



# A new analytical methodology for a fast evaluation of semi-volatile polycyclic aromatic hydrocarbons in the vapor phase downstream of a diesel engine particulate filter

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## ARTICLE INFO

### Article history:

Received 26 August 2010

Received in revised form

10 December 2010

Accepted 16 December 2010

Available online 23 December 2010

### Keywords:

Diesel particulate filter

Polycyclic aromatic hydrocarbons

Diesel exhaust sampling

Microwave assisted extraction

Ultra-traces analysis

Solid phase extraction

## ABSTRACT

A new sampling method was developed to collect vapor-phase polycyclic aromatic compounds (PAHs) downstream of a diesel engine equipped with a diesel particulate filter (DPF). This configuration allowed us to collect separately the particulate phase, which was trapped inside the DPF, and the vapor phase, which was sampled downstream of the DPF. PAHs, which were not predominantly adsorbed into the poor organic fraction of the diesel soot, but were rather physically sorbed on high energetic adsorption sites, should be extracted using very drastic extraction conditions. Microwave-assisted extraction using solvent mixtures composed of pyridine and diethylamine were used to desorb particulate PAHs, and the total PAH amounts corresponded to a very low value, i.e.,  $8 \mu\text{g g}^{-1}$  or  $0.24 \mu\text{g km}^{-1}$ , with a predominance of low weight PAHs. For collection of the vapor phase, gas bubbling in an aqueous medium was preferred to conventional methods, e.g., trapping on solid sorbents, for several reasons: aqueous trapping allowed us to use a solid phase enrichment process (SPE) that permitted PAH sampling at the sub-picogram levels. Consequently, low volume sampling was possible even if the sampling duration was very short (20 min). Additionally, the amount of time saved for the analysis was considerable when coupling SPE to the analytical system (liquid chromatography with fluorimetric detection). Solvent consumption for the overall sampling and analytical processes was also drastically reduced. Experiments on a diesel engine showed that vapor phase samples collected downstream of the DPF contained all of the 15 target priority PAHs, even the heaviest ones. The total vapor-phase PAH amount was  $6.88 \mu\text{g N m}^{-3}$  or  $10.02 \mu\text{g km}^{-1}$ , which showed that the gaseous fraction contains more PAHs than the particulate fraction. Partitioning coefficients ( $K_p$ ) were estimated showing the predominance in the vapor phase of all the PAHs. However, the DPF technology effects a considerable decrease in the total PAH emission when compared to non-equipped diesel vehicles.

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## 1. Introduction

Diesel engines emit not only gaseous pollutants but also carbonaceous particulates, which are heterogeneous materials consisting of an elemental carbon core with several organic and inorganic compounds adsorbed on the surface [1–4]. Included among these organic compounds, polycyclic aromatic hydrocarbons (PAHs) can be found in two forms due to their moderate volatility: sorbed on particles and in the gas phase. PAHs resulting from incomplete combustion of organic matter are known to adversely affect human health [5,6]. Unfortunately, the car-

cinogenic effects of native and pyrogenic PAHs compounds may potentially be increased by their sorption onto fine particles ( $<1 \mu\text{m}$ ), which can penetrate deep into the bronchioles and alveoli of the lungs. However, the lower molecular weight PAHs, which are known to be less toxic and may be found predominantly in the vapor phase, must be also considered because they can react with other pollutants, such as ozone or nitrogen oxides ( $\text{NO}_x$ ), to form direct and more toxic mutagens, such as nitrated PAHs [7]. Traffic has been shown to be one of the major sources of PAHs (or oxygenated PAHs) in urban area atmospheres, and the contribution of these contaminants by diesel vehicles is markedly higher than that of gasoline-powered cars [8–12]. However, the use of particulate traps in the exhaust pipe can minimize tailpipe emissions of particulate matter and can potentially eliminate carcinogenic PAHs through their binding on particulate matter. Areas of particular importance are to ensure that reduction of total particulate

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emission is also accompanied by destruction of the diesel soot soluble organic fraction (SOF), which contains the carcinogenic PAHs, and that gas phase aromatic hydrocarbons are also significantly reduced in tailpipe emissions. To date, there are non specific standards for PAHs emissions from motor vehicles, but as they are considered as hazardous air pollutants, recommendations are required about ambient air quality. In the European Union, a directive (96/62/EC) on ambient air quality assessment and management has been adopted and a 2004 daughter directive (2004/107/EC) sets a target limit value for benz[a]pyrene of  $1 \text{ ng m}^{-3}$  for the protection of human health.

Numerous analytical techniques and instruments are used to monitor and characterize particle-bound or gas-phase PAHs in the atmosphere or in diesel emissions. The sampling methods used for air sampling usually involve combinations of glass or quartz fiber filters for retaining the particle-bound PAH fraction, and sorbents like polyurethane foam plugs (PUF) and XAD resins are used to trap the volatile fractions [13–16]. Denuder-based sampling methods also showed good collection efficiencies for sampling of the most volatile PAHs [17]. In diesel exhaust sampling, exhaust gases are usually collected after being mixed and homogenized with the ambient air in a dilution tunnel connected to a constant volume sampling system. The collection system is also generally composed of glass fiber filters to trap the particulate matter, e.g., a Pallflex system, and of adsorbent resins, e.g., XAD-2, XAD-4 or XAD-16, coupled to PUF cartridges to collect the gaseous phase [5,18–20]. After sampling, extraction processes are usually performed using Soxhlet extraction or sonication [21,22], but other extraction procedures, such as supercritical fluid extraction (SFE), microwave-assisted extraction (MAE) or assisted solvent extraction (ASE) can favorably replace Soxhlet or sonication extractions and yield to cleaner extracts with minimal loss of volatile compounds and minimal use of solvents [23,24]. Solid phase micro-extraction (SPME) also provides a useful alternative to solvent extraction methods [25]. Extracts are then cleaned up (by solid phase extractions – SPE –, through silica gel columns, ...) and analyzed by gas chromatography/mass spectrometry (GC/MS) or high performance liquid chromatography (HPLC) with fluorescence detection, which have adequate resolution and sensitivity for quantification of trace levels of PAHs [26–29]. Our work was aimed at developing an original method to collect the gaseous phase downstream of a diesel engine, resulting in a minimal loss of semi-volatile PAHs [30]. This sampling method differs from conventional collection methods in that it consists of trapping PAHs in an aqueous solution by gas bubbling and not on a solid sorbent. The liquid solution that is employed must solubilize vapor-phase PAHs, and subsequent solid phase extraction coupled with on-line HPLC analysis must permit quantification of PAHs at the sub-picogram level. The diesel soot collected inside the particulate trap was also simultaneously analyzed in order to understand the partitioning behavior of PAHs between the gaseous phase and the particulate phase. Specific extraction conditions had to be utilized to quantitatively extract particle-bound PAHs. Microwave-assisted extraction and hot Soxhlet extraction methods were developed to reach this goal [31,32]. Additionally, the partitioning behavior of PAHs between the particulate matter and the gaseous fraction is discussed.

