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Determination of polycyclic aromatic hydrocarbons (PAHs) from organic aerosols using hollow fiber micro – porous membrane liquid – liquid extraction (HF-MMLLE) followed by gas chromatography–mass spectrometry analysis

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ABSTRACT

A method for determination of polycyclic aromatic hydrocarbons (PAHs) from aerosols was developed. Instead of conventionally used non-polar or slightly polar phenylmethylpolysiloxane column a highly polar, highly substituted, cyanopropyl column (VF-23 MS) was used for separation of PAHs. Based on hollow fiber micro-porous membrane liquid–liquid extraction (HF-MMLLE) a method was developed for sample clean up and pretreatment. An enrichment factor of 617–1022 was obtained with extraction efficiency 10.2–18.9% for different PAHs analyzed in this study. The optimized method was successfully applied to aerosol samples and limits of detection between 1.2 pg m^{-3} and 180 pg m^{-3} was obtained. Almost all PAHs were found in most of the aerosol samples.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) belong to a class of hydrophobic organic contaminants (HOC) comprised of two or more fused benzene rings [1]. PAHs have a variety of aspects: chemical, toxicological, engineering, technological, public health, economic, regulatory, and legislative. PAHs range from semi-volatile to high boiling points molecules. They are generally lipophilic, a property that increases with increasing complexity of the compounds [2].

There has been a worldwide increase in interest in PAHs because of their known carcinogenic and mutagenic properties [3,4]. PAHs have been measured extensively during the last few years throughout the environment, i.e., in aerosols, soil, water, sludge and sediment [5–9]. Due to their low aqueous solubility and their hydrophobic and lipophilic properties, PAHs, once emitted into the environment, can be easily bio-accumulated to such an extent that can threaten the safety of food chains for both man and animals [7]. PAHs condense and usually appear in the atmosphere as particles smaller than 3 μm. They mainly affect lungs and may cause lung cancer, but they have also been linked to skin and bladder cancer [8,10,11].

PAHs are the most stable form of hydrocarbons having low hydrogen-to-carbon ratio and usually occur in complex mixtures rather than single compounds [12]. The ubiquitous nature of these airborne PAHs is due to their emissions from a wide range of combustion sources, including combustion of fossil fuels in heat generation [13], diesel and gasoline engines [14], biomass burning of agricultural and forest fuels [15,16], outdoor wood smoke [17] and municipal incinerators [18]. PAHs are also common constituents of indoor air, arising from coal and [19], wood combustion [20], and tobacco smoke [21].

The total concentration of PAHs has been extensively studied in urban [9,22] and marine aerosols [23] as well as under background conditions [24]. Somewhat less attention has been paid to the size distribution of PAHs on aerosol particles. Sicre et al. found mass median diameters for total PAH content between 0.75 and 1.27 μm in marine aerosols [25]. They observed that most of the PAHs are adsorbed on particles having aerodynamic diameter ≤1.5 μm. Some other studies have shown that independent of the ring number, most of the PAHs are adsorbed on aerosol particles corresponding to aerodynamic diameters between 0.25 and 2.0 μm. The highest concentration in the 0.25–2.0 μm size range can be interpreted by the fact that PAHs are deposited mainly on

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soot particles of this size [26]. The PAHs level also changes with the seasons and the location. It is usually higher in urban than in rural areas. Changes in emission patterns and meteorological conditions are the main factors contributing to this difference [27].

Matrices of environmental samples are quite complex as; they exist in a variety of phases. Aerosols (generally particular matter) are a mixture of countless organic and inorganic species with a larger portion of inorganic and a considerable portion of organic species depending upon nature of sampling site. Organic matter in aerosol is also very complex consisting of various different classes of compounds, originating directly from processes at the source and complicated secondary processes in the atmosphere [28].

In recent years, sensitive, rapid and accurate methods have been developed to determine PAHs and their derivates in atmospheric particles. Gas chromatography with flame ionization detector (GC-FID) and high performance liquid chromatography with fluorescence detector (HPLC-FL) are the conventional analytical methods to determine the un-substituted PAHs. However, most of these methods lack specificity in their detection and give false positives when used to analyze complex mixtures. Due to this fact, GC–MS is recently the most used method for the determination of PAHs; it allows working with complex matrixes, giving a high specificity and sensitivity [29].

Numerous compounds in aerosols exist as trace constituents and cannot be detected by general analytical methods that are less sensitive. Therefore extraction and pre-concentration steps are of utmost importance prior to the analysis of compounds existing in very low level.

Hence, analysis of PAHs from complex particulate matter should include extraction of PAHs into a suitable solvent, pre-concentration, clean up, separation and detection techniques for multi-component mixtures.

Generally aerosol samples are extracted with large amount of organic solvent using sonication [30], microwave assisted extraction [31] or Soxhlet extraction [32,33]. After extraction, a time consuming and laborious pre-concentration step is needed that requires evaporation of a large portion of organic solvent into environment, using nitrogen flow [34] or rotary evaporator [31]. This step is not only having environmental concerns, but also may result in loss of target analytes during evaporation.

