Chapter from the book *Diesel Engine - Combustion, Emissions and Condition Monitoring*


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Analytical Methodologies for the Control of Particle-Phase Polycyclic Aromatic Compounds from Diesel Engine Exhaust

F. Portet-Koltalo and N. Machour

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1. Introduction

Diesel emissions contain complex mixtures of chemical constituents that are known to be (or possibly to be) human carcinogens, or that have adverse health effects [1]. Among these substances (formaldehyde, benzene, acrolein, dioxins, etc.), polycyclic aromatic hydrocarbons (PAHs) and their nitrated derivatives (nitro-PAHs) have been implicated as major contributors to the toxicity of diesel exhausts [2, 3]. However, these substances are currently non-regulated pollutants in engine exhaust. PAHs are a group of organic compounds consisting of two or more fused aromatic rings, which are produced as a result of the incomplete combustion of fossil fuels. These compounds are mainly derived from anthropogenic sources, particularly from mobile sources of emissions in urban areas [4]. The combustion of fuel in diesel engines results in the formation of a mixture of gaseous compounds (CO, CO₂, NO, NO₂, SO₂, etc.) and solid particles (carbonaceous matter, sulphates, trace metals, etc.). PAHs and their derivatives can be found in the gaseous or particulate phases of diesel exhaust fumes depending on their vapour pressure, but the distribution of particles between the two phases is also dependent on the total amount of particles, on the physical characteristics of the particles (particularly their specific surface area), and on the temperature.

The majority of particulate matter in diesel exhaust is composed of fine particles that are primarily formed from the condensation of organic matter on an elemental carbon core. These particles are generally called soot particles. The soluble organic fraction (SOF) is defined as the fraction that can be extracted from soot using an organic solvent; particulate PAHs and their derivatives are found in this fraction. The SOF primarily originates from unburned fuel and engine lubrication oil [5]. There is a wide range of SOF in the diesel particulate matter; it can range from less than 10 % to more than 90 % by soot mass. The
fraction of SOF in the particulate matter depends on the type of diesel vehicles (light or heavy-duty diesel vehicles, mopeds, etc.), on the concentrations of sulfur and aromatic compounds in the diesel fuel, on the test engine cycles and also, on the collecting procedure of diesel exhaust, which is less well described. In general, the SOF values are highest for light engine loads when exhaust temperatures are low [6].

Two methods are generally used for measuring vehicle emissions: dynamometer studies where tailpipe fumes are measured from one vehicle, and roadside or tunnel studies where mean traffic emissions values (daily, by vehicles, etc.) are obtained [7]. In this book chapter, only analytical methodologies developed for diesel emissions studies using dynamometer tests are described. Even if the exhaust particles produced in the tailpipe are distinct from those sampled in the ambient atmosphere, it is shown in this chapter that the trapping media are very similar. Conventional and less conventional sampling trains for collecting the particles are described. The classical (Soxhlet and ultra-sound extractions) and more recent methodologies (micro-wave assisted extractions, pressurised solvent extractions, supercritical fluid extractions, and solid phase extractions) are detailed; they are used for treating the collected samples from gaseous and particulate phases to obtain the fraction containing PAHs and their derivatives. Because the individual products present different health risks, information about total PAH emissions is less important than information about the composition of such emissions. Therefore, techniques that are developed for identifying and quantifying the individual PAHs and their nitrated derivatives found in the two phases are described.

Finally, the efficiency of the sample pretreatment step (before quantitation) is strongly dependent on the SOF fraction of diesel soot; therefore, it is shown in this chapter that when the optimisation of this important analytical step is neglected, it can lead to important analytical bias.

2. Properties, sources and toxicity of PAHs and nitro-PAHs

2.1. Physical and chemical properties of PAHs and nitro-PAHs

The name “polycyclic aromatic hydrocarbons” (PAH) commonly refers to a large class of organic compounds containing two or more fused aromatic rings; however, in a broad sense, non-fused ring systems should also be included. In particular, the term “PAH” refers to compounds containing only carbon and hydrogen atoms (i.e., unsubstituted parent PAH and their alkyl-substituted derivatives), whereas the more general term “polycyclic aromatic compounds” also includes the functional derivatives (e.g., nitro- and hydroxy-PAHs) and the heterocyclic analogues, which contain one or more hetero atoms in the aromatic structure (aza-, oxa-, and thia-arenes).