## 2. Material and methods

### 2.1. Solvents and samples

Acetonitrile, toluene, pyridine, diethylamine, propan-2-ol, methylene chloride (all of HPLC grade) and acetic acid (purity 99.5%) were obtained from Fisher Scientific France (Illkirsh, France). Cetyltrimethylammonium bromide (CTAB,

**Table 1**

Wavelength program as a function of time, which was used to detect the 16 target PAHs with fluorescence detection.

Wavelength time program (min)	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm)	Detected PAHs (with associated numbering)
0	220	330	Naphthalene (1)
7.4	220	315	Acenaphthene (2) Fluorene (3)
11.8	250	370	Phenanthrene (4) Anthracene (5)
18	235	420	Fluoranthene (6) Pyrene (7)
21.2	267	385	Benz[a]anthracene (8) Chrysene (9)
24.6	260	420	Benzo[e]pyrene (10) Benzo[b]fluoranthene (11) Benzo[k]fluoranthene (12) Benzo[a]pyrene (13)
28.6	290	410	Dibenz[ah]anthracene (14) Benzo[ghi]perylene (15)
30.6	245	500	Indeno[1,2,3-cd]pyrene (16)
35	220	330	

purity > 99%) and sodium chloride (purity > 99%) were purchased from Sigma–Aldrich France (Saint Quentin Fallavier, France). Water was purified and deionized using a Direct Q3 system from Millipore France (Molsheim, France). For HPLC–fluorimetry quantitative analysis, a standard solution of 16 PAHs was prepared in acetonitrile ( $20 \mu\text{g mL}^{-1}$ ) (see Table 1) which were all obtained from Sigma–Aldrich–Fluka, Interchim (Montluçon, France) or Supelco (Bellefonte, PA, USA). For GC–MS quantitative analysis of PAHs extracted from diesel particulate matter, a working stock solution was prepared from individual standards diluted in toluene ( $100 \mu\text{g mL}^{-1}$ ) and was composed of 18 PAHs (see Table 2). Deuterated phenanthrene, purchased from Sigma–Aldrich, was used as an internal standard ( $100 \mu\text{g mL}^{-1}$  in toluene) for GC–MS analysis. Diesel particulate matter was obtained from the CERTAM (Saint Etienne du Rouvray, France). Diesel soot was produced by a

**Table 2**

Mean concentrations and standard deviations ( $\mu\text{g g}^{-1}$ ) of PAHs extracted from 0.25 g or 0.2 g of diesel soot (accumulated inside the diesel particulate filter) using a hot Soxhlet or a microwave assisted extractor, respectively.

	Hot Soxhlet mean quantity and standard deviation ( $n=3$ ) ( $\mu\text{g g}^{-1}$ )	MAE mean quantity and standard deviation ( $n=3$ ) ( $\mu\text{g g}^{-1}$ )
Naphthalene (1)	3.71 ( $\pm 0.16$ )	4.29 ( $\pm 0.33$ )
Acenaphthylene (2)	0.36 ( $\pm 0.12$ )	0.71 ( $\pm 0.03$ )
Acenaphthene (3)	0.66 ( $\pm 0.10$ )	0.09 ( $\pm 0.06$ )
Fluorene (4)	0.08 ( $\pm 0.02$ )	0.07 ( $\pm 0.03$ )
Phenanthrene (5)	0.76 ( $\pm 0.15$ )	0.64 ( $\pm 0.08$ )
Anthracene (6)	0.08 ( $\pm 0.04$ )	0.14 ( $\pm 0.04$ )
Fluoranthene (7)	0.28 ( $\pm 0.10$ )	0.26 ( $\pm 0.05$ )
Pyrene (8)	0.35 ( $\pm 0.05$ )	0.23 ( $\pm 0.06$ )
Benz[a]anthracene (9)	0.24 ( $\pm 0.12$ )	0.22 ( $\pm 0.05$ )
Chrysene (10)	0.20 ( $\pm 0.06$ )	0.15 ( $\pm 0.07$ )
Benzo[b]fluoranthene (11)	0.31 ( $\pm 0.13$ )	0.29 ( $\pm 0.08$ )
Benzo[k]fluoranthene (12)	0.14 ( $\pm 0.06$ )	0.21 ( $\pm 0.10$ )
Benzo[e]pyrene (13)	0.20 ( $\pm 0.10$ )	0.31 ( $\pm 0.08$ )
Benzo[a]pyrene (14)	0.15 ( $\pm 0.04$ )	0.20 ( $\pm 0.04$ )
Perylene (15)	0.14 ( $\pm 0.07$ )	0.23 ( $\pm 0.05$ )
Indeno[1,2,3-cd]pyrene (16)	0.04 ( $\pm 0.04$ )	n.d. <sup>a</sup>
Dibenz[ah]anthracene (17)	0.05 ( $\pm 0.05$ )	n.d. <sup>a</sup>
Benzo[ghi]perylene (18)	0.07 ( $\pm 0.07$ )	n.d. <sup>a</sup>
$\Sigma$ PAH	7.82 $\pm$ 0.88	8.04 $\pm$ 0.15

<sup>a</sup> Non detected.

light duty four cylinder direct-injection engine equipped with an oxidation catalyst and a wall-through diesel particulate filter (DPF) impregnated by an oxidation catalyst. A European Euro 5 standard diesel engine was used as a test platform for the application of a new European driving cycle (NEDC), which consisted of four repeated urban driving cycles (maximum  $50 \text{ km h}^{-1}$ ) and an extra-urban driving cycle (maximum  $120 \text{ km h}^{-1}$ ), for a total of 11 km and 20 min for one complete cycle. A NEDC cycle is supposed to represent the typical usage of a car in Europe. The standard fuel used was a low content sulfur fuel, containing 2% PAHs, and it was mixed to yield 30% methylester content (B30). After several repeated cycles, the DPF soot was blown into glass flasks at  $100^\circ\text{C}$  and weighed, and then the soot sample was stored at  $-20^\circ\text{C}$ . During the combustion cycle, the temperature was continuously measured at the DPF outlet and inside the DPF. Sensors also continuously measured the pressure of air admitted into the diesel engine and the mass flow-rate at the engine exhaust. A scanning mobility particle sizer (SMPS) from TSI France (Marseille, France) was used to measure the number and the distribution of diesel soot particles upstream and downstream of the diesel particulate filter.

## 2.2. PAHs extractions from the particulate matter

### 2.2.1. Hot Soxhlet extractions

Hot Soxhlet extractions were performed with a Büchi B-811 Soxhlet extractor purchased from IMLAB (Lille, France). A sample size of 250 mg of collected diesel soot was extracted using 150 mL of a solvent mixture composed of pyridine and diethylamine in a ratio 83/17 (v/v) after 60 reflux cycles [32]. The extract was then concentrated by evaporation at  $45^\circ\text{C}$  and 50 mBar to approximately 3 mL and analyzed by GC–MS.