Liquid–liquid extraction (LLE) is a classical technique that has been often used for carrying out the extraction and pre-concentration of many environmental hydrophobic contaminants from various kinds of samples. For example, LLE is recommended in the draft US Environmental Protection Agency (EPA) method 1614 for analysis of PBDEs [35]. However LLE is a time consuming process with many drawbacks such as using large volumes of expensive, high purity organic solvents, loss of analytes while evaporating the organic solvent in pre-concentration step, intensive-labor, etc. To overcome these disadvantages some better techniques like solid-phase extraction (SPE) [36] and solid-phase microextraction (SPME) [37] have been introduced, but still with some limitations. A further improvement came by introduction of a novel technique termed solvent micro-extraction (SME) but also here, some practical considerations limit it [38,39].

Micro-porous membrane liquid–liquid extraction (MMLLE) is a suitable technique for extracting and concentrating hydrophobic compounds from aqueous samples. MMLLE is a two-phase membrane extraction technique based on an aqueous phase (donor or sample phase) and an organic (acceptor) phase. The organic phase is supported by a hydrophobic membrane, which keeps the solvent in position. The organic phase fills the membrane pores and the acceptor channel (in case a flat membrane is used) or the lumen (in case a hollow fiber (HF) membrane is used) [40].

In the present study we developed an environment friendly analytical method that uses only a few micro-liters of organic solvent and is very efficient in sample clean up, and pre-concentration. We used HF-MMLLE for pre-concentration and enrichment of analytes. Analytes were concentrated from large volume of aqueous phase to a few microliters of an organic solvent (n-undecane) in the lumen of the hollow fiber. Also instead of conventionally used slightly polar column, i.e., 5% phenylmethylpolysiloxane (DB-5 MS) and 50% phenylmethylpolysiloxane (DB-17 MS), we used a high polarity and highly substituted cyanopropyl column (VF-23 MS). This type of column has never been used for PAHs separation. This column not only gives symmetric peaks without any tailing, but also the co-eluting pairs of PAHs were well separated even at very low concentrations. We obtained an LOD ranging from 1.2 pg m^{-3} to 180 pg m^{-3} for 9 PAHs analyzed in this study.

2. Materials and methods

2.1. Reagents and standards

The standards of PAHs were purchased from Fluka (Steinheim, Germany) and consisted of naphthalene, acenaphthylene, fluoranthene, benz[e]acephenanthrylene, chrysene, 1,2-benzanthracene, phenanthrene, pyrene and acenaphthene.

1-Phenyldodecane (97%) was provided by Acros Organics (Geel, Belgium). Acetone (HPLC grade) and dihexyl ether (97%) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Methanol (HPLC grade) was provided from Fisher Scientific (Waltham, MA, USA). n-Hexane (≥99%) and undecane (≥99%) was purchased from Fluka (Stenheim, Germany). Dodecane (99%) was from BDH Laboratories Supplies (Poole, UK) and helium gas (99.9995%) was provided from Strandmøllen Lab Line (Denmark).

Ultrapure reagent water purified by a Milli-Q gradient system (Millipore, Bedford, MA, USA) was also used. The Q3/2 Accurel PP polypropylene hollow-fiber membranes (HF) (200 μm wall-thickness, 600 μm inner diameter, 0.2 μm pore size) were obtained from Membrana GmbH (Wuppertal, Germany).

Individual standard solutions of each PAH were prepared at concentrations of 1000 μg mL^{-1} in n-hexane. A mixture solution containing the nine PAHs was prepared at concentration of 50 μg mL^{-1} in methanol from each individual solution.

An internal standard solution of 500 μg mL^{-1} of 1-phenyldodecane was prepared in n-hexane. From this solution two solutions of 1 μg mL^{-1} were prepared. One of them was diluted with n-hexane and the other one with methanol.

The direct calibration curves were established from standard solutions in methanol at 12 different concentrations levels (8–2000 ng mL^{-1}) and injecting them directly in the GC–MS. 1-Phenyldodecane was used as an internal standard. Each level of concentration was analyzed in triplicate.

For the calibration curve after extraction, solutions with concentrations ranging 25–2000 ng mL^{-1} were also prepared from the 50 μg mL^{-1} mixture. However, in this case the internal standard (1-phenyldodecane) was added after the extraction using 1 μg mL^{-1} solution in n-hexane and adding the half volume of the volume obtained from the extraction. After this process, the solutions were injected into the GC–MS.

All the solutions were stored in the refrigerator at 4 °C.

2.2. Sample collection

The sampling site Vavihill is a EUSAAR and EMEP (European Monitoring and Evaluation Programme) background station situated in Southern Sweden (56°01′N, 13°09′E, 172 m a.s.l.). The station is not situated close to any local pollution sources, although the distances to the densely populated areas of Malmö, Copenhagen

Table 1
Retention time and selected ions for quantification and confirmation of PAHs.

Compound	t_R (min)	Target ion (m/z)	Confirmation ions (m/z)
Napthalene	3.35	128	102, 127, 129
Acenaphthene	6.74	154	77, 152, 153
Acenaphthylene	7.37	152	76, 150, 151
Phenanthrene	11.55	178	76, 89, 152, 176
Fluoranthene	14.71	202	100, 101, 200
Pyrene	15.21	202	100, 101, 200
1,2-Benzanthracene	19.32	228	114, 226, 229
Chrysene	19.49	228	114, 226, 229
Benzo[e]acephenanthrylene	27.63	252	113, 126, 250, 253

and Helsingborg west to southwest of the station are only 45, 50 and 25 km, respectively.

