Particle size distribution of polycyclic aromatic hydrocarbons in the urban air in Southern of Spain

A. Gutiérrez Dabán · A. J. Fernández Espinosa* · M. T. Rodríguez · F. Fernández Álvarez

Department of Analytical Chemistry "Profesor F. Pino Pérez", Faculty of Chemistry, University of Seville. C./ Profesor García González, s/n, E-41012, Seville, Spain.

*   A. J. Fernández-Espinosa

E-mail: anjose@us.es

Abstract Size distribution of PAHs was determined in airborne particles of a large city with high vehicular traffic. The analytical method has been optimised and validated using a NIST standard reference material (SRM 1649a Urban Dust). The 16 priority PAHs listed in the US-EPA were soxhlet extracted from filters of particulate matter and then fractionated using on-column chromatography. The aromatic fraction was quantified by gas chromatography-mass spectrometry (GC-MS). Real samples of particles collected in Seville (Spain) were analysed with the validated method. Values of total concentration of PAHs in the air, as well as concentrations of each PAH in six particle size ranges were provided. Values of PAHs in TSP, PM_{10} $PM_{2.5}$ and PM_1 were assessed.

Keywords Polycyclic aromatic hydrocarbons · benzo[a]pyrene · urban airborne particles · size distribution · SRM 1649a

Introduction

Polycyclic aromatic hydrocarbons (PAHs) have received considerable attention as an important class of environmental organic pollutants [1,2]. In fact, according to the classification of the International Agency for Research on Cancer (IARC) [3], some PAHs are major mutagenic and carcinogenic agents. As a result of the carcinogenic activity, sixteen of these PAHs have been listed as priority pollutants by the US-EPA [4].

Benzo[a]pyrene (BaP) concentration is a good marker or carcinogenic PAH levels in environmental samples [5]. Benzo[a]pyrene (BaP) is one of the most potent PAH embryotoxic and teratogenic in mice. Leukemia, gastric tumor and pulmonary adenoma or tumor developed in the strain of white Swiss mice that were fed BaP [6]. The exposure at BaP increase the incidence of papillomas, carcinoma of for estomach, esophagus and tongue.

PAHs are originated from products of incomplete combustion in industrial [7], domestic [8] activities and vehicular traffic [9]. Under oxygen-deficient conditions, highly condensed compounds are common products of combustion of carbon based materials, such as carbon, wood, coke, fuels or gasoline. Due to the location of these sources and the number of human exposure, especially in the urban environment, PAHs must be specially studied.

During combustion processes PAHs are initially emitted as gases. Heavier PAHs with 5 or 6 aromatic rings (vapor pressure $\approx 10^{-11}$ Torr) are rapidly associated with suspended particles, usually soot particles, by adsorption or condensation upon cooling of fuel gas. The most volatile PAHs (2 rings and vapor pressure $\approx 10^{-1}$ Torr) escapes from particulate incorporation and they exist in the gas phase [10]. Semivolatile PAHs with 3 or 4 rings can have significant fractions in both the gas and particulate phases, depending upon the particular compound.

The origin of PAHs in airborne particles is well known. The problem of atmospheric pollution by PAHs in Spain has been investigated in various cities [11,12,13]. However, any result exists in the southern of Spain. In consequence, this work constitutes a preliminary study of these atmospheric pollutants in Seville [14].

When PAHs are mostly sorbed on inhalable particles they have a high prevalence of airborne particles of sub-micron diameters [15]. Suspended atmospheric particles have long lifetimes depending on size and meteorological conditions. During the atmospheric lifetime the fine PAH-carrying particles may be transported over large distances. Size distribution depends on aerosol sources but it is also affected by prevailing meteorological conditions [16]. PAHs associated with fine particles can affect skin, lungs and urinary bladder. Consequently, the study of their size distributions is an important purpose to obtain a more productive information than with the determination of total concentrations in air [17].

Knowledge of size of particles is vital in understanding the effects on human health [18]. It has been observed that chemical compounds associated with natural sources, such as soil and ocean, are usually found in coarse particles, while those emitted from anthropogenic sources, such as traffic and industries, are associated with fine particles. Besides, the degree of penetration and retention in the respiratory way is a direct function of aerodynamic particle size and particle size distribution data is essential to assess the inhalation health hazard [19]. In general, particles with a diameter > 5 µm are filtered in the nose for the most part, while those < 1-2 µm in aerodynamic diameter (aed) predominantly gets deposited in alveolar regions of lung and can affect lung physiology, especially if particles contain biologically available toxic compounds. Determinations of size distributions are usually done by mechanical separation during the sampling. A type of separation system is the impactor. A cascade impactor coupled on a sampler permit to collect particles of different sizes [20].

Based on the bibliography [21-25] a modified methodology was developed to extract and quantify PAHs in urban airborne particles of different sizes. The analysis of different organic compounds at trace levels (PAHs, PCBs, alyphatic hydrocarbons, organic acids, etc.) in complex matrices usually involves several steps. Mainly, for each type of compound, an extraction step is followed by an extensive clean-up and by the fractionation of the extract. Such tedious and time-consuming procedures might be advantageously replaced by an appropriate clean-up of the same extract providing well-defined fractions containing different types of analytes.

PAHs studied were those listed as priority pollutants by the US-EPA. The aim of this study was also to present the procedure to optimise and validate this modified method which it has been applied then to some real samples of urban particles collected in the city of Seville.

Experimental

The analytical methodology to determine PAHs in airborne particles of different sizes was based in some determinant stages such as the sampling of particles, the extraction of organic compounds, the clean-up of the extract to select the PAHs and the instrumental method used. These methods are referenced in the EPA norms for organic extraction and sample preparation [23], analysis of semivolatile organic compounds by gas chromatography/mass spectrometry [24] and determination of PAHs in ambient air by gas chromatography/mass spectrometry [25]. Of these, several variables were optimised, such as the optimum time and volume of extraction of samples collected on glassfibre filters, the volume of different solvents used to clean-up extracts and chromatographic conditions. Then, the final method was validated using a certified reference material.

Chemicals and materials

Material for sampling

Glassfibre filters (GF/A) for particle sampling and were supplied by Whatman International Ltd. (Maidstone, England). For stages 1-5, five cut glassfibre filters were used (14.2 x 14.2 cm^2), and for the backup filter, a complete non-cut filter (20.3 x 25.4 cm^2) was used, i.e., a set of six filters for each sampling.

The use of filters as a collection media was an ineluctable inconvenience because of the impurities they contain, although the reference method for collection of particles recommends this type of sampling [26]. These impurities can cause errors in subsequent analysis [27]. Consequently, blank determinations are always necessary. Also, gravimetric determination of particles can be subject to error unless ambient conditions during weighing, mainly the temperature and humidity of the air, are carefully controlled.

Solvents

Residue analysis grade n-hexane and dichloromethane used in the extraction stage and acetone and methanol used in the clean-up stage were obtained from Merck (Darmstadt, Germany). Bank of heating mantle for soxhlet extraction was from J.P. Selecta (Barcelona, Spain). Rotavapor to evaporate extracts was from Büchi (Switzerland). Cellulose soxhlet extraction thimbles (Ad# 213379) for soxhlet extraction were supplied by Whatman International Ltd. (Maidstone, England).

Standards

To quantify each PAH a 16-PAHs standard was purchased from Agilent Technologies (Wilmington, DE) and an internal standard mix (mixture of acenafthene-d_{10}, phenanthrene-d_{10}, chrisene-d_{12}, perylene-d_{12}) and a standard of pyrene-d_{10} were purchased from Dr. Ehrenstorfer BmbH (Augsburg, Germany).

Adsorbents

Neutral silica gel (Kieselgel 40, 70-30 mesh) and alumina (aluminium oxide 90 active, 70-230 mesh) used in the fractionation stage were from Merck. Drying oven and high temperature oven for activation of stationary phases were from J.P. Selecta (Barcelona, Spain). Homogenisation of each product was carried out by shaker agitation with a vertical shaker (Vibromatic Model 384) from Selecta.

Reference material

The standard reference material SRM 1649a Urban Dust to validate the method was from the US National Institute of Standard and Technology (NIST) (Gaithersburg, MD, USA). Standard Reference Material (SRM) 1649a Urban Dust is constituted by 2.5 grams of a solid of an atmospheric particulate material collected in an urban area. It is used in evaluating analytical methods for the determination of selected polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCB) congeners, chlorinated pesticides, and total carbon in atmospheric particulate material and similar matrices [28].

Reference and information values are also provided for selected polychlorinated dibenzo-p-dioxin and dibenzofuran congeners, inorganic constituents, total extractable material, mutagenic activity, particle-size characteristics, and chemical and isotopic (^{14}C) carbon composition. The SRM 1649a Urban Dust airborne urban particles and it is certified for twenty-two PAHs, thirty-five PCBs congeners and eight chlorinated pesticides.

Sample collection

Airborne particulate matter (PM) was collected with a high-volume sampler (MCV, Model CAV-A/HF, Barcelona, Spain). For collecting different sizes of particles this Hi-Vol sampler was equipped with a five-stage standard cascade impactor plus a backup filter (MCV, Model IC/CAV, Barcelona, Spain). The cascade system allows collecting particulate matter distributed in six different ranges of size. Concentrations of PAHs can be determined in each size ranges to obtain different conclusions in relation with sources and grade of human health risk. Impactor system separates particles this way: suspended particulates enter the impactor at a fixed flow rate through the slots in the first impactor stage. Particles larger than the particle cut-off size of first stage impact on the slotted collection filter. The air stream then passes through the slots in the collection paper, accelerates through smaller slots in the second impactor stage, and the remaining particles greater than the particle cut-off size of second-stage impact on the second collection filter…and so on.

The different cut-off points of the impactor at 50% efficiency were the following equivalent aerodynamic diameters (Dp): stage 1, >10 µm; stage 2, 10–4.9 µm, stage 3, 4.9–2.7 µm, stage 4, 2.7–1.3 µm, stage 5, 1.3–0.6 µm, and stage 6, <0.6 backup (0.6–0.01) µm, at an aspiration flow of 68 m^3 h^{-1}. These granulometric fractions which were from manufacture specifications were in accordance with particle-size fraction definitions for health-related sampling [29]. The sampling periods were 24 hours. Total air volume sampled was about 1632 m^3. The aspired air passed through the impactor and the particles were trapped on filters by impact in stages 1–5 and by filtration in stage 6 (backup).

Five samples were collected in Seville. Sampling periods were from 0.00 a.m. to 23.59 p.m. Before sampling, filters used for dust collection were previously dried in a desiccator for 48 h in a dark room and weighed on an analytical balance according to the international recommendation [26]. Care was taken in handling micro-fibre filters to avoid contamination problems and all filter materials, samples, and reagents were handled within a vertical laminar airflow cabinet (Indelab with HEPA filter, Model IDL-48 V), for ensuring air cleanliness standards of class 100 according to Federal Standard 209E [30].