### 2.2.2. Microwave-assisted extractions

Diesel soot extractions were performed using a MARS X microwave-accelerated extraction system (CEM Corporation, Matthews, USA). A sample size of 200 mg of diesel particulate matter was extracted for 37 min at  $140^\circ\text{C}$  (power: 1200 W) using 30 mL of the pyridine/diethylamine solvent mixture (83/17 v/v) [31]. After filtration through  $0.45 \mu\text{m}$  Phenex Teflon filters (Phenomenex, Le Pecq, France) to remove soot particles, extracts were concentrated by evaporation to approximately 1.5 mL and analyzed by GC–MS.

## 2.3. Aqueous trapping at the outlet of the engine exhaust pipe

### 2.3.1. Generation of gaseous PAHs and collection tests

An experimental, home-made apparatus was composed of a flow-through vaporizer based on a non-volatile organic solvent (1 mL of diethylamine) that solubilizes a liquid PAH mixture (25  $\mu\text{L}$  of a  $0.1 \mu\text{g mL}^{-1}$  test solution) and releases it in the gas state (heating:  $250^\circ\text{C}$ ) in a carrier gas (nitrogen), with a controlled flow-rate ( $0.07\text{--}0.11 \text{ m}^3 \text{ h}^{-1}$ ) [30]. This part of the device is connected to the collection part by Teflon tubing, which is wrapped within a heating wire maintained at  $220^\circ\text{C}$  to avoid condensation after vaporization. Two or three glass bubbling bottles, each containing 125–250 mL of a trapping aqueous medium, constitute the collection assembly. The duration of the sampling tests was usually 30 min, and the PAH recoveries were determined in duplicate following concentration by solid-phase extraction (SPE) and on-line analysis by HPLC–fluorimetry.

### 2.3.2. Collection at the diesel engine exhaust pipe

Collection of gas-phase PAHs, which were present in undiluted exhaust gases, was performed at a post-DPF stainless steel junction placed 20 cm after the DPF. The three on-line glass bubbling bottles containing the optimized aqueous medium were connected to the

stainless steel junction by Teflon tubing. One glass bottle was added after the collection assembly as a safety bottle, and another bottle containing silica gel was employed to protect the flow-meter and the vacuum pump from humidity. The diameter of the diesel engine exhaust pipe (designated as  $D_1$ ) was 54 mm, and the internal diameter of all glass tubings of the sampling system (designated as  $D_2$ ) was 5 mm. Undiluted exhaust gases were collected at a volumetric flow-rate of  $Q_{v2} = 0.082 \text{ N m}^3 \text{ h}^{-1}$  during the 20 min duration of the NEDC cycle ( $0.09 \text{ m}^3 \text{ h}^{-1}$  at  $298 \text{ K}$ ). Volume flows were expressed by normal cubic meters per hour (with standard conditions defined as  $273.15 \text{ K}$  and  $10^5 \text{ Pa}$ ), permitting to be independent of the temperature and pressure of the gas flowing in the system. The mean value of the mass flow-rate during one NEDC cycle could be measured, i.e.,  $Q_{m1} = 0.017 \text{ kg s}^{-1}$ , the mean DPF internal temperature was  $296^\circ\text{C}$  and the mean admission pressure was near atmospheric pressure, i.e.,  $P_{ad} = 1.08 \times 10^5 \text{ Pa}$ . It is generally accepted that the volumetric mass of a diesel combustion gas can be compared to dry air, with a value equal to  $\rho = 1.3 \text{ kg N m}^{-3}$ . Thus the mean volumetric flow-rate ( $Q_{v1}$ ) during an NEDC cycle was approximately:

$$Q_{v1} = \frac{Q_{m1}}{\rho} = \frac{0.017}{1.3} = 0.0131 \text{ N m}^3 \text{ s}^{-1} = 47.08 \text{ N m}^3 \text{ h}^{-1}$$

To operate at constant linear speed between the diesel exhaust pipe and the sampling apparatus, the sampling volumetric flow-rate would have been:

$$Q_{v2} = \frac{Q_{v1} \times D_2^2}{D_1^2} = \frac{47.08 \times 5^2}{54^2} = 0.404 \text{ N m}^3 \text{ h}^{-1}$$

instead of  $0.082 \text{ N m}^3 \text{ h}^{-1}$ . Thus, a factor equal to 4.92 must be applied to the results obtained with our sampling apparatus to evaluate the real quantity of PAHs coming from the tailpipe.

## 2.4. Chromatographic analysis

### 2.4.1. GC–MS analysis of PAHs extracted from diesel particulate matter

After addition of  $10 \mu\text{L}$  of the deuterated internal standard ( $100 \mu\text{g mL}^{-1}$ ) to  $990 \mu\text{L}$  of each liquid extract,  $0.5 \mu\text{L}$  of this mixture was injected (splitless injection at  $250^\circ\text{C}$ ) in a gas chromatographer (model 6850) coupled to a mass spectrometer (model 5975C) from Agilent technologies (Santa Clara, USA). The detector operated at 70 eV with an electron voltage of 1400 V in positive ion mode (temperature of transfer line:  $290^\circ\text{C}$ ). Quantification was based on selected ion monitoring for better sensitivity. Chromatography was performed using a  $40 \text{ m} \times 0.15 \text{ mm}$  i.d. capillary column coated with a Factor Four VF-5MS phase ( $0.15 \mu\text{m}$  film thickness) from Varian (Palo Alto, USA) and with helium as a carrier gas ( $0.5 \text{ mL min}^{-1}$ ). The oven temperature was programmed at  $60^\circ\text{C}$  for 2 min and then increased to  $180^\circ\text{C}$  at  $40^\circ\text{C per minute}$ , followed by an increase to a maximum temperature of  $300^\circ\text{C}$  at  $3.7^\circ\text{C per minute}$ .

### 2.4.2. SPE concentration of vapor phase PAHs and HPLC–fluorimetry analysis

Solid phase extraction was performed using a short column ( $7.5 \text{ mm} \times 4.6 \text{ mm}$  i.d.) from Grace Davison (Templemars, France) that contained an octadecylsilane stationary phase ( $d_p = 5 \mu\text{m}$ ). The aqueous medium was percolated at  $2.5 \text{ mL min}^{-1}$  through the column with an auxiliary pump (model 126) from Beckman Coulter (Fullerton, USA). This short column was flushed and conditioned before percolation with a solvent sequence that included 10 min with pure water, 10 min with isopropanol, 10 min with acetonitrile, 10 min with a mixture of acetonitrile/methylene chloride in a 50/50 ratio (v/v), 10 min with acetonitrile and then 10 min with pure water. After percolation, the SPE column was directly

connected to the HPLC analytical column Vydac 201 TP 54 from Grace Davison (250 mm  $\times$  3.2 mm i.d.;  $d_p = 5 \mu\text{m}$ ). Concentrated PAHs were eluted by the mobile phase, composed of 50/50 (v/v) acetonitrile/water for 10 min, followed by a linear elution gradient and a final 100% acetonitrile mobile phase at  $t = 20$  min. The flow-rate ( $0.5 \text{ mL min}^{-1}$ ) was generated with a Beckman pump (model 126) and detection was obtained using a Prostar363 fluorimetric detector from Varian. To enhance the detection limit, we determined the optimal excitation length  $\lambda_{\text{ex}}$  and emission length  $\lambda_{\text{em}}$ , which were programmed as a function of time (Table 1).