Samples were collected weekly on 47 mm quartz filters (Pall Tissuquartz™, binder free) by an aerosol flow of 38 l/min from a PM10 inlet. Samples collected between April 2008 and April 2009 were used in this study. Filters were baked in 900 °C for 4 h prior to sampling. After sampling the filters were stored in a Petri dish, wrapped in aluminum foil in the refrigerator (+8 °C) or freezer (−30 °C).

2.3. Hollow-fiber microporous membrane liquid–liquid extraction (HF-MMLLE)

Prior to the extraction, hollow fibers were cut into pieces of 3.8 cm length and sealed at the two ends using a hot surface. After that the fiber pieces were cleaned with acetone and dried overnight. Then, the fiber pieces had a length of 3.5 cm with sampling phase volume of 10 μL in the lumen. The fibers were filled with the solvent by sonication, placing them in a vial filled with the solvent (n-undecane) for 2 h. Then, the fiber pieces (now solvent bars) were ready for the extraction.

Each aerosol-sampling filter was added to the aqueous phase (100 mL reagent water) for extraction and stirred for 3 h (optimized time) at 1000 rpm. Then, the fiber was immersed in water and briefly shaken to wash away any excess of organic solvent on the surface. After that, the prepared hollow fiber was put into the aqueous phase for the extraction. During the extraction the solution was stirred at 600 rpm for 30 min (parameters optimized in this study). For the extraction, a magnetic stirrer model D-79219 (IKA-WERKE, Staufen, Germany) and an Agilent Gold Standard Syringe (Agilent Technologies, Palo Alto, USA) were used.

After the extraction, the HF was taken out. In order to collect the volume in the lumen one of the HF ends was punctured with a 10 μL GC syringe, while the other end was cut. Approximately 10 μL of solvent was obtained and put in a vial. The syringe was cleaned several times with acetone to avoid interferences from one sample to other one.

In this vial, 1 μg mL^{-1} solution of internal standard was added. Its volume was half of the volume obtained from the HF. In this way, the concentration of the internal standard was kept at 333 ng mL^{-1} and all the samples were diluted 1.5 times after the extraction process. The solution was properly mixed and injected in the GC–MS.

2.4. GC–MS analysis

All the analyses were performed using a 6890 Series gas chromatograph equipped with a split/splitless 7683 Series injector, an autosampler and a 5973-N Mass Selective detector (Agilent Technologies, Palo Alto, USA).

Analytes were separated using a VF-23 ms Factor Four™ capillary column (Model CP8822) of 30 m × 0.25 mm with a phase thickness of 0.25 μm (Varian, Darmstadt, Germany).

The final temperature program was: 120 °C, hold 0.5 min, increased at 10 °C min^{-1} to 143 °C, increased at 2 °C min^{-1} to 147 °C and increased at 10 °C min^{-1} to a final temperature of 255 °C and hold 15 min (total analysis time: 30.60 min). The carrier gas used was helium (99.9995%) with a flow rate of 1.5 mL min^{-1}. The injector temperature was 250 °C, and the injection was done in split mode with a split ratio of 26.5 and a split flow of 40.0 mL min^{-1}.

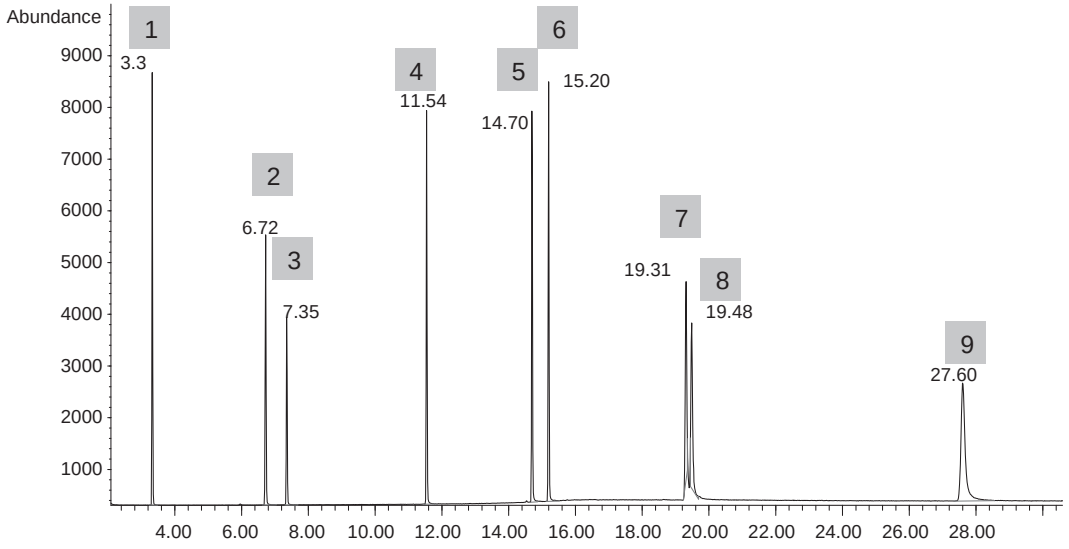

Fig. 1. SIM chromatograms with all the nine PAHs (Approx 4 fg of each compound) (1: naphthalene; 2: acenaphthene; 3: acenaphthylene; 4: phenanthrene; 5: fluoranthene; 6: pyrene; 7: 1,2-benzanthracene; 8: chrysene; 9: benzo[e]acephenanthrylene).