Sample extraction

The mixture of solvents used to extract all organic compounds by the soxhlet system was the acetone : dichloromethane 5:1 mixture [31]. Samples were spiked in the cellulose extraction thimble with 25 µl of the deuterated standard pyrene-d_{10} 10 mg l^{-1} in order to determine analytical efficiencies. With this volume a final concentration of 250 ng $µl^{-1}$ should obtain in the measurements. The same spiking was applied to the SRM 1649a to evaluate the goodness of the method. After the Soxhlet extraction the most volume –about 250 ml– of extracts was reduced by rotavaporization and the rest –about 5 ml– was concentrated until almost dryness with a stream of nitrogen. No lost of analytes during the evaporation were verified by analysing of the evaporating flask.

Clean-up

After volume reduction, extracts were fractionated and purified by on-column chromatography. Neutral silica gel and alumina were used as stationary phase. The treatment of both adsorbents consisted in heat in drying oven at 120ºC and in high temperature oven at 350ºC respectively overnight for activation. After cooling in a desiccator, they were deactivated by addition of water in a proportion (5%, w/w). Homogenisation of each product was carried out by shaker agitation for 2 hours and they were kept in closed containers in a desiccator before use.

A set of glass columns (20 cm length x 1 cm i.d.) filled with 1 g each of alumina (top) and silica gel (button) was used for the clean-up. The column was carefully handled to ensure an exact synchronisation between the volume eluted and its time consuming, that is the reproducibility. In order to avoid retention of air-bubbles, the adsorbent was suspended in n-hexane and introduced in

4

the glass column with gentle lateral tapping. Prior to use, the column was conditioned adding 25 ml of n-hexane.

Then it was performed the fractionation. The extract from the evaporation was transferred to the column and left to penetrate into adsorbents. Then, successive mixtures of solvents were added: the non-polar fraction which contains aliphatic hydrocarbons were eluted with n-hexane and then it was discarded for the present work; the aromatic hydrocarbons were then collected in the second fraction eluting with 20% DCM in n-hexane; the third fraction, 5% methanol in DCM, containing polar compounds was discarded for the present work.

Finally, the aromatic fraction was nitrogen concentrated to 1 ml in a volumetric flask adding here the deuterated standard mixture as internal standards and transferring the final content to a 2 ml chromatographic vial.

Quantification of PAHs

16-PAHs were determined by gas chromatography mass spectrometry (GC-MS) using a gas chromatograph Agilent Serie 6890A and a mass selective detector (MSD) Agilent Serie 5973N from Agilent Technologies (Wilmington, DE). A DB-5MS capillary column (J&W Scientific, Folsom, CA, USA) of 0.25 mm i.d. x 60 m fused silica capillary column with 5% (mole fraction) phenyl-substituted methylpolysiloxane phase (0.25 mm film thickness) was the chromatographic column used. This was the same column used by the NIST institute in PAHs analyses of SRM 1649a. Helium was the carried gas used at a column head pressure of 20 p.s.i. (constant pressure conditions).

Injections were pulsed splitless with split opened after 30 seconds and the injector temperature was 270ºC. The oven temperature program was as follows: 60ºC for 1 minute; 30ºC min^{-1} to 190ºC; 5ºC min^{-1} to 290ºC and hold time 30 min. The MSD was operated in electron impact mode with electron energies of 70 eV and being the ion source temperature of 230ºC.

The identification of PAHs was based on retention times and mass spectra, comparing these data with those of PAHs standards. In order to improve the sensitivity and asseverate the identification, final identification and quantitative analysis for PAH was performed in the selected ion monitoring (SIM) mode, selecting the corresponding molecular ions of different PAHs. The SIM mode was applied in each range of retention times. Monitored ions were shown in Table 1. Figure 1 shows the full-scan chromatogram of a real sample.

The deuterated standard mixture used as internal standard was transferred to the 1 ml volumetric flask before its bringing. A volume of 25 µl of 10 mg l^{-1} of the mixture was added to obtain a final concentration of 250 ng µl^{-1}. Each PAH was quantified using as signal the ratio 'response of PAH / response of internal standard'. Each one of the16-PAHs was quantified regarding one of four deuterated PAHs (Table 1).

Optimisation and validation of the method

In order to optimise the variables of the methodology a similar procedure to one proposed in the literature [32] was followed. Results of experimental assays and parameters validated are presented in the following sections. Several quality parameters were determined, such as the linearity, accuracy and precision, limits of detection, limits of quantitation and sensitivity.

The optimised method was validated using a certified reference material for establishing analytical requirements of the method to be adequate for determination of PAHs in airborne particles of different sizes.

Expression of results

Concentrations of PAHs were expressed in mg Kg^{-1} for the results of the reference material. Concentrations of PAHs were expressed in ng m^{-3} for the results of real samples collected in the city. Individual concentrations of each of the 16-PAHs but also the sum of 16-PAHs (total PAHs concentration) were presented, as well as the sum of six size ranges for each PAHs and total PAHs (Sum, TSP). Besides, indicative concentrations of PAHs in ng m^{-3} in PM_{10} were obtained from the sum of fractions corresponding to stages 2–6. Indicative concentrations in $PM_{2.5}$ and PM_1 were obtained from the sum of stages 4–6 and 5-6 respectively.

Results and discussion

Optimisation

Clean-up

Because the soxhlet extraction was not a selective method to extract PAHs, extracts of airborne particles obtained from her contain high co-extracted materials, such as many aliphatic hydrocarbons, different polar compounds or other aromatic substances. Therefore, in order to avoid possible interferences in the MSD detection it was necessary clean-up and fractionate the organic extracts. Fractionation allows to determine PAHs in a fraction but also other fractions corresponding to aliphatic hydrocarbons, other aromatic compounds or other polar organic compounds, such as sterols, organic acids, etc., in the same sample.

The clean-up and fractionation of organic extracts has been carried out by on-column chromatography in three fractions as it was described previously. A similar procedure as one found in the literature [33] was developed to optimise the volume of each mobile phase in the column. In order to test the efficiency of fractionation, 500 ng of the 16-PAHs standard was laid on the top of the column and then eluted according to the same clean-up procedure. PAHs were quantified in each fraction in order to estimate the amount of PAH fractionated.

The volume of n-hexane was optimised for the first fraction adding 50 µl of 10 mg l^{-1} of the 16-PAHs standard and pyrene-d_{10} (final concentration of 500 ng $µl^{-1}$) to five chromatographic columns and eluting by increasing volumes of n-hexane (2 to 6 ml) in each consecutive column. Percentages of recovery of the 16-PAHs fractionated in each column for the elution of first mobile phase are presented in Figure 2. Because the 16-PAHs should elute in the second fraction these percentages must be zero. Figure 2 shows that a volume above 4 ml of n-hexane elutes several PAHs, such as naphtalene, acenaphthylene and acenaphthene. Higher percentages were found for naphtalene, acenaphthylene, acenaphthene for 5 ml and fluorene, phenanthrene, anthracene, fluoranthene and pyrene for 6 ml. Therefore, volumes of 5 or 6 ml were discarded because there are evidences of elution for some PAHs of low molecular weight in the first fraction. Consequently a volume of 4 ml was better. For 4 ml a percentage of naphtalene, 13%, was eluted, consequently this PAH must be considered the only that it was not recovered at 100%. Then, the optimum volume for the first fraction was fixed for 4 ml of n-hexane. Although this fraction was rejected in the present work it contains alyphatic hydrocarbons and other non-polar compounds useful to be determined in airborne particles.

The aromatic fraction was optimised adding 50 µl of 10 mg l^{-1} of the 16-PAHs standard and pyrene-d_{10} (final concentration of 500 ng $µl^{-1}$) to six chromatographic columns and eluting by increasing volumes of the 20:80 DCM/n-hexane mixture (3 to 8 ml) in each consecutive column. Previously the first fraction was eluted with 4 ml of n-hexane to elute non-polar organic compounds, according to the previous optimisation. Percentages of recovery of the 16-PAHs obtained in each column for the elution of second mobile phase are shown in Figure 3. The percentage of PAHs eluted reached 100% when the volume of mixture tends to 7 ml, for all PAHs except for naphtalene (only 77%). Figure 3 shows that a volume lower than 7 ml of mixture of solvents elute insufficiently several PAHs, such as naphtalene, pyrene and benzo[ghi]perylene for 6 ml. Then, lower volumes than 7 ml

were discarded and the optimum volume for aromatic fractions was evaluated for 7 ml of DCM/n-hexane mixture.

In order to corroborate that any PAH must be eluted after the second fraction and with the aim of optimise another fraction containing other interesting compounds, the third fraction was also optimised with the same procedure. The polar fraction was optimised adding 50 µl of 10 mg l^{-1} of the 16-PAHs standard and pyrene-d$_{10}$ (final concentration of 500 ng µl^{-1}) to five chromatographic columns and eluting by increasing volumes of the 5% methanol in DCM mixture (2 to 6 ml) in each consecutive column. Previously the first fraction was eluted with 4 ml of n-hexane to elute non-polar organic compounds and the second fraction was eluted with 7 ml of the 20:80 DCM/n-hexane mixture to elute PAHs, according to the previous optimisation. Percentages of recovery of the 16-PAHs obtained in each column for the elution of second mobile phase are shown in Figure 4. The percentage of practically all PAHs eluted were 0% in the third phase. Only again naphtalene was eluted in a low grade less than 2%. Consequently an optimum value of 4 ml of 5% methanol in DCM mixture was chosen to elute the third fraction. Because of the loss found for naphtalene in the first and third fractions with regard to the other PAHs, it considered that it was the only PAH with a poorer recovery estimated in less than 80%.

Soxhlet extraction time

Cut and non-cut glassfibre filters have different sizes and areas. Cut filters are smaller than non-cut filters. Besides, cut and non-cut glassfibre filters collect different quantity of particles. Cut filters collect fewer amounts of particles than non-cut filters. Consequently, the size and weigh of samples introduced in the soxhlet for the cut filter plus particles is smaller than the sample of non-cut filter plus particles. Therefore, the volume of solvent used in the extraction can be optimised keeping in mind the size and weigh of solid samples introduced in the soxhlet apparatus. Samples of particles were extracted using Soxhlet apparatus with 100 ml and 250 ml for both types of samples. The results were the same for both types of samples and a Soxhlet apparatus with 250 ml of solvent for both types of samples was selected.

The optimisation consisted in perform the extraction of airborne samples on eight soxhlet apparatus simultaneously at different times in each apparatus, increasing the time of extraction and assessing the maximum of PAHs extracted. It was necessary to apply the extraction stage on real samples of urban airborne particles collected on glassfibre filters. Extractions at different times were applied on different portions of the same filter. Because of this, real samples of particles used to optimise the extraction were obtained from accumulative samplings of 24 hours on the same filter support of impactor until the amount of particles collected be sufficiently high. This amount should be equivalent at 5-8 times the usual amount of particles collected in one sampling of 24 hours, because later on these filters are fractionated on eight homogeneous portions for evaluation of the soxhlet extraction time. The amount of particles in each one of the eighth should be equivalent at the usual amount of particles collected in one sampling of 24 hours. Each portion was extracted in similar conditions at one complete filter. All this experience was performed six times, each one on the five size fraction filters and on a fourth (1/4 area) of the backup filter. The mixture of solvents used, acetone : dichloromethane 5:1, was different to others usual mixtures, but with excellent results [31].