### 3. Results and discussion

#### 3.1. Analysis of PAHs from the diesel particulate matter

The mass of diesel particulate matter, which accumulated inside the DPF, was evaluated after 40 NEDC cycles by differential weighing of the filter, and the mean mass accumulated during one cycle was calculated, which was approximately 1 g per hour or 0.33 g per cycle. Analysis of particulate PAHs was performed using two extraction techniques, i.e., hot Soxhlet and microwave-assisted extraction (MAE), which were optimized and validated previously [31,32]. Hot Soxhlet, in which heating is also applied to the extraction cavity, was preferred to classical Soxhlet because this method was more efficient to desorb the heavy PAHs [32]. The diesel soot collected from the DPF has a particularly poor soluble organic fraction (SOF), which is less than 10%. When a vehicle is used without a DPF, the SOF can reach markedly higher values, e.g., 20% for diesel soot standard reference materials such as SRM 1650, and even larger SOF values for vehicles like two-stroke mopeds, which may reach 72% of the particulate mass [33]. These very high proportions of the SOF suggest that absorption into the organic fraction, which includes unburned and partially burned fuel and lubricating oil, is the main partitioning mechanism for PAHs. But in the case of a poor SOF, the dominant mechanism affecting the gas-particle partitioning of PAHs seems more likely to be physical adsorption on highly energetic sites of the particle surface [34]. Consequently, when the fraction of organic carbon is much higher than the fraction of elemental carbon (for high SOF values), PAHs are much easier to desorb from the soot particle than in the case of strong adsorption on the carbonaceous surface. In the first case, conventional Soxhlet extractions with classical organic solvents, such as methylene chloride or hexane, can be used to desorb and analyze particulate PAHs; in the case of strong adsorption on highly retentive sites, conventional extraction conditions are not sufficient to desorb the heaviest PAHs. That is why our poor SOF diesel soot, which is collected inside the DPF, had to be extracted using nonclassical organic solvent mixtures (containing pyridine), which are not usually used in such applications. In fact, the aromatic character of the pyridine in conjunction with its basic character, which is reinforced by mixing it with diethylamine, could promote quantitative desorption of the heavy PAHs strongly adsorbed on the soot  $\pi$ -electron acceptor retention sites. Fig. 1 shows an example of a chromatographic analysis of a real sample after MAE extraction and Table 2 shows the mean results of the analysis of particulate PAHs. Comparable results are obtained from hot Soxhlet and MAE extractions, except for the three lightest PAHs which results were biased when hot Soxhlet extraction was used: indeed naphthalene and acenaphthylene concentrations are slightly underestimated because the solvent evaporation step is longer, leading to losses by volatilization. On the other hand, acenaphthene is overestimated when hot Soxhlet extraction is used because some interfering species, which appear between 6 and 10 min on the chromatographic analysis, co-elute with this PAH. Standards deviations may appear important,

but they are of the same order of magnitude than those presented in a previous work [32].

Overall, there is a very small proportion of extracted PAHs from the soot collected inside the particulate filter. The total sum of particulate PAHs is around  $8 \mu\text{g g}^{-1}$ , which corresponds to a mean value of  $0.17 \mu\text{g N m}^{-3}$  or  $0.24 \mu\text{g km}^{-1}$ . Lower values were reported in a previous paper [32] that demonstrated that the soot collected inside the DPF is markedly poorer in PAH levels than a standard reference soot (SRM 1650) directly emitted in exhaust gases without any filtration process. Thus, the diesel particulate filter seems efficient at reducing the total PAH amounts adsorbed on diesel soot. This can be explained by the catalytic oxidative process, which also reduces the total soot mass. The high temperature reached inside the DPF during the NEDC cycle (250–400 °C) can also explain the poor condensation of PAHs on the soot surface. Consequently, the second part of this study determines if a large portion of the PAHs is found in the exhaust gas downstream of the particulate filter.

#### 3.2. Analysis of PAHs in the exhaust gas downstream of the DPF

Aerosol pollutants can be collected by means of high volume sampling apparatus (HVS,  $15\text{--}30 \text{ m}^3 \text{ h}^{-1}$ ) connected to a dilution tunnel that allows dilution of the diesel exhaust gases. However, losses of volatile or semi-volatile PAHs can occur during high volume sampling through partial sublimation [35]. Moreover, following gas phase collection, an additional step is necessary before chromatographic analysis: desorption of aerosol PAHs from the polyurethane foams or resin sorbents by means of a Soxhlet apparatus must be accomplished. This step is time consuming and large volumes of organic solvents are also consumed. Even if faster and less solvent-consuming extraction techniques can be performed, as mentioned previously, a large portion of the extraction solvent must be eliminated afterwards by evaporation to concentrate samples for analysis. This last step is also quite critical for obtaining quantitative results for the most volatile PAHs. For all of these reasons, we chose to collect gaseous PAHs downstream of the DPF directly into an aqueous medium and not on a solid support in order to avoid sample loss through solvent evaporation after the extraction step. Then a solid phase extraction process (SPE) was utilized to concentrate traces of PAHs trapped in the aqueous phase during the very short sampling duration. Indeed, when optimized, this technique is well-suited for concentrating ultra-trace levels of compounds without any sample loss, and SPE can also be used as a sample cleanup procedure. On-line coupling of SPE and HPLC allowed us to analyze PAHs at levels as low as parts per trillion (a few  $\text{ng L}^{-1}$ ). These very low detection levels were absolutely required due to the short duration of an NEDC cycle and low volume sampling was preferred to avoid sample losses. Consequently, the way in which we chose to concentrate ultra-trace PAHs involved percolating the solubilizing aqueous medium through a short column containing hydrophobic packing material which was the same used in the analytical column. The nonpolar PAHs were then eluted from the short column by the solvent-rich mobile phase required for the HPLC analysis and were detected using a sensitive fluorescence detector. The main difficulty involved in aqueous trapping of PAHs is due to their very low solubility in water. To enhance PAH solubility, we added the cationic surfactant cetyltrimethyl ammonium bromide (CTAB) to the aqueous phase. Indeed, above the critical micellar concentration (CMC), surfactant micelles are capable of increasing the solubilization of sparingly soluble solutes into water. This surfactant also eliminated PAH losses through adsorption on the walls of tubing and glass vessels, which is a very significant phenomenon when ultra-trace levels of compounds must be analyzed. As described in a previous paper, the efficiency of the trapping process was enhanced by adding an inor-