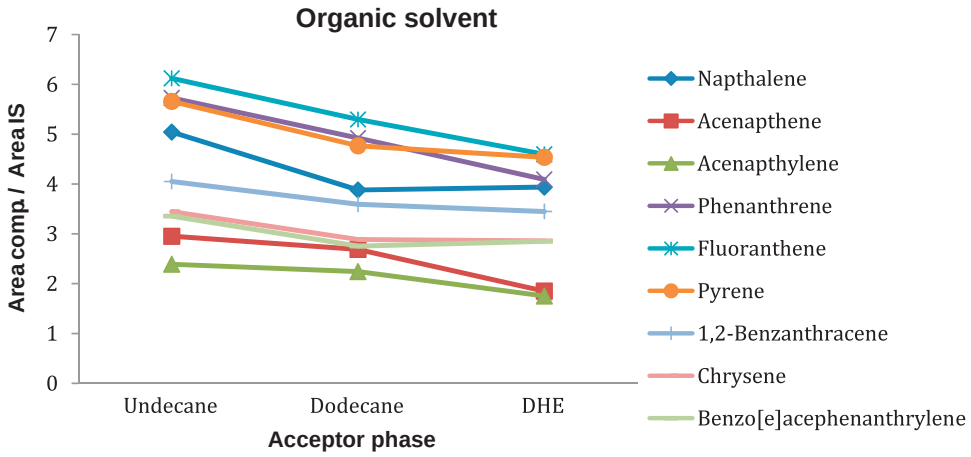

Fig. 2. Effect of the organic solvent with extraction time 1 h at 800 rpm stirring speed, while reagent water was spiked at a concentration of 10 ng L^{-1}.

The injection volume was 1 μL. The transfer line, quadrupole and ion source temperatures were 260 °C, 180 °C and 240 °C, respectively. The MS operated in the electron impact ionization mode (EI) at 70 eV. Scan mode was used for the standard and for the identification of each compound. The scan mass range was set to 50–300 *m*/*z*. For the quantification of PAHs in the samples selective ion monitoring mode (SIM) was used. The most abundant ion was used for quantification in each case, while the other two or three most abundant ions were usually used for the identification of the analyte (see Table 1).

Under the above-mentioned conditions even for very low concentrations of PAHs a good separation was obtained with symmetric peaks without tailing, see Fig. 1.

3. Results and discussion

3.1. Method optimization

In HF-MMLLE, mass transfer of the analyte from the aqueous sample to the organic solvent in the hollow fiber and the partition coefficient of the analyte between the aqueous sample and the organic phase play key role in extraction of required analytes. There are several parameters, such as type of organic solvent, sample pH, extraction time, and stirring speed that have an impact on the extraction process. In the present study samples were in form of particulate matter on a filter paper. So as a first step a suitable piece of filter paper was stirred in reagent water for a period of 3 h to dissolve the PAHs in aqueous media. Then a method was optimized for the extraction of PAHs from reagent water to organic solvent [41].

3.2. Selection of the organic solvent

For the selection of the organic solvent, several factors must be considered: high partition coefficient for the desired compounds compared to the matrix components to get a high selectivity, low solubility in water to prevent the dissolution in the aqueous phase, low volatility to avoid the evaporation during the extraction process and similar polarity of the solvent and the fiber to facilitate the immobilization within the pores of the hollow fiber [42].

In this study, three solvents accomplishing these characteristics were tried as possible acceptor solvents: dodecane, n-undecane and dihexyl ether. The selection of the organic solvent was based on the ability of the solvent to extract the analytes.

While the acceptor phase was changed, all the other parameters where kept constant. Firstly, several fibers were prepared and then three of them were filled with each solvent. The extraction time used was 1 h, the stirring speed was 800 rpm and no organic solvent was added to the aqueous phase. 10 μL of a mixture of PAHs at 1 μg mL^{-1} was spiked in the aqueous phase for this optimization.

As is shown in Fig. 2, comparing the ratios between the areas of each compound and the internal standard, n-undecane shows higher response than the other solvents. Dihexyl ether (DHE) was not a suitable solvent; the ether group gives polarity to the solvent decreasing the interaction of these non-polar compounds with the solvent. In addition, this group, containing oxygen is differing from the nature of PAH molecules.

The difference between undecane and dodecane is not too high, but there is a slightly higher response with undecane. Furthermore, the separation of our analytes from the solvent peak was also more difficult with dodecane and DHE than using n-undecane.

Toluene is also known as a good extraction solvent because of its selectivity towards the analytes and its GC performance, but it was not tried due to its high volatility.

The easiest extracted compound is naphthalene; meanwhile the most difficult PAH to be extracted is acenaphthylene. The tendency of each compound to be extracted does not change when the solvent varies.