The six different size fractions gave the same result. The average result for six replicates is shown in Figure 5. The percentage of PAHs extracted was represented for the sum of the 16 measured PAHs, because the optimum time was the same for all individual PAHs. The concentration increases with the time of extraction until the maximum that was reached at 10 hours. There was not a significant increase of concentration over 10 hours for the soxhlet extraction. Therefore, the optimum time to extract the maximum of PAHs from airborne particles on filter supports was fixed at 10 hours.

The complete analytical method is schematically presented in Figure 6.

Validation

Analytical calibration

A multipoint calibration and internal standard method using eight standard solutions of increasing concentrations were the technique used to obtain calibration curves. Compounds are quantified using the ratio of analyte and internal standard response. The internal standard was added to the sample extract just prior to the instrumental analysis. Quantification of studied compounds must be conducted in the linear range of calibration curves. In order to determine the linear range of the detector, several standard solutions were prepared and injected at different concentration levels. According to usual PAH airborne levels, concentrations of the 16-PAHs and pyrene-d_{10} ranged between 5 and 800 ng µl^{-1}. The concentration of the deuterated standard mixture was 250 ng µl^{-1} for all points. Within these linearity ranges, calibration curves plotted from eight points were obtained for all compounds by regression analysis of peak areas versus injected concentrations. In all cases, regression coefficients were higher than r = 0.999 for all analytes.

Limit of detection and limit of quantitation

The parameters of calibration corresponding to the 16-PAHs were shown in Table 1. The instrumental LOD, expressed in ng µl^{-1} was obtained from the standard error of estimate of the regression ($S_{y/x}$) multiplied by 3 and divided by the slope (intercept of the regression) and the LOQ was obtained from the same standard error of estimate using a factor of 10. The values of LODs and LOQs were averaged from data of five regressions done in different days. Limits of detection (LOD) ranged from 0.17 ng µl^{-1} for benzo[b]fluoranthene to 1.41 ng µl^{-1} for pyrene. Limits of quantitation (LOQ) ranged from 0.58 ng µl^{-1} for benzo[b]fluoranthene to 4.69 ng µl^{-1} for pyrene.

Accuracy and precision of PAHs determinations

The complete analytical method was applied to the NIST certified reference material SRM 1649a Urban Dust. The reference material has been certified for 12 of the 16 priority PAHs of the US EPA [34,35]. Fifteen aliquots of 100 mg of material were analysed. Results obtained were shown in Table 2. The experimental mean concentration obtained for each PAH with its uncertainty at 95% level of confidence was presented in the table of results. The recovery, the interval of the AOAC criteria and the relative standard deviation are also presented in the table. Recoveries of each PAH were calculated as percent of the certificated value (100%). The recovery provides an estimation of the accuracy of the whole procedure.

The relative standard deviation shows the precision of the determination of each PAH. The interval of the AOAC criteria from the American Organisation of Analytical Chemistry is another measure of the accuracy of determinations.

The recoveries for all analysed PAHs ranged from 93.6 to 102.1% and they were very close to the expected values, giving an average value of 97%. The lowest recovery was obtained for benzo[a]anthracene and the highest was for chrysene, however both values were close to the true value. Practically all PAHs have good recoveries between 95 and 100% and all percentages were within the range 80-110% recommended by the A.O.A.C. for their levels of concentration [36]. Results on benzo[b]fluoranthene and benzo[k]fluoranthene show the good resolution obtained with the use of a 60 m capillary column, instead a 30 m column, which not resolve satisfactorily in some cases both PAHs [37].

Values of relative standard deviation obtained were in agreement with certified data of SRM 1649a material except for chrysene, benzo[k]fluoranthene and benzo[a]pyrene, which they obtained higher values of RSD than the reference, but always lower than 5%. RSD values ranged from 1.9%

for phenanthrene and 19.5 for fluorene. All RSDs were lower than 5% except fluorene that was the only PAH with a reference value, not certified. The mean value obtained for our work (4.7%) was also lower than 5%.

The study of this reference material was of particular interest. The results obtained indicate that the methodology is suitable for the nature of samples at trace levels and that it allows the determination of most compounds at different concentration levels with a recovery very close to 100%. Besides, low values of relative standard deviations are indicative of a good precision for the whole methodology.

Application to airborne particles collected in Seville

Once the final method was optimised and validated with the CRM it was applied to real samples of airborne particles to test in real situations. In the present work samples of airborne particles were collected of different particle size by the impactor system. They represented the air pollution of a Mediterranean urban city high polluted by vehicular traffic. According with the aim of this work the results should give us the type of size distribution of PAHs found in these real samples. These samples were collected in different situations, such as in sites high trafficked (HT) and low trafficked (LT), located in the centre (C) of the city and in its periphery (P) and sites with industrial (I) influence (Table 3). Five samples of airborne particles of six different size ranges were collected by the cascade impactor. HTP corresponds to a sample collected in a high trafficked site located in the periphery of the city; HTC corresponds to a sample collected in a high trafficked site located in the centre of the city; LTP corresponds to a sample collected in a low trafficked site located in the periphery; LTC corresponds to a sample collected in a low trafficked site located in the centre; LTIP corresponds to a sample collected in a low trafficked site located in the periphery very close to the more important industrial zone.

Seville is the more populated city of Andalucia. It covers an area of over 142 Km^2 and is located 10 m. a.s.l. on a large plain alongside the Guadalquivir River. Seville is also the more trafficked city of the southern of Spain. The vehicular traffic constitutes the main source of anthropogenic air pollution because this city is less polluted by industries than other Andalucian cities such as Huelva or Algeciras. It must keep in mind that the South of Spain receives an important influence of a natural crustal source from the north of Africa, which sometimes has high contributions to total suspended particles. On the other hand these natural contributions also come from the resuspension of not cultivated lands of the periphery of Seville, usually dry lands.

PAHs concentrations were analysed in the six filters of five samples. PAHs levels in TSP, PM_{10}, $PM_{2.5}$ and PM_1 were obtained summing the corresponding fractions. PAHs concentration in TSP (sum, TSP) resulted from the sum of levels quantified on the six fractions. TSP, PM_{10}, $PM_{2.5}$ and PM_1 values represent the usual cut points having the inlets of samplers to collect suspended particles. These values of cut points are useful to compare with the corresponding values obtained by the inlets in other cities.

Total PAHs concentrations

The concentrations of PAHs detected are shown in Table 3. Levels of Total PAHs (sum of the 16 congeners) in TSP (sum of the 6 size fractions) determined in Seville vary from 2.1 ng m^{-3} to 14.6 ng m^{-3} for the five samples analysed. The average value for Total PAHs in TSP was 8.6 ng m^{-3}. These values correspond to usual concentrations of PAHs characteristic of urban air in other cities of Spain. These results are higher than levels of Jinámar [13] and Zaragoza [11]. Nevertheless a more populated city, Barcelona [21], shows PAHs levels higher than those found in this present work. Benzo[a]pyrene, considered as a representative marker of total PAHs [10], presented values ranged from 0.11 ng m^{-3} to 0.98 ng m^{-3} in TSP with an average value of 0.56 ng m^{-3}. The PAH more abundant

was benzo[ghi]perylene with a mean of 2.8 ng m^{-3} in TSP. Other PAHs high concentrated were benzo[b]fluorantene and chrysene (1.1 ng m^{-3}), indeno[1,2,3-cd]pyrene (0.76 ng m^{-3}) and benzo[a]pyrene (0.56 ng m^{-3}). The other values were lower than 0.4 ng m^{-3} (benzo[a]anthracene and pyrene).

Size distribution of PAHs

With regard to the size distribution, concentrations of the 16-PAHs were different in different range sizes, as it was expected. Table 4 presents the distribution as percentage of the sum of the six size fractions. Higher concentrations of PAHs were accumulated in the finest size range of submicron particles (<0.6 μm, stage 6 of the impactor), however in a higher grade (average of 75% for Total-PAHs) than for particulate matter concentrations (45%). It has found 82% of PAHs in particles less than 1.3 μm (stages 5 and 6). That is, there was low amount of PAHs in particles greater than 1 micrometer. The highest concentrations in finest particles was for the heaviest PAHs benzo[ghi]perylene (2.4 ng m^3, 84%). That is, this PAH was the most abundant in the air in addition to the most accumulated in finest particles, the more harmful for human health. The other PAHs high concentrated in the air in finest particles were benzo[b]fluoranthene (0.89 ng m^3, 80%), Chrysene (0.81 ng m^3, 78%), Indeno[1,2,3-cd]pyrene (0.60 ng m^3, 79%) and Benzo[a]pyrene (0.44 ng m^3, 79%), all these heavier PAHs. Other values were lower than 0.3 ng m^{-3} (benzo[a]anthracene, 77%). The higher percentages in finest particles were also found for the heaviest PAHs Benzo[a]anthracene to benzo[ghi]perylene (Table 4) from 67% (dibenzo[b]anthracene) to 84% (benzo[ghi]perylene).

There are an evident change starting from fluoranthene, with 53% of accumulation grade, regarding the previous PAHs, from fluorene (33%) to anthracene (43%). The increase in accumulation grade in finest particles is related with the change in physical-chemical properties, such as the molecular weight, boiling and melting points, vapour pressure and water solubility. As it can see in Figure 7 the vapour pressure and water solubility properties become minimum starting from anthracene, meanwhile the other properties continue increasing. Both properties are the most related with meteorological variables and they could be correlated with temperature, humidity and atmospheric pressure. A more extensive study collecting more samples for a long time should be performed to found these relationships.

PM$_{10}$, PM$_{2.5}$ and PM$_1$ results

The results of PAHs levels in the different size cut points PM$_{10}$, PM$_{2.5}$ and PM$_1$ (see Table 5) shows that PAHs with higher molecular weight trend to associate with fine particles less than 1 μm (PM1). For example, 89.3% of benzo[ghi]perylene was accumulated on PM$_1$ and 86.5% of benzo[a]pyrene was quantified too in PM$_1$. High percentages of accumulation starting from benzo[a]anthracene. For the average of PAHs 82% was in PM$_1$. This means that only 5.9% of PAHs are in particles between 2.7 and 1.3 μm and only 8.7% of PAHs are in particles between 10 and 2.7 μm. Therefore, is more useful to study PAHs in fine particles using a commercial PM$_1$ inlet, because this range of size is the most harmful for the health. PM$_1$ particles can penetrate and deposit in the alveolar region of lungs. The high content in PAHs in PM$_1$ regarding the total of suspended particles is a serious risk for the population, which must be more frequently controlled. There are many works that have studied PAHs and their size distribution by impactor systems but there is a little number of works that has studied PAHs in PM$_1$ particles by PM$_1$ inlets [38,39].