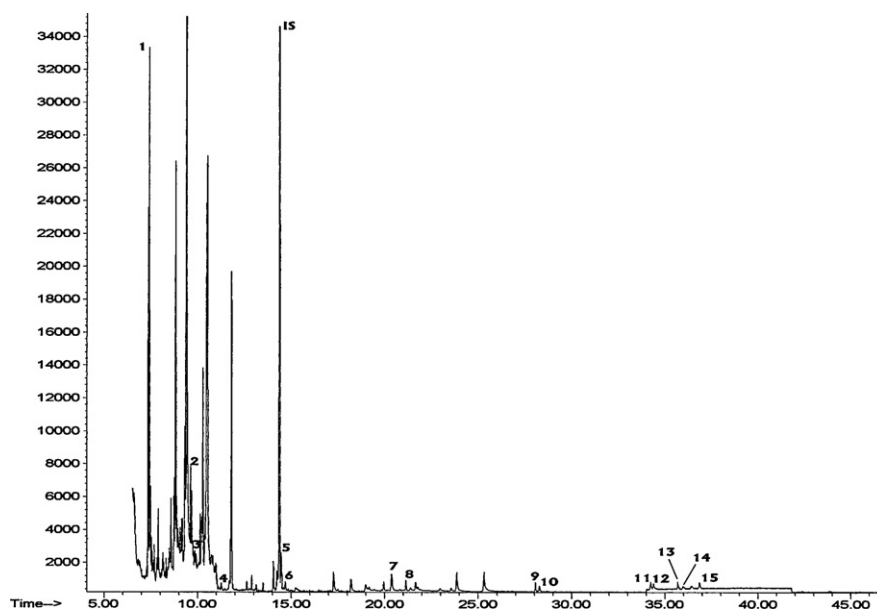


Fig. 1. GC-MS analysis of the target PAHs extracted by MAE from 0.2 g of real soot obtained after NEDC cycles; IS: internal standard; numbering: see Table 2.

ganic salt to the aqueous medium, which decreases the surfactant CMC [30]. After experiment evaluation, NaCl was preferred over  $\text{NH}_4\text{Cl}$  or  $\text{MgCl}_2$ , and its effect was more favorable at  $10^{-2} \text{ mol L}^{-1}$  than at  $2 \times 10^{-2} \text{ mol L}^{-1}$  (data not shown). Fig. 2 shows the recovery yields obtained with SPE-HPLC analysis when 2.5 ng of a mixture of 16 PAHs was spiked into 250 mL of water containing CTAB at various concentrations. The CMC of CTAB is  $8.3 \times 10^{-4} \text{ mol L}^{-1}$ , and this solubilizing surfactant was tested below its CMC. Indeed, the foam produced by the surfactant, which reaches a maximum near the CMC, is a considerable drawback for this application. Consequently, we decided to work slightly below the CMC at concentrations where pre-micellar aggregates already form, to decrease the foaming phenomenon and overflow problems that could occur during the bubbling process. As seen in Fig. 2, recoveries of a few nanograms of PAHs in water, with NaCl and CTAB as additives, are more satisfac-

tory when CTAB is increased to a concentration of  $2 \times 10^{-4} \text{ mol L}^{-1}$ . However, only light PAHs from acenaphthene to anthracene are quantitatively concentrated. Recoveries of naphthalene are not satisfactory because CTAB, which induces significant peak tailing at dead volume, is an obstacle for its detection by fluorimetry. Finally, to enhance aqueous solubility of the high molecular weight PAHs, we introduced an organic additive. Because the SPE process is not compatible with high levels of organic solvents, we chose to test several co-solvents at levels ranging from 1 to 10% in the aqueous medium. The addition of the organic co-solvent had an optimal effect at 5% in the aqueous phase, and among all the tested solvents, the recovery yields increased in this order: ethanol < acetonitrile < tetrahydrofuran < pyridine. Fig. 2 shows that the addition of 5% pyridine markedly increases the enrichment recovery yields of the high molecular weight PAHs, which

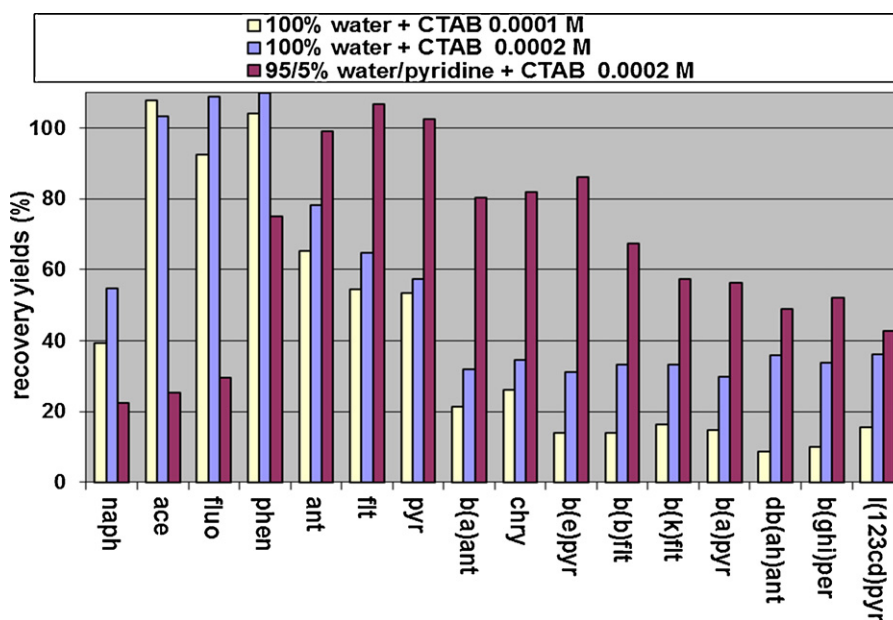


Fig. 2. PAH recovery yields (initial concentration:  $10 \text{ ng L}^{-1}$ ) after SPE enrichment and HPLC-fluorimetry analysis, as a function of additives present in the solubilizing aqueous medium.

**Table 3**  
Recovery yields, limits of detection (LOD) and quantification (LOQ), mass and concentration linearity for the complete sampling process, i.e., PAH vaporization ( $m_0 = 1 \text{ ng}$  to  $10 \text{ ng}$ ), aqueous phase bubbling ( $0.09 \text{ m}^3 \text{ h}^{-1}$ ), SPE trace enrichment and HPLC-fluorimetry on-line coupling.

	Mean recovery <sup>a</sup> and standard deviation (%)	LOD <sup>b</sup> (pg)	LOQ <sup>b</sup> (pg)	Mass linearity (ng)	Concentration linearity <sup>c</sup> (ng L <sup>-1</sup> )
Naphthalene	46.1 ( $\pm 6.0$ )	1.5	5	0.005–3	0.025–15
Acenaphthene	79.1 ( $\pm 11.5$ )	0.9	3	0.003–5	0.015–25
Fluorene	79.7 ( $\pm 11.1$ )	0.6	2	0.002–4	0.010–20
Phenanthrene	109.5 ( $\pm 3.9$ )	1.2	4	0.004–5	0.020–25
Anthracene	93.6 ( $\pm 5.0$ )	1.5	5	0.005–5	0.025–25
Fluoranthene	93.9 ( $\pm 12.5$ )	9	30	0.03–10	0.15–50
Pyrene	102.7 ( $\pm 6.5$ )	9	30	0.03–10	0.15–50
Benz[a]anthracene	74.6 ( $\pm 3.9$ )	1.2	4	0.004–7	0.020–35
Chrysene	68.6 ( $\pm 8.3$ )	0.9	3	0.003–6	0.015–30
Benzo[e]pyrene	48.9 ( $\pm 4.5$ )	4.5	15	0.015–10	0.075–50
Benzo[b]fluoranthene	39.1 ( $\pm 2.5$ )	0.9	3	0.003–8	0.015–40
Benzo[k]fluoranthene	34.3 ( $\pm 4.1$ )	1.2	4	0.004–5	0.020–25
Benzo[a]pyrene	35.2 ( $\pm 3.9$ )	2.4	8	0.008–7	0.040–35
Dibenz[ah]anthracene	30.6 ( $\pm 3.3$ )	4.5	15	0.015–8	0.075–40
Benzo[ghi]perylene	24.6 ( $\pm 3.5$ )	7.5	25	0.025–8	0.125–40
Indeno[1,2,3-cd]pyrene	21.5 ( $\pm 2.5$ )	15	50	0.050–10	0.25–50

<sup>a</sup>  $n = 3$  replicates,  $m_0 = 2.5 \text{ ng}$ .