3.3. Addition of methanol to donor phase

PAHs are known as hydrophobic compounds with very low water solubility, which also decreases when the molecular weight of the PAH increases. It could be a problem during the extraction because the analytes might not be properly dissolved in the donor phase and perhaps be adsorbed to container walls, etc.

To increase this solubility, an organic solvent such methanol or acetonitrile is often added to the sample. The concentration of the organic solvent is a critical parameter because if it is too high PAHs will be too soluble in the donor phase and extracting them to the acceptor phase will be a more difficult step [43].

In this work, the influence of methanol content was studied by adding 0–20% methanol to the aqueous phase. The extraction time was kept constant at 60 min, the stirring speed was also constant at 800 rpm and the fibers were filled with n-undecane. Again, 10 μL of a mixture of PAHs at 1 μg mL^{-1} was spiked in the aqueous phase for this optimization.

The response decreased with the addition of organic solvent. It means that addition of methanol increases the organic contents of donor phase making it more likely to dissolve PAHs. It results in decrease of extraction efficiency. Hence we did not use methanol in donor phase.

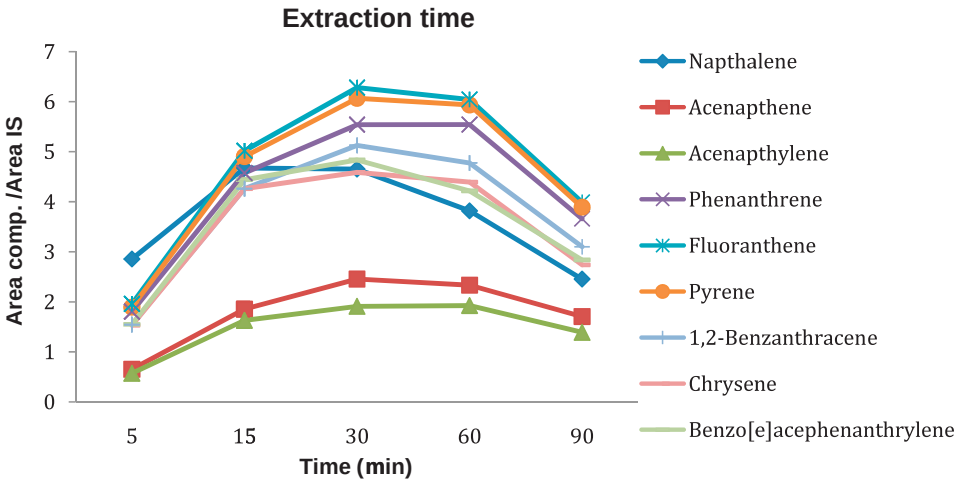

Fig. 3. Effect of the extraction time with stirring speed 800 rpm, n-undecane solvent and reagent water spiked with a concentration of 10 ng L^{-1}.

3.4. Extraction time

Hollow fiber extraction is a time-dependent dynamic process during which there is a partitioning of the target compounds between the hollow fiber and the sample solution. The extraction time is also one of the most important factors to be optimized [44].

To determine the influence of the extraction time, aqueous standard solutions were spiked with 10 μL of a mixture of 1 μg mL^{-1} containing all the PAHs. The extraction solvent was n-undecane, organic solvent was not added to the aqueous phase and the stirring speed was kept constant at 800 rpm.

The response increased with the extraction time until 30 min, see Fig. 3. After this time, the response slightly decreased until 60 min but later on the decrease was considerable. This behaviour of the PAHs can be explained because long extraction times increase solvent loss and thus a decrease in the amount extracted. Finally, 30 min was selected as the optimum time.

3.5. Stirring speed

The agitation of the sample reduces the time to reach the thermodynamic equilibrium, especially for the analytes with high molecular weight [43]. To optimize the stirring speed, all other parameters were kept constant (undecane as extraction solvent, no addition of methanol in the aqueous phase and extraction time of 30 min) and 10 μL of the mixture of PAHs (1 μg mL^{-1}) was added.

In Fig. 4 is shown that the response with the stirring speed increases until 600 rpm, but after that the response remains almost constant and for some compounds, it also decreases a little. So, the selected stirring speed was 600 rpm.

The amount of PAHs extracted increases with the stirring speed because it enhances the mass transfer from the bulk of the sample to the hollow fiber surface. Furthermore, when the stirring speed is too high, the amount of analytes decreases due to a generation of bubbles on the surface of the hollow fiber and the loss of organic solvent. Higher velocity (1000 rpm) was also tried and the result was that most of the fibers were destroyed causing a leakage of solvent to the aqueous phase and loss of analytes. In this case the extraction did not work.

The following optimized conditions were selected for the further experiments: hollow fibers of 3.8 cm length and an inner diameter 600 μm impregnated with n-undecane (about 10 μL in the lumen of fiber). The fibers were put in the aqueous phase (100 mL of water) without adding any organic solvent and stirred at 600 rpm for 30 min.

3.6. Method validation

For the analytical method validation, water samples spiked at different levels were analyzed. Linearity, method precision and limits of detection (LODs) were calculated. These parameters are shown in Table 2.

