	7.3	1.2
Benzo(k)fluoranthene	0.3	0.4	11,3	5.0	3.9	3.2	25.1	8.4	9.7	2.5
Benzo(a)pyrene	0.3	0.4	11,0	5.7	8.0	4.9	-3.3	2.5	0.3	0.1
Indeno(1,2,3-cd)pyrene	0.6	0.8	22,9	10.7	13.9	11.2	-6.0	1.8	1.1	1.7
Dibenz(a,h)anthracene	0.3	0.4	12,1	4.9	4.1	0.4	4.5	13.5	1.4	0.7
Benzo(ghi)perylene	0.7	0.4	26,5	2.5	8.0	3.7	0.2	1.8	0.7	0.8
Coronene	0.1	0.2	4,4	1.7	4.4	1.4	4.7	14.3	2.1	0.7

(a) Accuracy and precision calculated from filters spiked with standard solution. See Table 6 for values of accuracy and precision calculated from the extraction of SRM 1649a.

Table 6. Certified and experimental concentrations, precision and accuracy of SRM 1649a

Compound	Certified Concentration (mg kg ⁻¹)	Certified Variability (mg kg ⁻¹)	Mean Experimental Concentration (mg kg ⁻¹)	Standard Deviation (mg kg ⁻¹)	Precision (%) (RSD)	Accuracy # (%)
Phenanthrene	4.140	0.370	4.50	0.73	16.2	8.7
Anthracene	0.432	0.082	0.58*	0.16	27.5	34.3
Fluoranthene	6.450	0.180	6.75	1.24	18.3	4.7
Pyrene	5.290	0.250	5.49	0.90	16.4	3.8
Benzo(a)anthracene	2.208	0.073	2.15	0.40	18.4	-2.6
Chrysene	3.049	0.060	4.03**	0.90	22.3	32.2
Benzo(b)fluoranthene	6.450	0.640	6.74	1.21	17.9	4.5
Benzo(k)fluoranthene	1.913	0.031	2.85*	1.08	38.0	49.0
Benzo(a)pyrene	2.509	0.087	2.47	0.10	3.9	-1.6
Indeno(1,2,3-cd)pyrene	3.180	0.720	3.17	0.28	8.9	-0.3
Dibenz(ah)anthracene	0.288	0.023	0.40*	0.14	35.3	38.9
Benzo(ghi)perylene	4.010	0.910	4.00	0.34	8.6	-0.2

Expressed as (mean measured concentrations minus certified value) / Certified Value x 100

* Certified and experimental concentration are significantly different at p<0.05 level

** Certified and experimental concentration are significantly different at p<0.01 level