<sup>b</sup>  $m_0 = 1 \text{ ng}$ .

<sup>c</sup> Concentrations in 200 mL of aqueous medium.

were quantitative ( $\geq 80\%$ ) from anthracene to benzo[e]pyrene. Only fair recovery yields (45–67%) could be attained for the ultra-trace enrichment of the high molecular weight PAHs with 5–6 rings. Relative standard deviations, which were evaluated from the SPE enrichment of a mixture of 16 PAHs at  $10 \text{ ng L}^{-1}$ , ranged from 2.1 to 13.2% for semi-volatile PAHs (from acenaphthene to pyrene) and from 1.3 to 14.1% for high molecular weight PAHs (from benz[a]anthracene to indeno[1,2,3-c,d]pyrene). As regards the very low concentrations of PAHs which could be measured after SPE, these results of RSD were not at all excessive and contribute to a relatively good precision of the enrichment methodology and consequently of the overall analytical tool.

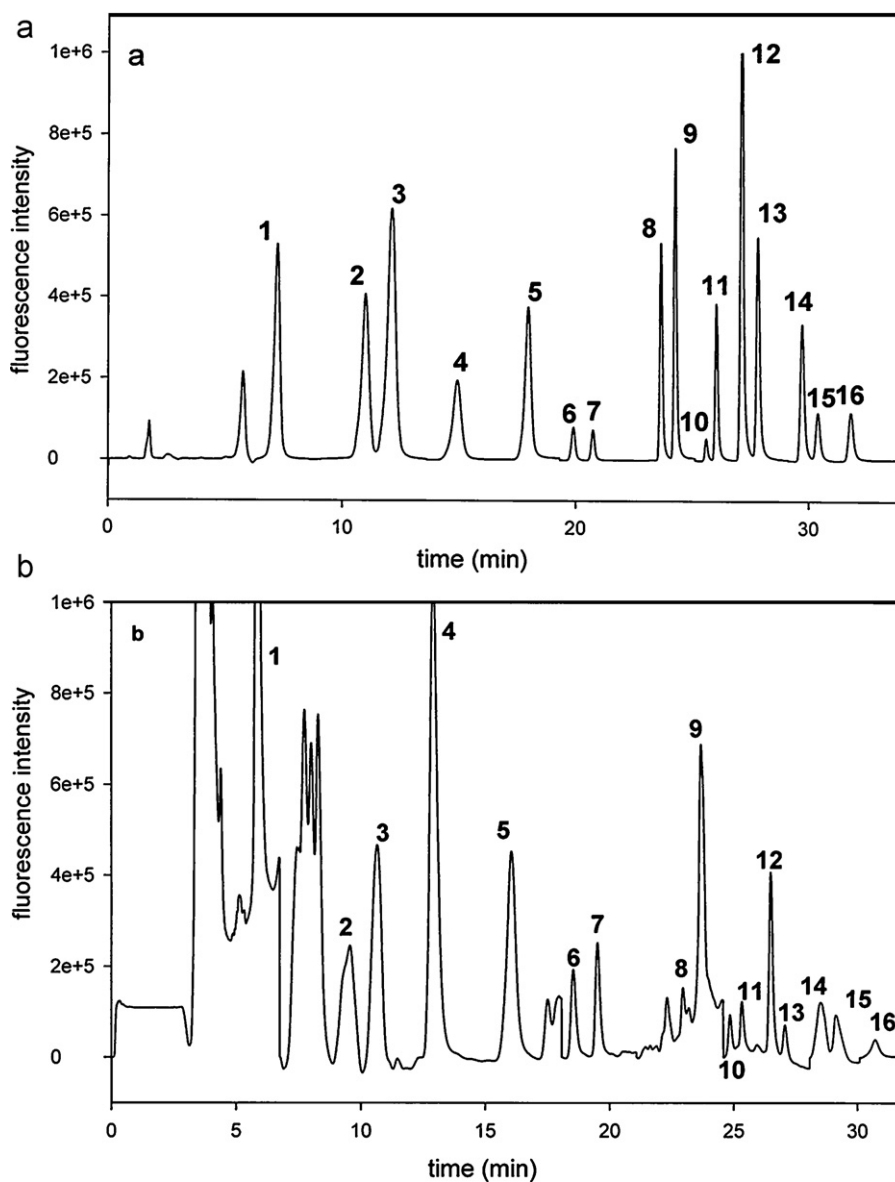
The collection efficiency of the bubbling process for gaseous PAHs was studied next using an home-made experimental device (see Section 2.3.1). To better solubilize the less volatile PAHs, the two initial bubbling bottles contained 150 mL of the mixture of water/pyridine (95/5 v/v), CTAB at  $2 \times 10^{-4} \text{ mol L}^{-1}$  and NaCl at  $10^{-2} \text{ mol L}^{-1}$ , and the third one lacked only the organic additive (to better solubilize the volatile PAHs). The collection recovery yields were quantitative for semi-volatile PAHs (from acenaphthene to pyrene). However, although fair recovery yields ( $>50\%$ ) were obtained from benz[a]anthracene to benzo[e]pyrene, the heaviest PAHs were not quantitatively trapped ( $<40\%$ ). But we do emphasize that these PAHs can be detected at very low concentrations (pg–ng range) in a short sampling time. Table 3 summarizes the best recovery yields and their associated standard deviations attained using the aqueous trapping process followed by SPE enrichment and on-line HPLC-fluorimetry analysis. Limits of detection and quantification mentioned in this Table 3 report the minimal quantity of each vapor PAH which could be detected or quantified, respectively. The limits of detection and quantification could be evaluated from tests performed with initial quantities of 1 ng of each PAH vaporized in a gas stream, and an order of magnitude in detection at the picogram level was obtained. The masses of PAHs that could be analyzed in less than 30 min of gas phase sampling ranged from a few picograms to few nanograms (see Table 3).

Additionally, several gas flow-rates were tested, and we could conclude that the results were not significantly altered by a flow-rate fluctuation in the range  $0.09 \pm 0.02 \text{ m}^3 \text{ h}^{-1}$ .