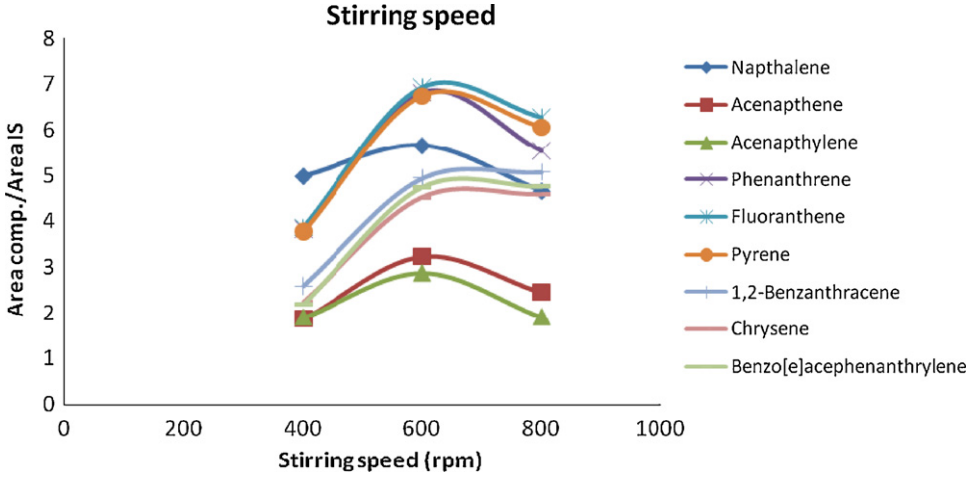

Fig. 4. Effect of the stirring speed with extraction time 1 h, solvent n-undecane, stirring speed 800 rpm and reagent water spiked with 10 ng L^{-1}.

Table 2
Parameters for the analytical performance.

Compound	Linearity range (ng L^{-1})	R^2	LOD (ng L^{-1})	LOD (pg m^{-3})[a]	Repeatability (%RSD, $n=3$)	Reproducibility (%RSD, $n=3$)
Napthalene	16.6–1333	0.9916	1	12	9.2	11.1
Acenaphthene	16.6–1000	0.9946	5	60	18.2	20.0
Acenaphthylene	16.6–1333	0.9954	5	60	10.7	11.2
Phenanthrene	16.6–1000	0.9970	0.1	1.2	5.8	7.5
Fluoranthene	16.6–1000	0.9937	2	24	3.6	4.3
Pyrene	16.6–1000	0.9972	3	36	2.7	4.2
1,2-Benzanthracene	33.3–1000	0.9978	6	72	0.8	2.9
Chrysene	66.6–1000	0.9924	8	96	15.8	16.5
Benzo[e]ace-phenanthrylene	66.6–1000	0.9929	15	180	12.0	12.6

[a] Concentrations in term of pg m^{-3} were calculated by assuming that the filter paper was exposed to 100 m^3 air.