Conclusions

Experimental conditions of the method have been optimised in the extraction and purification stages of PAHs. Ten hours of soxhlet extraction with 250 ml of acetone : dichlorometane 5:1 mixture was sufficient to obtain extracts from filters with particles of different sizes. A fractionation of the extract consisting on eluting with 4 ml of n-hexane the first fraction, rejecting this, and then, it elutes the aromatic fractions with 7 ml of DCM/n-hexane mixture, analysing this by GC-MS. The optimised analytical method has been tested and validated with the SRM 1649a Urban dust reference material, giving good recoveries >93% for all PAHs and good RSD for all PAHs except for chrysene, benzo[k]fluoranthene and benzo[a]pyrene. Therefore, the modified method is valid to analyse PAHs in samples of airborne particles of different sizes.

Finally, the method was applied on real samples collected in Seville. It has allowed us to determine concentrations off each one of the 16 priority PAHs of the US-EPA in six size ranges of particles. Concentrations in urban air were in the same order as in other cities, although the levels not indicate a high pollution grade. Benzo[a]pyrene level not reach the European target value of 1 ng m^{-3} that the actual proposal for the Fourth Daughter Directive [40]. Results on the size distribution of PAHs demonstrate the importance that has the use of impactor systems to find the size mode in which the pollutants have the major incidence.

PAHs concentrations were determined in TSP, PM_{10}, $PM_{2.5}$ and PM_1. PAHs levels detected in Seville were similar as other cities of traffic influence. PAHs with highest molecular weight are associated with finest particles, consequently $PM_{2.5}$ and mainly PM_1 inlets should be more frequently used.

References

1. Fenger J (1999) Urban air quality. Atmospheric Environment 33: 4877-4900.
2. Ray E, CPW Yang (2001) Environmental Analysis. Analytical Chemistry 73: 2761-2790.
3. International Agency for Research on Cancer (IARC), (1991) IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, vols. 43-53. Lyon.
4. US EPA (1977) Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutans, U.S. Environmental Protection Agency, Environment Monitoring and Support Laboratory, Cincinnati, OH.
5. Culp SJ, Gaylor DW, Sheldon WG, Goldstein LS, Beland FA (1988) Carcinogenesis 19: 117-124.
6. Weyand EH, Chen YC, Wu Y, Koganti A, Dunsford HA, Rodríguez LV (1995) Chemical Research in Toxicology 8: 949-954.
7. UBA Berlín (1998) Investigation of emission and abatement measures for persistent organic pollutants in the Federal Republic of Germany. Texte 75/98, Research Report 295 44 365 Umweltbundesamt.
8. Kim Oanh NT, Reutergardh LB, Dung NT (1999) Environmental Science and Technology 33: 2703-2709.
9. CONCAWE (1998) Polycyclic aromatic hydrocarbons in automovile exhaust emission and fuels. Report 98/55.
10. Pankow JF (1987) Atmospheric Environment 21: 2275-2283.
11. Mastral AM, Callén MS, López JM, Murillo R, García T, Navarro MV (2003) Fuel Processing Technology 80: 183-193.
12. Leal-Granadillo IA, García Alonso JI, Sanz-Medel A (2000) Journal of Environmental Monitoring 2: 218-222.
13. López Cancio JA, Vera Castellano A, Navarro Trujillo R, Corujo Jiménez J (2002) Water, Air and Soil Pollution 136: 93-103.
14. Gutiérrez Dabán A (2003) Study of the atmospheric pollution by Polycyclic aromatic hydrocarbons and their particle size distributions in the city of Seville. Ph. Dr. Thesis. Department of Analytical Chemistry. University of Seville.
15. Thysen J, Althoff JKG, Mohr U (1981) J. Nat. Cancer Inst. 66: 575-577.
16. Fernández AJ, Ternero M (2004) Idojaras 108: 11-32.
17. Fernández Espinosa AJ, Ternero Rodríguez M, Barragán de la Rosa FJ, Jiménez Sánchez JC (2001) Atmospheric Environment 35: 2595-2601.
18. Kawanaka Y, Matsumoto E, Sakamoto K, Wang N, Yun S (2004) Atmospheric Environment 38: 2125 –2132.
19. Pope CA, Burnett RT, Thun MJ (2002) Air Man Assoc 287: 1132–1141.
20. Sáez FS, Cabañas A, González A, Murillo JM, Martínez JM, Rodríguez JJ, Dorronsoro JL (2003) Biosystems Engineering 86: 103 –111.
21. Aceves M, Grimalt JO (1993) Environmental Science and Technology 27: 2896-2908.
22. Odabasi M, Vardar N, Sofuoglu A, Tasdemir Y, Holsen TM (1999) The Science of the Total Environment 227: 57-67.
23. Environmental Protection Agency (EPA) (1996) Organic extraction and sample preparation. Method 3500B. Revisión 2.
24. Environmental Protection Agency (EPA) (1996) Semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS). Method 8270c. Revision 3.
25. Environmental Protection Agency (EPA) (1999) Determination of polycyclic aromatic hydrocarbons (PAHs) in ambient air using gas chromatography/mass spectrometry (GC/MS). Method TO-13A. Compendium of Methods for Determination of Toxic Compounds in Ambient

Air. Center for Environmental Research Information, Oficce of Research and Development, U.S. Environmental Protection Agency.

26. European Commision of Normalization (CEN) (1999) EN 12341:1999: Air quality. Determination of the PM10 fraction of suspended particulate matter. Reference method and field test procedure to demonstrate reference equivalence of measurement methods.

27. International Organization for Standarization (ISO) (1993) ISO 9855: ambient air-determination of the particulate lead content of aerosols collected in filters. Atomic absorption spectroscopy method. ISO Publications.

28. Certificate of Analysis, Standard Reference Material (SRM) 1649a, Urban Dust (2001) National Institute of Standards and Technology, Gaithersburg, MD, January 31.

29. International Organization for Standarization (ISO) (1995) ISO 7708: 1995 (E): Air quality – particle size fraction definitions for health-related sampling. ISO Publications, First Edition 1995-04-01.

30. FED-STD-209E (1988) General services administration. Federal standard FED-STD-209E: airborne particulate cleanliness classes in cleanrooms and clean zones.

31. Bomboí Mingarro MT (1987) Investigación sobre la contaminación por hidrocarburos y ácidos grasos en las aguas de escorrentía superficial urbana y sus efectos sobre los procesos biológicos. Tesis Doctoral. Departamento de Salud Pública e Historia de la Ciencia. Facultad de Farmacia, Universidad Complutense de Madrid.

32. Jaouen-Madoulet A, Abarnou A, Le Guellec AM, Loizeau V, Leboulenger F (2000) Journal of Chromatography 886: 153-173.

33. Jang JK, Li A (2001) Chemosphere 44: 1439-1445.

34. Schubert P, Schantz MM, Sander LC, Wise SA (2003) Anal. Chem. 75: 234-246.

35. Shu YY, Tey SY, Wu DKS (2003) Analytica Chimica Acta 495: 99–108.

36. AOAC (2003) Peer Verifed Method Program, Manual on Policies and Procedures, Arlington, VA, November 2003.

37. Bamford HA, Bezabeh DZ, Schantz MM, Wise SA, Baker JE (2003) Chemosphere 50: 575 –587.

38. Hauck H, Berner A, Frischer T, Gomiscek B, Kundi M, Neuberger M, Puxbaum H, Preining O, AUPHEP-Team (2004) Atmospheric Environment 38: 3905 –3915.

39. Wingfors H, Sjödin A, Haglund P, Brorström-Lundén E (2001) Atmospheric Environment 35: 6361 –6369.

40. Commission of the European Communities (COM) 2003. Proposal for a directive of the european parliament and of the council relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. Brussels, July 16, COM 423 final, 2003/0164 Cod.

Captions of the figures

1. Chromatogram of a real sample. Peaks: 1= naphthalene; 2=acenaphthylene; 3=acenaphthene; 4= acenaphthene-d10; 5=fluorene; 6=phenanthrene-d10; 7=phenanthrene; 8=anthracene; 9=fluoranthene; 10=pyrene-d10; 11=pyrene; 12=benz[a]anthracene; 13=crysene-d12; 14=crysene; 15=benzo[b]fluoranthene; 16=benzo[k]fluoranthene; 17=benzo[a]pyrene; 18=perylene-d12; 19=indeno[1,2,3-cd]pyrene; 20=dibenz[ah]anthracene; 21=benzo[ghi]perylene.

2. PAH recoveries as function of first mobile phase volume elution.

3. PAH recovery as function of second mobile phase volume elution.

4. Total PAHs extracted with the acetone : dichloromethane 5 : 1 mixture as function of time. The percentage is referred to the maximum of PAHs extracted.