The complete analytical process described herein is not time-consuming when compared to conventional methods of gas-phase PAH trapping. In this latter case, 24 h of pre-cleaning for the

polyurethane foam is required before sampling, more than 8 h of Soxhlet extraction are required to extract the PAHs, 30–60 min of evaporation are needed to concentrate the large sample and a purification step on a silica gel column is performed before gas chromatography analysis. In our method, only 50 min were required for the pre-cleaning/conditioning step of the SPE short column and 3 h were necessary to concentrate (and purify) the sample by SPE before chromatographic analysis. In addition, the cleaning step of the sampling apparatus (PTFE tubing and glass vessels) was particularly easy. Another advantage to this method was that the consumption of organic solvents (less than a total of 100 mL of various solvents for SPE and HPLC analysis) was drastically reduced compared to the conventional sampling methods, which require 10 times more solvent quantities for the pre-cleaning step of the PUFs, the subsequent extraction of the PAHs by Soxhlet and purification on a silica gel column.

After validation of our collection and analytical process, the three bubbling bottles were connected to the diesel exhaust pipe of a diesel engine, 20 cm downstream of the DPF outlet. The sampling pump was started at the same time as the NEDC cycle; the diesel engine was conditioned beforehand. After 20 min of bubbling, all of the glass and PTFE tubing was rinsed twice and the rinse solution was mixed with the aqueous solution before further concentration by SPE and analysis by HPLC. Fig. 3 presents a comparison between a typical analysis of the 16 target PAHs (Fig. 3a) and an example of analysis of the first and second bubbling bottles (media assembled) after one diesel engine NEDC cycle (Fig. 3b). In the second case, the solution injected in the analytical system contained also a small proportion of pyridine, salt and surfactant, so a slight shift of the retention times could be observed as regards the analysis of standard PAHs. Moreover, even if fluorimetric detection is selective, many fluorescent interfering species could be detected (see Fig. 3b), particularly between naphthalene and acenaphthene, which are probably biphenyl and methylated naphthalenes. Importantly, all of the target PAHs were detected in the trapping aqueous medium after one complete NEDC cycle, even the heaviest ones. This result was initially astonishing because we are collecting gaseous-phase PAHs. Three complete NEDC cycles were performed on three different days, and the mean result is shown in Fig. 4. Considering the variation introduced by the analytical method, which includes two SPE enrichments followed by two HPLC analyses for each NEDC cycle, and the considerable variations introduced during an engine test (not quantified here), the standard deviations reported



**Fig. 3.** (a) Analysis of the 16 target PAHs by HPLC-fluorimetry; conditions:  $C_{18}$  column (250 mm  $\times$  0.32 mm,  $d_p = 5 \mu\text{m}$ ), mobile phase gradient composed of acetonitrile and water, flow-rate:  $0.5 \text{ mL min}^{-1}$ ; detection and numbering: see Table 1. (b) Analysis of the first and second bubbling bottles (assembled) after one NEDC cycle, following SPE enrichment and on-line analysis by HPLC-fluorimetry.

in Fig. 4 were realistic and not particularly excessive. The mean sum of all PAHs measured in the gaseous phase downstream of the DPF was  $6.86 \pm 0.66 \mu\text{g N m}^{-3}$  ( $n=3$  tests), which represents  $110.2 \mu\text{g}$  of PAHs per cycle or  $10.02 \mu\text{g km}^{-1}$ . Notably, this value is certainly underestimated because although semi-volatile PAHs are quantitatively trapped in the aqueous medium, this is not completely the case for the heaviest PAHs. Regardless, it appears that the gaseous fraction is predominant with respect to the particulate phase ( $0.24 \mu\text{g km}^{-1}$ ), which shows the great importance of sampling the gas phase. Particulate collection alone underestimates PAHs, especially when the diesel engine is equipped with a particulate filter.

### 3.3. Gas-particle partitioning of PAHs

Bosteels et al. have demonstrated that for a diesel engine with a DPF, vapor phase PAH emissions during an NEDC cycle were comparable to particulate-phase PAH emissions: levels of the vapor phase were lower than  $1.2 \mu\text{g km}^{-1}$  while particulate-phase PAHs were

around  $1 \mu\text{g km}^{-1}$  [36]. In our study, the DPF was approximately four times more efficient in reducing the total amount of adsorbed PAHs, but gaseous PAHs that passed through the DPF were eight times more concentrated.

Importantly, the sampling system that was used allowed the measurement of PAHs directly at the outlet of the DPF, and consequently, of the PAHs which were not adsorbed on the trapped soot. At the sampling point, the exhaust gas was still at high temperature, so the gaseous phase was particularly rich in vaporized PAHs. A sensor was used to measure the temperature of the gas stream 20 cm downstream of the DPF outlet, and the mean temperature value was  $260^\circ\text{C}$  during an NEDC cycle. If some of the vapor-phase PAHs could thereafter condense at the tailpipe outlet, where the temperature decreases to approximately  $50^\circ\text{C}$ , the mass balance remains the same: a large portion of the PAHs do not adsorb on the diesel particulate matter trapped inside the DPF and remain in the gaseous phase, which passes through the DPF.

Our results also demonstrate that lower molecular weight PAHs were predominant in both gaseous and particulate phases. Volck-

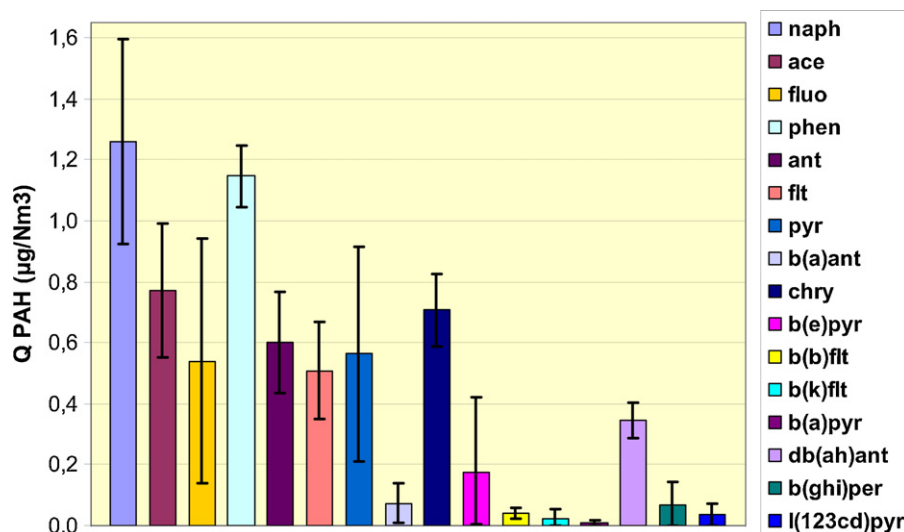


Fig. 4. Quantification of vapor-phase PAH amounts collected at the tail pipe 20 cm downstream of the DPF, following 3 NEDC cycles on 3 different days.