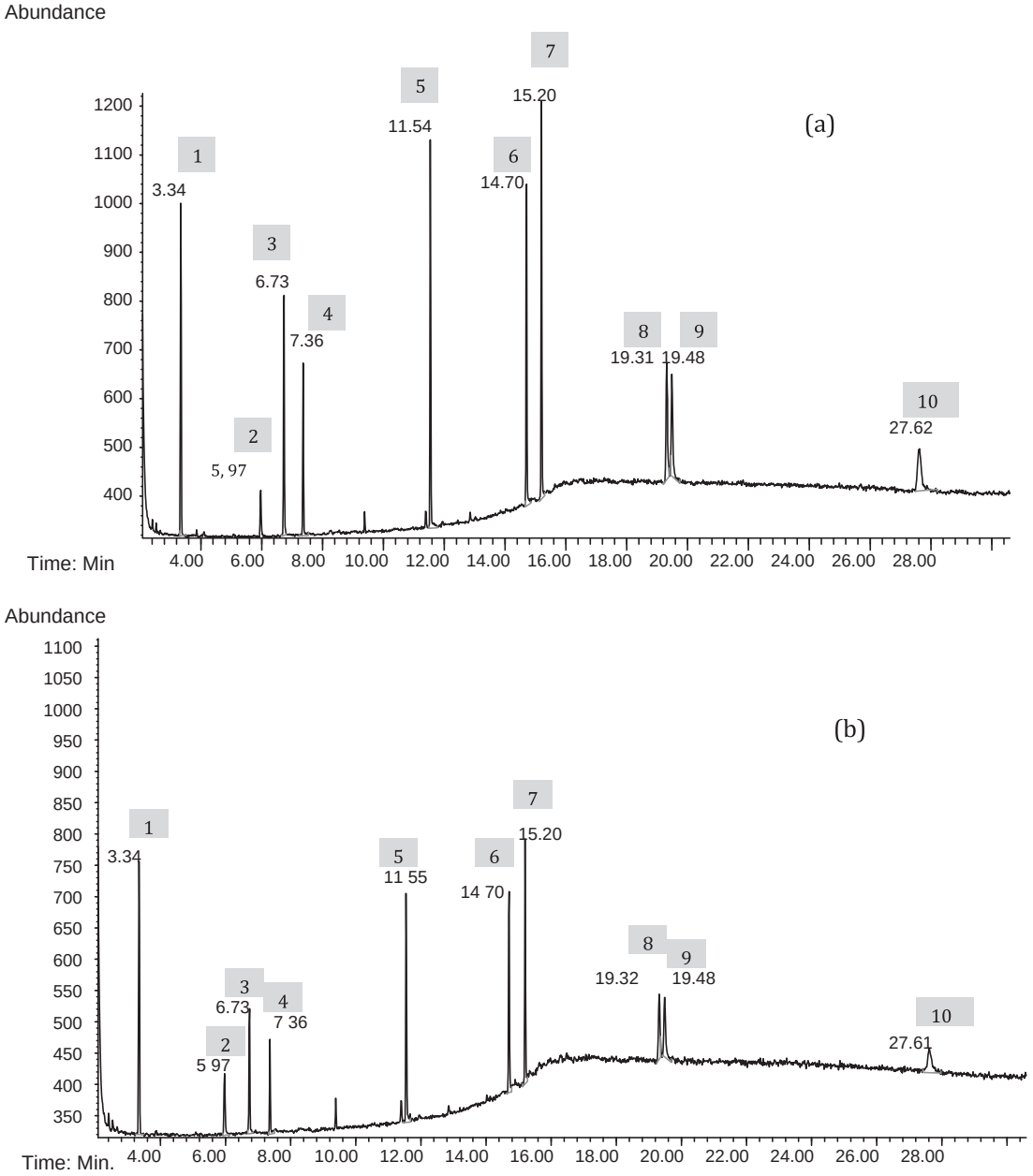

Fig. 5. SIM chromatograms with all the nine PAHs and the internal standard (1: naphthalene; 2: 1-phenyldodecane (IS); 3: acenaphthene; 4: acenaphthylene; 5: phenanthrene; 6: fluoranthene; 7: pyrene; 8: 1,2-benzanthracene; 9: chrysene; 10: benzo[e]acephenanthrylene). (a) is a chromatogram from a pure water sample extract spiked with 100 ng L^{-1} of PAHs and (b) is a chromatogram from a spiked filter, so that the aqueous extract gets same concentration as in (a) if all is extracted from filter paper.

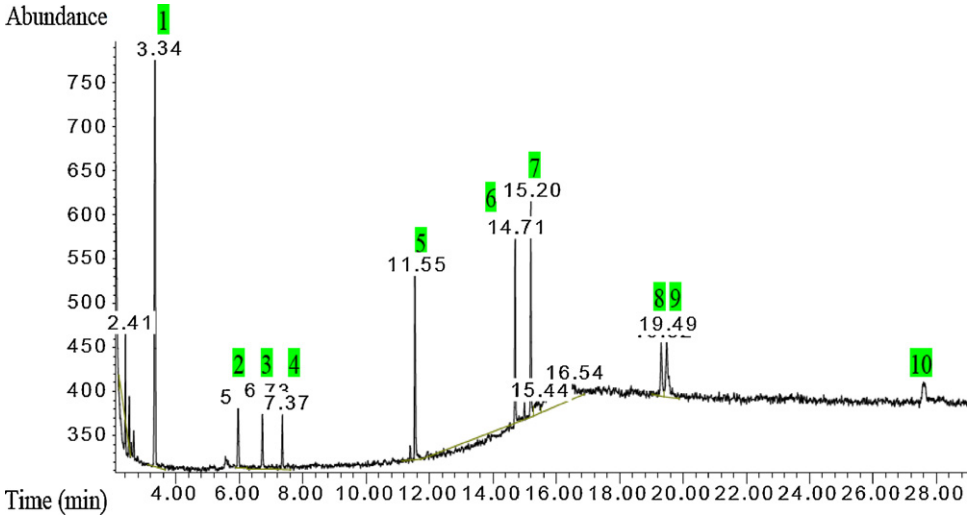

Fig. 6. SIM chromatogram of AJ-8 sample (collected on 7th January 09'). All the nine studied PAHs could be found in the sample. Also the internal standard was added for the quantification. Peak identification (1: naphthalene; 2: 1-phenyldodecane (IS); 3: acenaphthene; 4: acenaphthylene; 5: phenanthrene; 6: fluoranthene; 7: pyrene; 8: 1,2-benzanthracene; 9: chrysene; 10: benzo[e]acephenanthrylene).

Table 3
Enrichment factors and extraction efficiencies.

Compound	Enrichment factor	Extraction efficiency (%)
Napthalene	1017	18.9
Acenaphthene	711	12.7
Acenaphthylene	618	10.2
Phenanthrene	861	14.1
Fluoranthene	768	12.8
Pyrene	751	12.2
1,2-Benzanthracene	820	11.5
Chrysene	832	11.9
Benzo[e]acephenanthrylene	1022	12.3

The calibration curves were established by spiking the reagent water at eight different concentration levels (2.5–2000 ng L^{-1}). The extraction was performed using the optimal parameters and the internal standard was added after the extraction. Each level of concentration was analyzed in triplicate. The ratios of the peak area of each analyte versus the peak area of the internal standard were used for the calibration curve. All the analytes showed good linearity with squared regression coefficients between 0.9916 and 0.9978.

The LODs were calculated at a signal to noise ratio of 3 and ranged from 1.2 to 180 pg m^{-3}.