5. Analytical procedure to PAHs quantification.
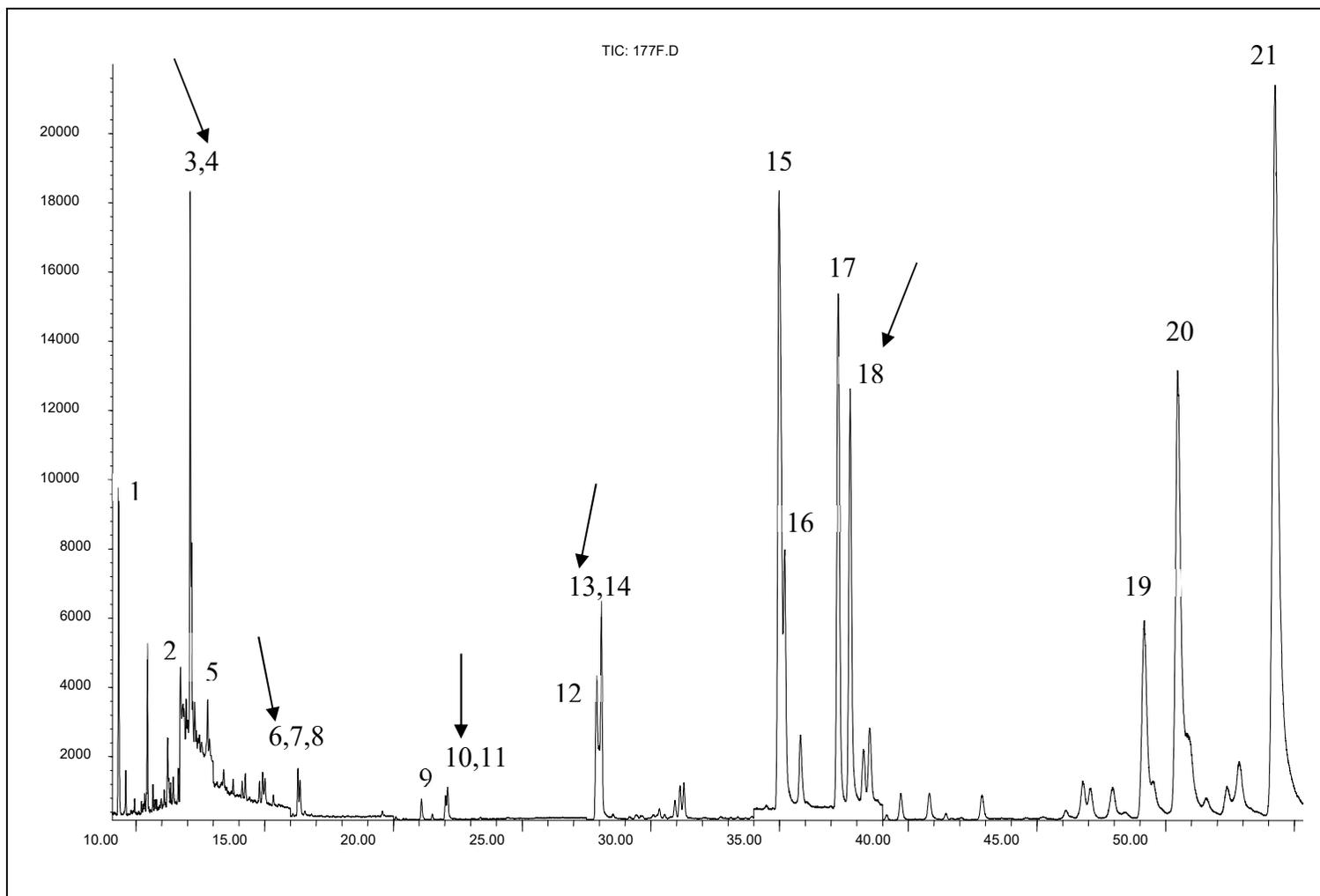
Figure 1. Chromatogram of a real sample. Peaks: 1= naphthalene; 2=acenaphthylene; 3=acenaphthene; 4= acenaphthene-d10; 5=fluorene; 6=phenanthrene-d10; 7=phenanthrene; 8=anthracene; 9=fluoranthene; 10=pyrene-d10; 11=pyrene; 12=benz[a]anthracene; 13=crysene-d12; 14=crysene; 15=benzo[b]fluoranthene; 16=benzo[k]fluoranthene; 17=benzo[a]pyrene; 18=perylene-d12; 19=indeno[1,2,3-cd]pyrene; 20=dibenz[ah]anthracene; 21=benzo[ghi]perylene.