ens and Leith [37] described the use of a partitioning coefficient,  $K_p$  ( $\text{m}^3 \text{g}^{-1}$ ) to describe the distribution of semi-volatile compound concentrations between the particle phase ( $F$ ,  $\text{ng m}^{-3}$ ) and the gas phase ( $A$ ,  $\text{ng m}^{-3}$ ):

$$K_p = \frac{F}{A \times \text{TSP}}$$

where TSP is the amount of total particulate matter ( $\mu\text{g m}^{-3}$ ). When the ratio of the particle to gas phase concentrations ( $F/A = K_p \times \text{TSP}$ ) is greater than 1, the compound partitions predominantly into the particulate phase. When  $K_p \times \text{TSP}$  is less than 1, partitioning is primarily into the gas phase. Table 4 shows the results obtained for all of the measured PAHs, and all of the values of  $K_p \times \text{TSP}$  are much less than 1, even for the heavy PAHs and even with the consideration that the amounts of gas-phase heavy PAHs are certainly underestimated. These latter PAHs were found predominantly in the vapor phase downstream of the DPF, and one might conclude that a large amount of fine particles could pass through the DPF

and could contribute to a considerable measurement bias, in which particle phase compounds are measured as gas phase constituents. Thus, soot particles were also measured upstream and downstream of the DPF with a scanning mobility particle sizer (SPMS): this permitted measurement of the full particle size distribution of diesel soot between 5 nm and 1000 nm, and the total number of particles obtained upstream and downstream of the DPF could be compared. In our case, 99.99% of the soot particles were trapped inside the DPF, which implies that the contribution of the heaviest particulate PAHs passing through the DPF and solubilized into our trapping aqueous solution was negligible.

The fact that heavy PAHs were less concentrated than expected on the soot particulate matter and that light PAHs were predominant in both particulate and gas phases could also be linked to the nature of the fuel blend used during our engine tests. Indeed, Karavalakis et al. [38] showed that the addition of biodiesel led to a substantial increase in low molecular weight PAHs. Our fuel blend contained 30% methyl ester (B30), which could

**Table 4**  
Evaluation of the partitioning coefficients  $K_p$  at 260 °C for each PAH present simultaneously in the particulate phase (diesel soot material) and the vapor phase downstream of the DPF, following three NEDC driving cycles.

PAHs	Mean particulate PAHs concentration <sup>a</sup> ( $\text{ng N m}^{-3}$ ) <sup>d</sup>	Mean gaseous PAHs concentration <sup>b</sup> ( $\text{ng N m}^{-3}$ ) <sup>d</sup>	$\text{Log } K_p^c$ ( $\text{N m}^3 \mu\text{g}^{-1}$ ) <sup>d</sup>	$K_p \times \text{TSP}^c$
Naphthalene	83.00	1259	−5.50	0.0659
Acenaphthene	7.78	771	−6.31	0.0100
Fluorene	1.56	539	−6.86	0.0029
Phenanthrene	14.53	1147	−6.21	0.0127
Anthracene	2.28	601	−6.74	0.0038
Fluoranthene	5.60	508	−6.27	0.0110
Pyrene	6.02	563	−6.29	0.0107
Benz[a]anthracene	7.26	72	−5.31	0.1008
Chrysene	5.71	707	−6.41	0.0081
Benzo[b]fluoranthene	6.23	41	−5.14	0.1520
Benzo[k]fluoranthene	3.63	22	−5.10	0.1650
Benzo[e]pyrene	5.29	173	−5.83	0.0306
Benzo[a]pyrene	3.63	8	−4.66	0.4538
Indeno[1,2,3-cd]pyrene	0.83	34	−5.93	0.0244
Dibenz[ah]anthracene	1.04	344	−6.84	0.0030
Benzo[ghi]perylene	1.45	69	−6.00	0.0210
$\Sigma$ PAHs	155.84	6858		

<sup>a</sup> Mean value ( $n=6$ ) of Soxhlet and MAE extractions.

<sup>b</sup>  $n=3$ .

<sup>c</sup>  $\text{TSP} = 20.75 \times 10^3 \mu\text{g m}^{-3}$ .

<sup>d</sup>  $\text{N m}^{-3}$ : unit for normalized volumes of gases in standard conditions of temperature (273 K) and pressure ( $10^5$  Pa).



explain the predominance of low weight PAHs over high weight PAHs.

Finally, if we assess the total amount of PAHs emitted by a Euro 5 diesel engine equipped with a DPF, this device noticeably reduces the total PAH amount emitted at the tailpipe. Particulate PAHs are known to reach around 50–60  $\mu\text{g km}^{-1}$  during an NEDC cycle on an Euro 3 diesel engine without a DPF [39,40], and the gaseous fraction is predominant with regard to the particulate fraction [41]: consequently, the use of a DPF with a biodiesel blend fuel is clearly a major way to reduce the total emission of PAHs, particularly the heaviest ones.

#### 4. Conclusions

The use of a diesel particulate filter downstream of a diesel engine permitted us to collect the particulate phase and the vapor phase separately during an NEDC standard driving cycle. It was an advantage compared to conventional sampling systems which trap simultaneously the two phases, that can disturb the gas-particle partitioning of PAHs and induce artefacts [17]. The soot particulate phase, which hydrocarbon-based soluble organic fraction was poor, had to be analyzed using rigorous extraction conditions to quantitatively desorb strongly sorbed PAHs. Indeed, previous studies demonstrated that adsorbed high weight PAHs could not be quantitatively extracted using conventional extraction techniques (Soxhlet) and common solvents (hexane, methylene chloride) [31]. Thus, microwave-assisted extraction was used (but alternative methods such as SFE or ASE could have been also employed [32]), in association with pyridine and diethylamine extraction solvents. Results showed that very low levels of PAHs were adsorbed on the soot surface and that low-weight PAHs were surprisingly predominant. To evaluate the vapor phase, an original collection method was optimized that trapped the vapor-phase PAHs by gas bubbling in an aqueous medium. The optimized aqueous collection solution contained a cationic surfactant, organic and inorganic additives, which quantitatively absorbed semi-volatile PAHs, from acenaphthene to benz[*a*]anthracene, at sub-picogram levels after only 20 min of low-volume sampling downstream of the diesel engine. The overall method (vapor phase collection associated to the highly sensitive analytical tool), was rapid, easy to perform and not expensive, firstly because it did not require a special apparatus for the gas phase collection (unlike conventional trapping systems [17]) and secondly, because only few organic solvent volumes were used. The heaviest PAHs, from chrysene to indeno[1,2,3-*c,d*]pyrene, could also be trapped and detected in the vapor phase, but 10–60% loss of these samples was observed. However, these results demonstrated that the vapor phase, which was collected 20 cm downstream of the DPF at 260 °C, contained not only volatile PAHs but also high molecular weight PAHs such as dibenz[*a,h*]anthracene. Consequently, the heavy PAHs that were not found on the soot particulate phase passed through the particulate filter, and a DPF may be considered to be a particulate filter but not a PAH filter. However, it must be also concluded that the DPF is an efficient device that considerably reduces the total PAH emission when compared to non-equipped diesel vehicles. Moreover, when using a biodiesel blend fuel with a particulate filter, the total emission is not only reduced but low-

weight PAHs are predominant, and these PAHs are known to be less dangerous than the heavy PAHs for human health and the environment.

#### Acknowledgement

The authors express their gratitude towards the “Région Haute Normandie” for financial support within the context of TOPAASE research program.

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