The method repeatability and reproducibility were calculated from water samples spiked with 10 ng L^{-1} of a mixture of PAHs.

For the repeatability, the final extracts were injected three times, and for the reproducibility, the process was repeated three consecutive days. The results are expressed as relative standard deviation values (RSD). The precision of the process (RSD) was 0.8–18% for repeatability and 2.9–20% for reproducibility.

3.7. Enrichment factor and extraction efficiency

To obtain the enrichment factor and the extraction efficiency, direct calibration curves for the GC–MS analysis were established by injection of methanol solutions without extraction. In these curves, all the analytes showed good linearity with squared regression coefficients between 0.9950 and 0.9995.

For the calculation of the enrichment factors, the aqueous phase was spiked with 10 μL of a 1 μg mL^{-1} solution (the final donor concentration was thus 100 ng L^{-1}). Meanwhile, for the calculation of the efficiency in the filter extraction some blank quartz filters (similar to those used in aerosol sampling) were spiked also with 10 μL of the same solution and kept overnight at 4 °C. After that, the filter was stirred for 3 h at 1000 rpm and the extraction was performed. The chromatograms obtained are shown in Fig. 5.

Shorter stirring times were tried but the extraction efficiencies were lower (results not shown). Trying longer times than 3 h did not produce better results. The peak areas of the extracts obtained by spiking the filters are lower than the areas obtained by spiking the aqueous sample directly. It means that not all the analytes could pass from the filter to the aqueous phase.

The extraction efficiency was evaluated using the direct calibration curves. The values are shown in Table 3. This parameter takes values from 10 to 19%. This is because analytes are lost in two ways: from the filter to the aqueous phase and from the aqueous phase to the acceptor phase. The enrichment factors (increase in concentration from the aqueous solution to that in the organic extract) ranged between 618 and 1017 times.

3.8. Analysis of aerosol samples

After optimizing the method, it was used for the quantification of PAHs in some aerosol samples. The selected samples were taken in the South of Sweden at different dates. As described above, the filters were extracted with water, HF-MMLLE was applied to all the samples using the optimized parameters, and then they were injected to the GC–MS.

In Fig. 6 is shown a chromatogram of the sample AJ-8. The chromatogram was obtained using the SIM mode. The only peaks that can be seen are nine peaks of the PAH compounds. In this sample all the nine PAHs could be identified. All the retention times coincide with the retention times in Fig. 5, referring to the spiked standard solutions.

Table 4 shows also the results obtained for all the analyzed samples. The name of each sample, the date when it was collected, and the amount of each PAH in each sample are included in this table.

According to the results, the most important PAH in aerosol samples from the South of Sweden is naphthalene and the less common PAHs are 1,2-benzanthracene and benzo[e]acephenanthrylene. The nine studied PAHs were found in all the samples extracted. However, in some of them the concentration obtained was below the quantification limits (LOQ).

Table 4
Amount of PAHs in aerosol samples, expressed in ng m^{-3}.

	AJ-13 27.05.08	AJ-15 30.06.08	AJ-19 01.08.08	AJ-20 01.09.08	AJ-9 09.09.08
Napthalene	11.40	9.82	33.58	7.78	11.05
Acenaphthene	1.09	0.72	3.71	1.02	1.54
Acenaphthylene	2.23	0.86	6.57	1.54	2.36
Phenanthrene	1.34	0.70	3.30	1.12	2.29
Fluoranthene	0.67	0.17	1.68	0.34	1.21
Pyrene	1.18	0.49	3.82	1.08	1.95
1,2-Benzanthracene	0.69	<LOQ	<LOQ	<LOQ	<LOQ
Chrysene	1.12	<LOQ	<LOQ	1.73	0.24
Benzo[e]acephenanthrylene	0.79	<LOQ	<LOQ	<LOQ	<LOQ
	AJ-21 15.10.08	AJ-8 07.01.09	AJ-29 25.02.09	AJ-10 09.04.09	AJ-30 22.04.09
Napthalene	10.02	6.54	2.06	5.83	6.84
Acenaphthene	0.91	0.85	<LOQ	0.34	0.86
Acenaphthylene	1.46	1.89	0.13	0.74	1.17
Phenanthrene	1.38	1.85	0.69	2.34	1.06
Fluoranthene	1.26	2.93	1.16	2.44	0.68
Pyrene	1.67	3.09	1.07	2.90	1.25
1,2-Benzanthracene	0.45	2.20	<LOQ	0.73	0.33
Chrysene	1.12	3.71	1.01	2.22	0.69
Benzo[e]acephenanthrylene	0.63	1.71	0.23	0.90	0.37

4. Conclusion

In this study an efficient method with high sensitivity for the quantification of PAHs in aerosol samples by GC–MS has been developed. The technique is based on hollow fiber micro-porous membrane liquid–liquid extraction (HF-MMLLE). This is a simple technique that has some advantages compared with others, such as higher capacity of clean up, a minimum use of solvent and low cost of the technique. There are several parameters to be optimized in this kind of extraction to improve the extraction efficiency. The best results were achieved using n-undecane as organic solvent, stirring for 30 min at 600 rpm and without organic solvent addition to the aqueous phase. The method was successfully applied to some aerosol samples finding all the studied PAHs in them.

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