15
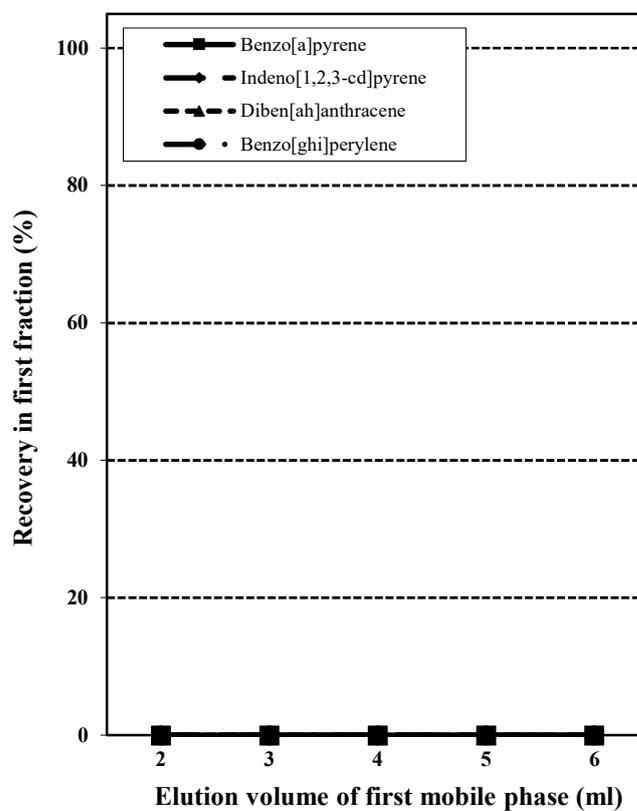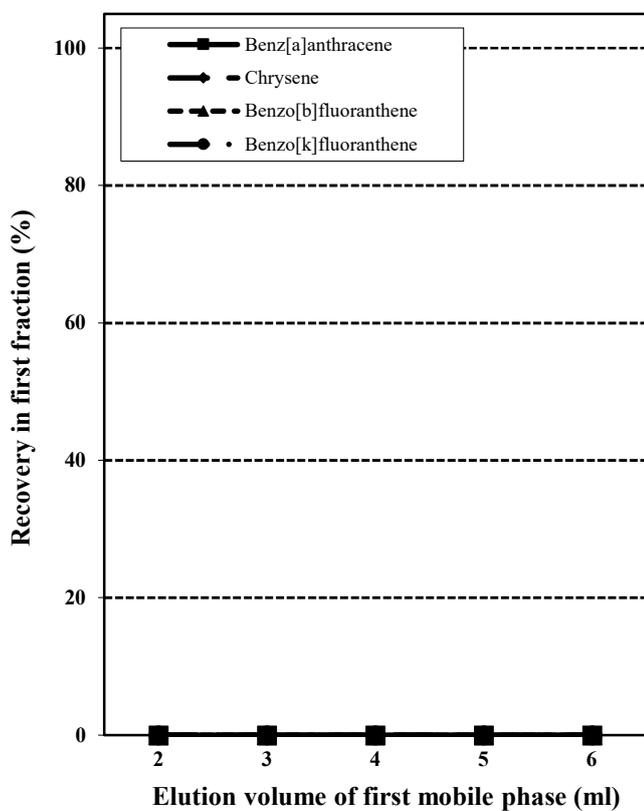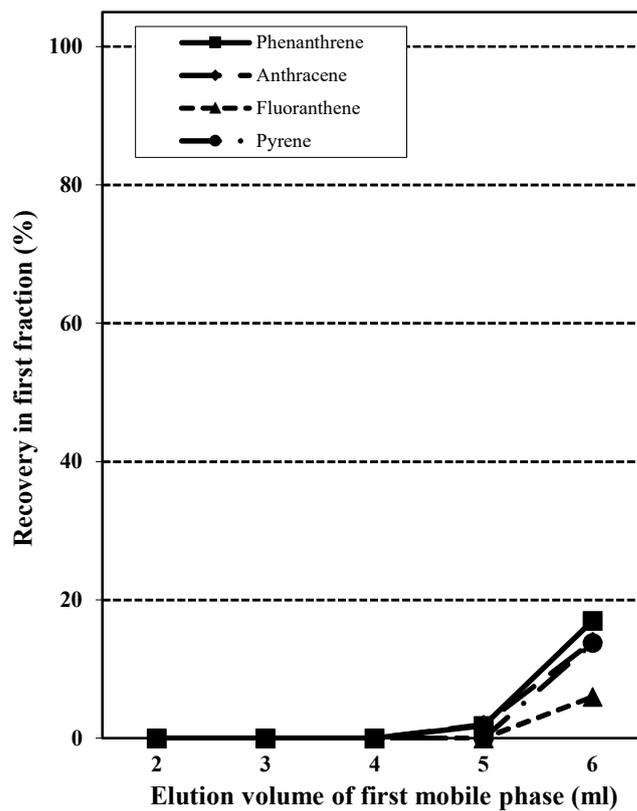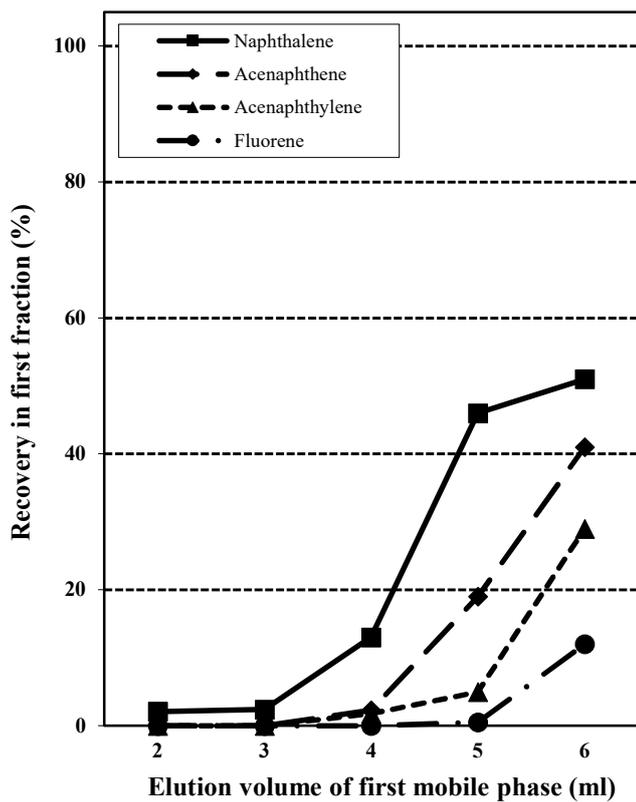
Figure 2. PAH recoveries as function of first mobile phase volume elution.
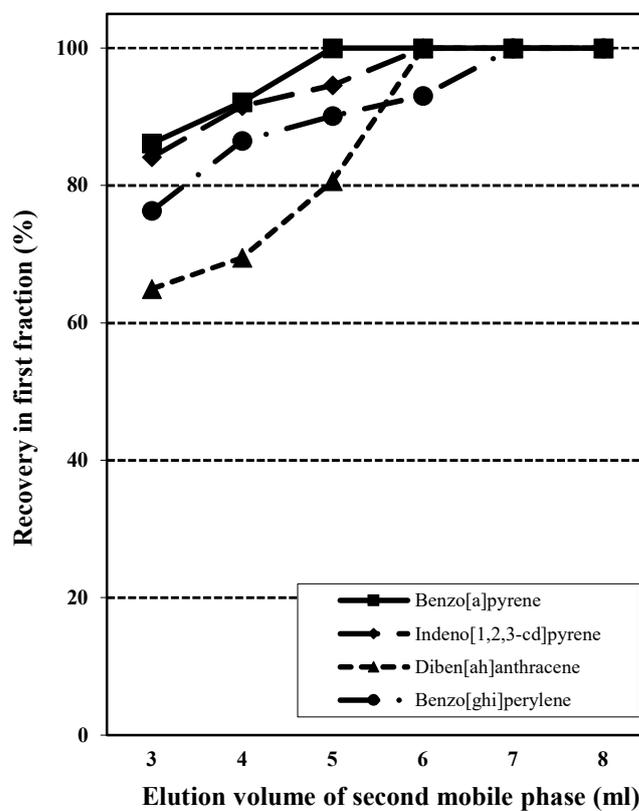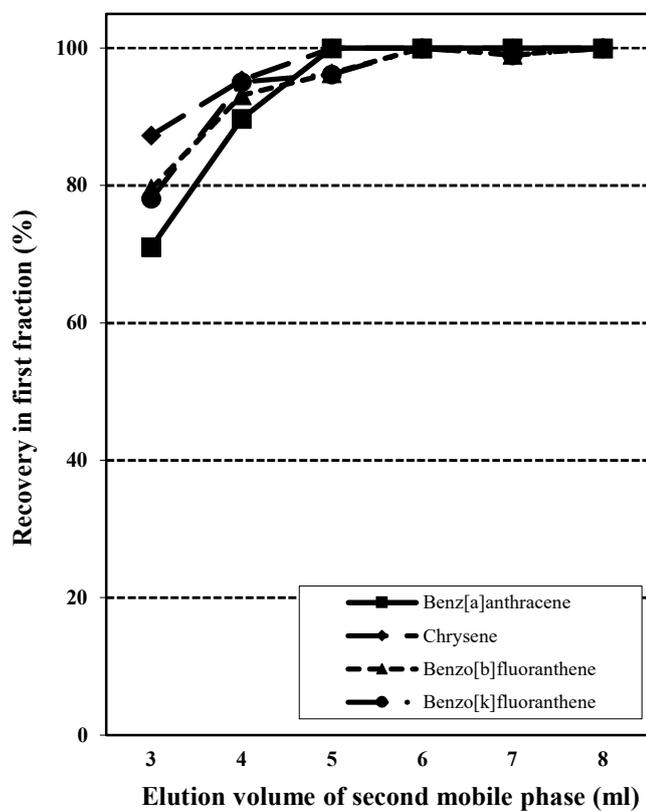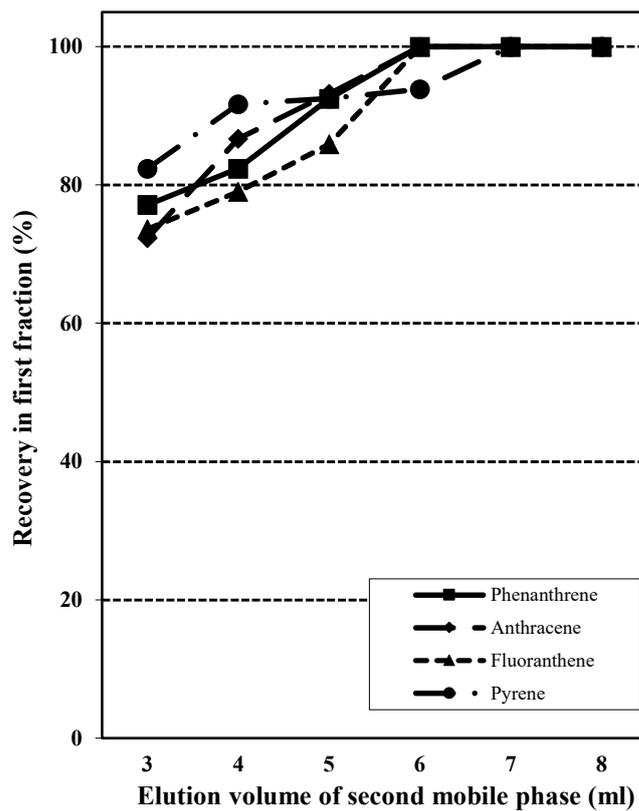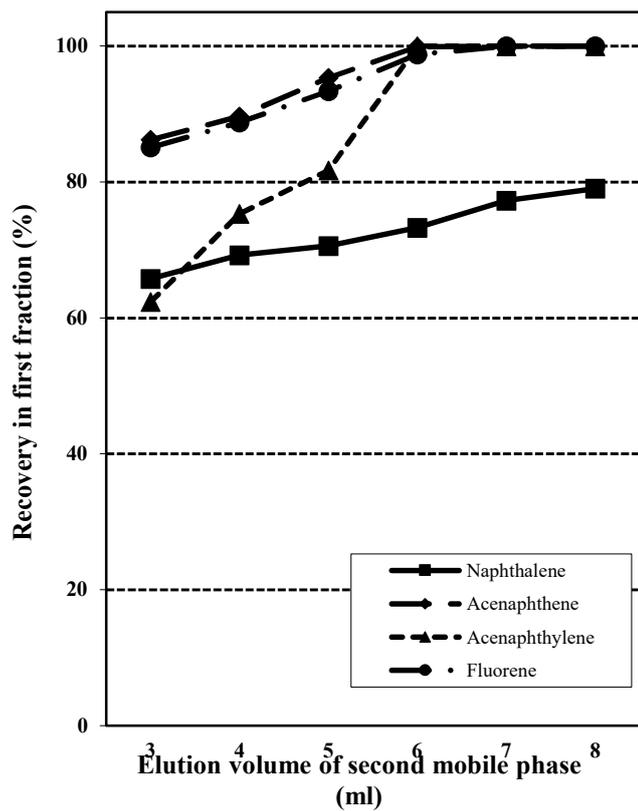
Figure 3. PAH recoveries as function of second mobile phase volume elution.
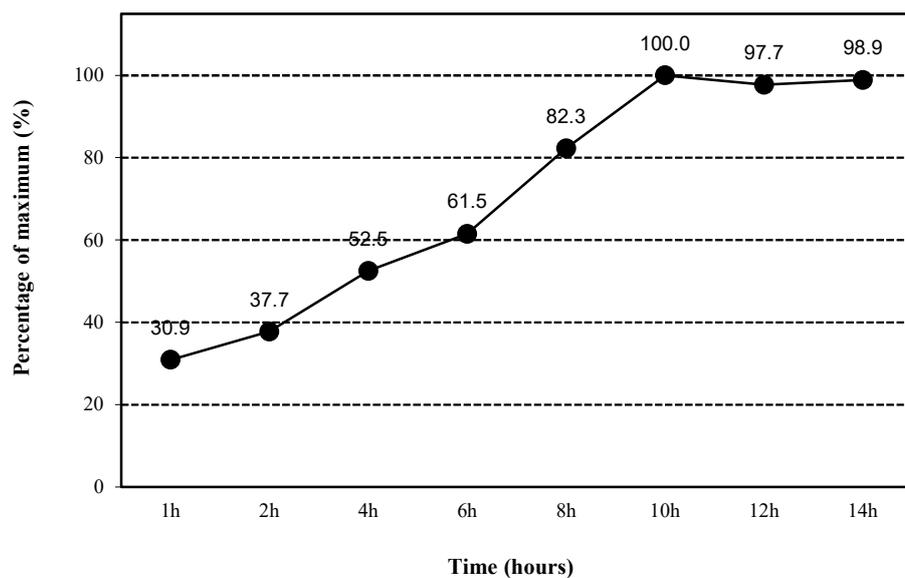
Figure 4. Total PAHs extracted with the acetone : dichloromethane 5 : 1 mixture as function of time. The percentage is referred to the maximum of PAHs extracted.
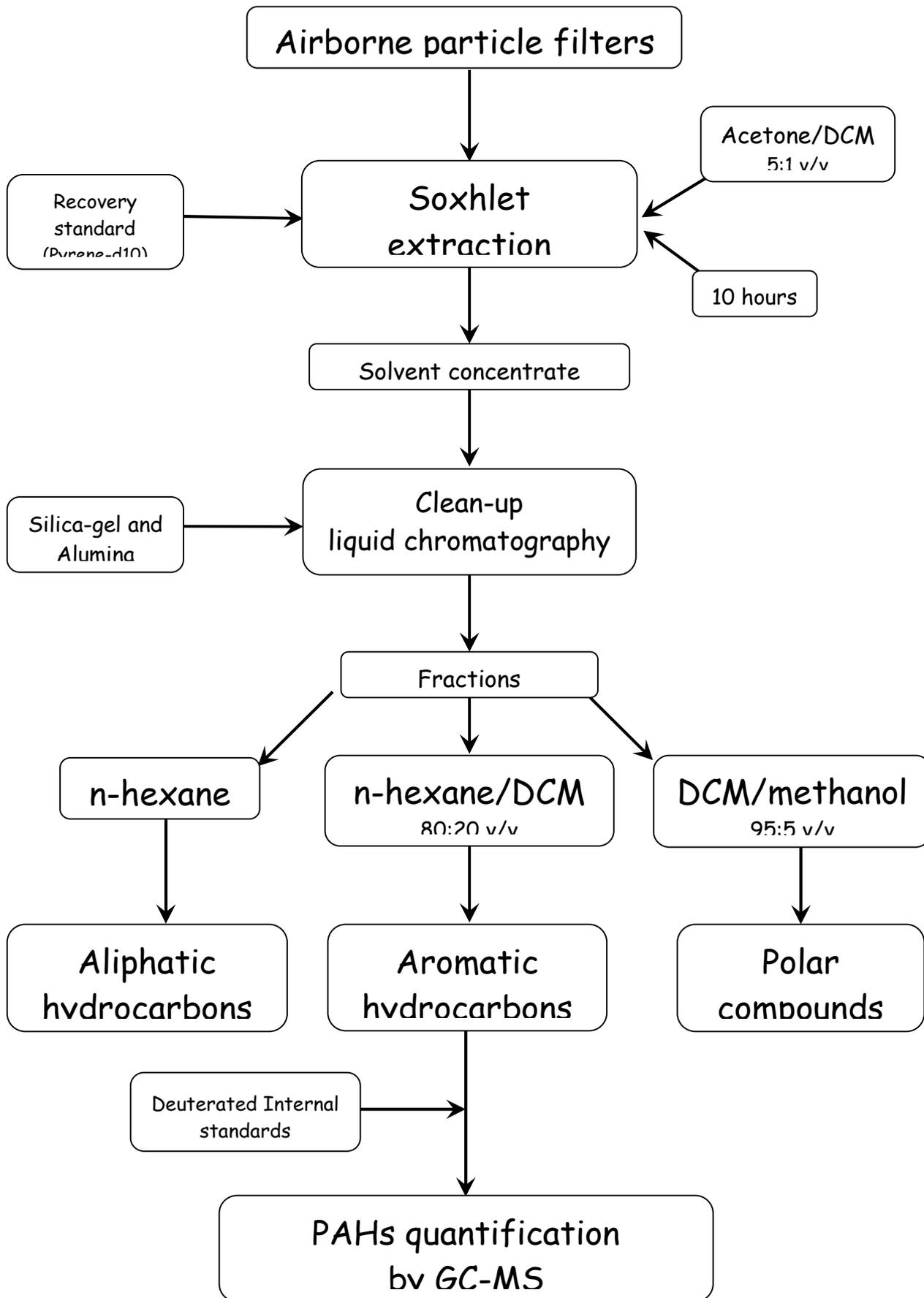
Figure 5. Analytical method to PAHs analysis.

Table 1 Calibration parameters, LODs and LOQs for the 16 PAH analysed, with deuterated PAH used as internal standard

PAH	Target + Qualifier	Linear range (pg μl^{-1}) (ppb)	Internal standard	r Coefficient	Slope (sensitivity, pg^{-1} μl)	Slope RSD (%)	LOD (pg μl^{-1}/pg m^{-3})	LOQ (pg μl^{-1}/pg m^{-3})
Naphthalene	128	5–800	Acenaphthene-d_{10}	0.9996	0.01361	1.16	8.59/5.26	28.63/17.54
Acenaphthene	153 + 154	5–800	Acenaphthene-d_{10}	0.9996	0.00875	1.19	2.45/1.50	8.18/5.01
Acenaphthylene	152	5–800	Acenaphthene-d_{10}	0.9996	0.00560	1.19	7.46/4.57	24.86/15.23
Fluorene	166 + 165	5–800	Acenaphthene-d_{10}	0.9995	0.00469	1.33	5.90/3.61	19.66/12.04
Phenanthrene	178	5–800	Acenaphthene-d_{10}	0.9995	0.00531	1.32	8.88/5.44	29.60/18.13
Anthracene	178	5–800	Acenaphthene-d_{10}	0.9993	0.00476	1.50	6.08/3.72	20.26/12.41
Fluoranthene	202	5–800	Acenaphthene-d_{10}	0.9995	0.00268	1.27	10.04/6.15	33.47/20.50
Pyrene	202	5–800	Phenanthrene-d_{10}	0.9991	0.00822	1.77	14.06/8.61	46.86/28.71
Benzo[a]anthracene	228	5–800	Chrysene-d_{12}	0.9996	0.00247	1.22	3.70/2.26	12.35/7.56
Chrysene	228	5–800	Chrysene-d_{12}	0.9993	0.00500	1.52	8.36/5.12	27.85/17.06
Benzo[b]fluoranthene	252	5–800	Perylene-d_{12}	0.9996	0.00293	1.12	1.74/1.06	5.81/3.56
Benzo[k]fluoranthene	252	5–800	Perylene-d_{12}	0.9991	0.01263	2.49	2.23/1.36	7.43/4.55
Benzo[a]pyrene	252	5–800	Perylene-d_{12}	0.9996	0.01423	2.18	4.38/2.68	14.59/8.93
Indeno[1,2,3-cd]pyrene	276	5–800	Perylene-d_{12}	0.9997	0.00849	2.12	4.08/2.50	13.59/8.32
Dibenz[a,h]anthracene	276	5–800	Perylene-d_{12}	0.9991	0.00553	2.54	4.01/2.45	13.36/8.18
Benzo[ghi]perylene	278	5–800	Perylene-d_{12}	0.9994	0.00247	3.91	4.86/2.97	16.21/9.93

Table 2 Certified and measured concentrations of PAH in SRM 1649a: accuracy and precision results

PAH	Certified values (mg kg^{-1})	RSD[b] (%)	Experimental mean[a] (mg kg^{-1})	Recovery (%)	RSD[b] (%)	AOAC criteria (%)
Fluorene[c]	0.23 ± 0.05[c]	21.7[c]	0.22 ± 0.03	93.7	19.5	80–110
Phenanthrene	4.14 ± 0.37	8.9	4.02 ± 0.04	97.2	1.9	80–110
Anthracene	0.432 ± 0.082	19.0	0.419 ± 0.008	97.1	3.2	80–110
Fluoranthene	6.45 ± 0.18	2.8	6.14 ± 0.01	95.2	2.7	80–110
Pyrene	5.29 ± 0.25	4.7	5.06 ± 0.07	95.7	2.4	80–110
Benzo[a]anthracene	2.208 ± 0.073	3.3	2.066 ± 0.036	93.6	2.8	80–110
Chrysene	3.049 ± 0.060	2.0	3.114 ± 0.088	102.1	4.7	80–110
Benzo[b]fluoranthene	6.45 ± 0.64	9.9	6.29 ± 0.10	97.6	2.6	80–110
Benzo[k]fluoranthene	1.913 ± 0.031	1.6	1.838 ± 0.037	96.1	3.4	80–110
Benzo[a]pyrene	2.509 ± 0.087	3.5	2.403 ± 0.069	95.8	4.7	80–110
Indeno[1,2,3-cd]pyrene	3.18 ± 0.72	22.6	3.04 ± 0.08	95.7	4.6	80–110
Dibenz[a,h]anthracene	0.288 ± 0.023	8.0	0.287 ± 0.007	99.8	4.1	80–110
Benzo[ghi]perylene	4.01 ± 0.91	22.7	4.05 ± 0.11	100.9	4.3	80–110
Mean		10.1		97.0	4.7	

[a]Mean for $n = 15$
[b]Relative standard deviation in percentage (%)
[c]Reference value, not certified

Table 3 Size distribution of particulate matter (PM, $\mu g\ m^{-3}$) and PAH (pg m^{-3}) in airborne particles in Seville

Sample	Size/PAH	PM	Naph	Ace	Acey	Flu	Phen	Ant	Flua	Pyr	BaA	Chry	BbF	BkF	BaP	InP	DbA	Bper	Total PAH
HTC	> 10 μm	16.3	19	6	18	7	40	6	35	45	17	52	38	18	19	27	16	105	468
	10–4.9 μm	15.3	19	6	22	9	60	8	39	46	20	60	54	24	25	38	21	134	585
	4.9–2.7 μm	9.1	16	5	19	8	86	6	76	94	24	70	73	30	36	50	21	142	756
	2.7–1.3 μm	8.8	16	5	23	7	47	4	56	92	27	89	138	46	59	95	32	298	1,034
	1.3–0.6 μm	7.0	15	5	19	8	48	5	42	55	34	115	166	44	75	106	36	329	1,102
	< 0.6 μm	43.0	48	17	64	19	158	20	192	260	407	1,252	1,572	371	691	1,047	263	4,309	1,690
	Sum (TSP)	100.0	133	44	165	58	439	49	440	592	529	1,638	2,041	533	905	1,363	389	5,317	14,635
HTP	> 10 μm	9.4	13	4	6	7	34	6	23	21	10	23	17	12	10	15	10	42	253
	10–4.9 μm	12.7	14	5	6	7	36	4	25	29	13	34	26	14	15	22	11	79	340
	4.9–2.7 μm	4.6	11	4	6	6	28	4	18	22	11	26	24	13	13	20	11	63	280
	2.7–1.3 μm	3.1	13	5	6	7	35	5	22	23	16	37	39	18	23	35	13	118	415
	1.3–0.6 μm	2.8	12	5	6	6	32	3	15	21	18	49	53	22	31	46	16	163	498
	< 0.6 μm	19.5	39	14	14	18	141	23	147	229	324	896	769	200	422	608	124	2,841	6,809
	Sum (TSP)	52.1	102	37	44	51	306	45	250	345	392	1,065	928	279	514	746	185	3,306	8,595
LTC	> 10 μm	6.3	14	4	15	6	41	2	30	33	8	20	15	11	9	12	11	28	259
	10–4.9 μm	7.0	14	4	20	6	38	5	22	21	8	20	19	12	10	15	11	35	260
	4.9–2.7 μm	3.2	14	5	17	7	42	5	22	21	7	18	19	13	10	15	11	35	261
	2.7–1.3 μm	3.1	17	5	25	8	49	4	31	33	9	23	31	16	15	24	13	59	362
	1.3–0.6 μm	3.2	16	5	22	8	47	4	26	25	10	30	48	20	23	39	16	106	445
	< 0.6 μm	26.2	38	13	72	17	130	15	102	123	79	279	546	158	221	404	118	1,518	3,833
	Sum (TSP)	49.0	113	36	171	52	347	35	233	256	121	390	678	230	288	509	180	1,781	5,420
LTP	> 10 μm	12.8	15	9	11	10	23	7	4	6	10	16	13	9	11	14	14	19	191
	10–4.9 μm	10.4	15	9	11	10	24	6	9	6	9	12	12	9	10	13	11	16	182
	4.9–2.7 μm	4.4	13	8	10	10	22	5	3	3	8	10	12	8	10	13	11	16	162
	2.7–1.3 μm	5.1	14	11	12	11	25	5	4	2	10	12	16	10	12	17	12	24	197
	1.3–0.6 μm	4.2	14	10	12	11	22	4	4	1	10	13	18	10	13	19	11	35	207
	< 0.6 μm	36.5	34	21	23	22	69	13	26	39	32	81	123	41	52	122	34	434	1,166
	Sum (TSP)	73.4	105	68	79	74	185	40	50	57	79	144	194	87	108	198	93	544	2,105
LTIP	> 10 μm	12.9	12	4	5	7	36	6	31	37	18	38	22	13	12	15	12	48	316
	10–4.9 μm	16.6	13	5	5	7	38	4	45	50	39	86	36	17	20	22	14	75	476
	4.9–2.7 μm	6.8	12	5	7	7	44	7	22	28	32	69	41	17	23	27	14	75	430
	2.7–1.3 μm	4.5	12	5	7	7	43	6	24	30	37	92	59	24	36	41	20	110	553
	1.3–0.6 μm	4.4	12	5	8	7	42	6	44	45	52	128	98	34	59	62	28	163	793
	< 0.6 μm	32.3	45	17	15	21	161	26	296	379	661	1,557	1,449	393	831	844	280	2,817	9,792
	Sum (TSP)	77.5	106	41	47	56	364	55	462	569	839	1,970	1,705	498	981	1,011	368	3,288	12,360
Average	> 10 μm	11.5	15	5	11	7	35	5	25	28	13	30	21	13	12	17	13	48	297
	10–4.9 μm	12.4	15	6	13	8	39	5	28	30	18	42	29	15	16	22	14	68	369
	4.9–2.7 μm	5.6	13	5	12	8	44	5	28	34	16	39	34	16	18	25	14	66	378
	2.7–1.3 μm	4.9	14	6	15	8	40	5	27	36	20	51	57	23	29	42	18	122	512
	1.3–0.6 μm	4.3	14	6	13	8	38	4	26	29	25	67	77	26	40	54	21	159	609
	< 0.6 μm	31.6	41	16	38	19	132	19	153	206	301	813	892	233	443	605	164	2,384	6,458
	Sum (TSP)	70.4	112	45	101	58	328	45	287	364	392	1,041	1,109	325	559	765	243	2,847	8,623

LT Low traffic, *HT* High traffic, *I* Very close to industries, *P* Periphery, *C* Centre of the city

Table 4 Comparison of total PAHs and BaP concentrations (ng m^{-3}) in airborne particles in cities around the world

Country	Sampling site	Character	Survey year	Particle Size	Total PAHs	BaP	References
Spain	Sevilla	Traffic	2000–2001	TSP	8.6	0.56	Present work
	Zaragoza	Traffic	1999–2001	TSP	5.67	0.78	43
	Jinámar (Canarias)	Traffic/Power station	1999–2000	TSP	7.80	0.34	44
	Barcelona	Industrial/Traffic	1993	Particle-size	82.80	10.82	11
			1991	TSP	47.7	22.0	12
Italy	Naples	Traffic	1996–1997	PM_{10}	31.39	1.72	45
	Rome	Traffic	1994	TSP	21.17	1.73	46
				PM_{10}	19.43	1.56	
Greece	Athens	Traffic	2000	TSP	3.01	0.17	47
France	Paris	Traffic	1999–2000	Deposition	357.01	15.23	48
Germany	Munich	Traffic/industrial	1996–1998	TSP	3.48	0.45	49
United Kingdom	London	Traffic/Industrial	1991–1992	TSP	825	10	50
USA	Chicago	Traffic	1995	TSP	451.6	1.6	14
	Postdan (New York)	Rural	2000	$PM_{2.5}$	2.796	0.013	51

23

Table 5 Particle-size distribution of PAH, expressed as a percentage of the sum of TSP

Sample	Size/PAH	Naph	Ace	Acey	Flu	Phen	Ant	Flua	Pyr	BaA	Chry	BbF	BkF	BaP	InP	DbA	Bper	Total PAH
HTC	>10	14.3	13.6	10.9	12.1	9.1	12.2	8.0	7.6	3.2	3.2	1.9	3.4	2.1	2.0	4.1	2.0	3.2
	10–4.9	14.3	13.6	13.3	15.5	13.7	16.3	8.9	7.8	3.8	3.7	2.6	4.5	2.8	2.8	5.4	2.5	4.0
	4.9–2.7	12.0	11.4	11.5	13.8	19.6	12.2	17.3	15.9	4.5	4.3	3.6	5.6	4.0	3.7	5.4	2.7	5.2
	2.7–1.3	12.0	11.4	13.9	12.1	10.7	8.2	12.7	15.5	5.1	5.4	6.8	8.6	6.5	7.0	8.2	5.6	7.1
	1.3–0.6	11.3	11.4	11.5	13.8	10.9	10.2	9.5	9.3	6.4	7.0	8.1	8.3	8.3	7.8	9.3	6.2	7.5
	<0.6	36.1	38.6	38.8	32.8	36.0	40.8	43.6	43.9	76.9	76.4	77.0	69.6	76.4	76.8	67.6	81.0	73.0
	Sum (TSP)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
HTP	>10	12.7	10.8	13.6	13.7	11.1	13.3	9.2	6.1	2.6	2.2	1.8	4.3	1.9	2.0	5.4	1.3	2.9
	10–4.9	13.7	13.5	13.6	13.7	11.8	8.9	10.0	8.4	3.3	3.2	2.8	5.0	2.9	2.9	5.9	2.4	4.0
	4.9–2.7	10.8	10.8	13.6	11.8	9.2	8.9	7.2	6.4	2.8	2.4	2.6	4.7	2.5	2.7	5.9	1.9	3.3
	2.7–1.3	12.7	13.5	13.6	13.7	11.4	11.1	8.8	6.7	4.1	3.5	4.2	6.5	4.5	4.7	7.0	3.6	4.8
	1.3–0.6	11.8	13.5	13.6	11.8	10.5	6.7	6.0	6.1	4.6	4.6	5.7	7.9	6.0	6.2	8.6	4.9	5.8
	<0.6	38.2	37.8	31.8	35.3	46.1	51.1	58.8	66.4	82.7	84.1	82.9	71.7	82.1	81.5	67.0	85.9	79.2
	Sum (TSP)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
LTC	>10	12.4	11.1	8.8	11.5	11.8	5.7	12.9	12.9	6.6	5.1	2.2	4.8	3.1	2.4	6.1	1.6	4.8
	10–4.9	12.4	11.1	11.7	11.5	11.0	14.3	9.4	8.2	6.6	5.1	2.8	5.2	3.5	2.9	6.1	2.0	4.8
	4.9–2.7	12.4	13.9	9.9	13.5	12.1	14.3	9.4	8.2	5.8	4.6	2.8	5.7	3.5	2.9	6.1	2.0	4.8
	2.7–1.3	15.0	13.9	14.6	15.4	14.1	11.4	13.3	12.9	7.4	5.9	4.6	7.0	5.2	4.7	7.2	3.3	6.7
	1.3–0.6	14.2	13.9	12.9	15.4	13.5	11.4	11.2	9.8	8.3	7.7	7.1	8.7	8.0	7.7	8.9	6.0	8.2
	<0.6	33.6	36.1	42.1	32.7	37.5	42.9	43.8	48.0	65.3	71.5	80.5	68.7	76.7	79.4	65.6	85.2	70.7
	Sum (TSP)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
LTP	>10	14.3	13.2	13.9	13.5	12.4	17.5	8.0	10.5	12.7	11.1	6.7	10.3	10.2	7.1	15.1	3.5	9.1
	10–4.9	14.3	13.2	13.9	13.5	13.0	15.0	18.0	10.5	11.4	8.3	6.2	10.3	9.3	6.6	11.8	2.9	8.6
	4.9–2.7	12.4	11.8	12.7	11.9	12.5	12.5	6.0	5.3	10.1	6.9	6.2	9.2	9.3	6.6	11.8	2.9	7.7
	2.7–1.3	13.3	16.2	15.2	14.9	13.5	12.5	8.0	3.5	12.7	8.3	8.2	11.5	11.1	8.6	12.9	4.4	9.4
	1.3–0.6	13.3	14.7	15.2	14.9	11.9	10.0	8.0	1.8	12.7	9.0	9.3	11.5	12.0	9.6	11.8	6.4	9.8
	<0.6	32.4	30.9	29.1	29.7	37.3	32.5	52.0	68.4	40.5	56.3	63.4	47.1	48.1	61.6	36.6	79.8	55.4
	Sum (TSP)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
LTIP	>10	11.3	9.8	10.6	12.5	9.9	10.9	6.7	6.5	2.1	1.9	1.3	2.6	1.2	1.5	3.3	1.5	2.6
	10–4.9	12.3	12.2	10.6	12.5	10.4	7.3	9.7	8.8	4.6	4.4	2.1	3.4	2.0	2.2	3.8	2.3	3.9
	4.9–2.7	11.3	12.2	14.9	12.5	12.1	12.7	4.8	4.9	3.8	3.5	2.4	3.4	2.3	2.7	3.8	2.3	3.5
	2.7–1.3	11.3	12.2	14.9	12.5	11.8	10.9	5.2	5.3	4.4	4.7	3.5	4.8	3.7	4.1	5.4	3.3	4.5
	1.3–0.6	11.3	12.2	17.0	12.5	11.5	10.9	9.5	7.9	6.2	6.5	5.7	6.8	6.0	6.1	7.6	5.0	6.4
	<0.6	42.5	41.5	31.9	37.5	44.2	47.3	64.1	66.6	78.8	79.0	85.0	78.9	84.7	83.5	76.1	85.7	79.2
	Sum (TSP)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Mean	>10	13.1±1.3	11.9±1.7	10.9±2.2	12.7±0.9	10.6±1.4	12.1±4.3	8.6±2.4	7.8±2.9	3.2±4.4	2.9±3.8	1.9±2.2	3.9±3.1	2.2±3.7	2.2±2.3	5.2±4.8	1.7±0.9	3.4±2.7
	10–4.9	13.4±1.0	12.8±1.1	12.6±1.4	13.4±1.5	11.9±1.4	12.1±4.0	9.8±3.8	8.4±1.1	4.5±3.3	4.1±2.0	2.7±1.6	4.7±2.7	2.9±2.9	2.9±1.8	5.6±3.1	2.4±0.4	4.3±2.0
	4.9–2.7	11.8±0.7	11.9±1.2	11.7±1.9	13.1±0.8	13.5±3.9	12.1±2.0	9.8±5.0	9.2±4.5	4.2±2.8	3.7±1.7	3.0±1.6	5.0±2.2	3.3±2.8	3.3±1.6	5.6±3.1	2.3±0.4	4.4±1.8
	2.7–1.3	12.9±1.4	13.7±1.8	14.4±0.7	13.7±1.4	12.1±1.4	10.7±1.6	9.5±3.4	9.9±5.2	5.1±3.6	4.9±1.8	5.1±2.0	7.0±2.5	5.2±2.9	5.5±1.9	7.4±2.8	4.3±1.0	5.9±2.0
	1.3–0.6	12.3±0.3	13.3±1.3	13.2±2.1	13.7±1.5	11.6±1.2	9.8±1.9	9.1±1.9	8.1±3.2	6.3±3.1	6.4±1.6	6.9±1.5	8.0±1.7	7.2±2.5	7.1±1.4	8.8±1.6	5.6±0.7	7.1±1.6
	<0.6	36.5±4.0	36.3±3.9	37.2±5.4	33.3±2.9	40.2±4.6	43.3±7.1	53.2±9.1	56.6±11.7	76.7±17.1	78.1±10.7	80.4±8.6	71.5±11.9	79.3±14.7	79.0±8.7	67.4±15.1	83.7±2.9	74.9±9.8
	Sum (TSP)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

LT Low traffic, *HT* High traffic, *I* Very close to industries, *P* Periphery, *C* Centre of the city

Table 6 PAH[a] concentrations (ng m^{-3}) in equivalent PM inlets

	PM$_{10}$	PM$_{2.5}$	PM$_1$
Particulate matter (µg m^{-3})	58.9 (83.6)	40.8 (58.0)	35.9 (51.0)
Naphthalene (Naph)	0.097 (86.9)	0.069 (61.7)	0.055 (48.8)
Acenaphthene (Ace)	0.040 (88.1)	0.029 (63.3)	0.022 (49.6)
Acenaphthylene (Acey)	0.090 (89.1)	0.066 (64.8)	0.051 (50.4)
Fluorene (Flu)	0.051 (87.3)	0.035 (60.8)	0.027 (47.1)
Phenanthrene (Phen)	0.293 (89.4)	0.210 (63.9)	0.170 (51.8)
Anthracene (Ant)	0.039 (87.9)	0.029 (63.8)	0.024 (53.1)
Fluoranthene (Flua)	0.262 (91.4)	0.206 (71.8)	0.179 (62.3)
Pyrene (Pyr)	0.335 (92.2)	0.271 (74.6)	0.235 (64.7)
Benzo[a]anthracene (BaA)	0.379 (96.8)	0.345 (88.1)	0.325 (83.0)
Chrysene (Chry)	1.012 (97.1)	0.931 (89.4)	0.880 (84.5)
Benzo[b]fluoranthene (BbF)	1.088 (98.1)	1.025 (92.4)	0.968 (87.3)
Benzo[k]fluoranthene (BkF)	0.313 (96.1)	0.281 (86.5)	0.259 (79.5)
Benzo[a]pyrene (BaP)	0.547 (97.8)	0.513 (91.7)	0.484 (86.5)
Indeno[1,2,3-cd]pyrene (InP)	0.749 (97.8)	0.702 (91.7)	0.659 (86.2)
Dibenz[a,h]anthracene (DbA)	0.230 (94.8)	0.203 (83.6)	0.185 (76.2)
Benzo[ghi]perylene (Bper)	2.799 (98.3)	2.665 (93.6)	2.543 (89.3)
Total PAH	8.326 (96.6)	7.579 (87.9)	7.067 (82.0)

a The proportion of the TSP level (in %) is given in parentheses