The physical and chemical properties of PAHs are dependent on the number of aromatic rings and on the molecular mass (Table 1). The smallest member of the PAH family is naphthalene, a two-ring compound, which is mainly found in the vapour phase in the atmosphere, because of its higher vapour pressure and Henry’s law constant $K_H$ (ratio
between the partial pressure of a gas above a solution and the amount of gas solubilized in solution). Three to five ring-PAHs can be found in both the vapour and particulate phases in air. PAHs consisting of five or more rings tend to be solids adsorbed onto other particulate matter in the atmosphere. For instance, the resistance of PAHs to oxidation, reduction, and vaporisation increases with increasing molecular weight, whereas the aqueous solubility of these compounds decreases (their \( n \)-octanol/water partition coefficient \( \log K_{ow} \) is higher). As a result, PAHs differ in their behaviour, their distribution in the environment, and their effects on biological systems.

<table>
<thead>
<tr>
<th>Compounds/Abbreviations</th>
<th>Chemical structure</th>
<th>Molecular mass (g mol(^{-1}))</th>
<th>Melting/Boiling points (°C)</th>
<th>Vapour Pressure (Pa at 25°C)</th>
<th>( \log K_{ow} )</th>
<th>Solubility in water at 25°C (mg L(^{-1}))</th>
<th>( K_{H} ) at 25°C (Pa.m(^3) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene* NAPH</td>
<td>![Naphthalene structure]</td>
<td>128.18</td>
<td>81 / 218</td>
<td>10.4</td>
<td>3.4</td>
<td>31.7</td>
<td>49</td>
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<tr>
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<td>![Acenaphthylene structure]</td>
<td>152.18</td>
<td>92 / 270</td>
<td>0.89</td>
<td>4.07</td>
<td>-</td>
<td>114</td>
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<tr>
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<td>154.21</td>
<td>95 / 279</td>
<td>0.29</td>
<td>3.92</td>
<td>3.9</td>
<td>15</td>
</tr>
<tr>
<td>Fluorene* FLUO</td>
<td>![Fluorene structure]</td>
<td>166.22</td>
<td>116 / 295</td>
<td>0.08</td>
<td>4.18</td>
<td>1.68</td>
<td>9.81</td>
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<tr>
<td>Anthracene* ANT</td>
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<td>178.24</td>
<td>216.4 / 342</td>
<td>8.0 (10^{-4})</td>
<td>4.5</td>
<td>0.073</td>
<td>73</td>
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<td>Phenanthene* PHEN</td>
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<td>178.24</td>
<td>100.5 / 340</td>
<td>0.016</td>
<td>4.52</td>
<td>1.29</td>
<td>4.29</td>
</tr>
<tr>
<td>Fluoranthene* FLT</td>
<td>![Fluoranthene structure]</td>
<td>202.26</td>
<td>108.8 / 375</td>
<td>0.00123</td>
<td>5.20</td>
<td>0.26</td>
<td>1.96</td>
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<td>Pyrene* PYR</td>
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<td>0.0006</td>
<td>5.18</td>
<td>0.135</td>
<td>1.1</td>
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<td>Chrysene* CHRYYS</td>
<td>![Chrysene structure]</td>
<td>228.29</td>
<td>253.8 / 436</td>
<td>-</td>
<td>5.86</td>
<td>0.00179</td>
<td>0.53</td>
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<td>Benz[a] Anthracene* B(a)ANT</td>
<td>![Benz[a] Anthracene structure]</td>
<td>228.29</td>
<td>160.7 / 400</td>
<td>2.8 (10^{-5})</td>
<td>5.61</td>
<td>0.014</td>
<td>1.22</td>
</tr>
<tr>
<td>Benzo[b] Fluoranthene* B(b)FLT</td>
<td>![Benzo[b] Fluoranthene structure]</td>
<td>252.32</td>
<td>168.3 / 481</td>
<td>-</td>
<td>5.78</td>
<td>0.0015</td>
<td>0.051</td>
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<tr>
<td>Benzo[k] Fluoranthene* B(k)FLT</td>
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<td>252.32</td>
<td>215.7 / 480</td>
<td>-</td>
<td>6.11</td>
<td>0.0008</td>
<td>0.044</td>
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<td>178.1 / 496</td>
<td>7.3 (10^{-7})</td>
<td>6.50</td>
<td>0.004</td>
<td>0.034 (20°C)</td>
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<td>Benzo[e]pyrene* B(e)PYR</td>
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<td>252.32</td>
<td>178.7 / 493</td>
<td>7.4 (10^{-7})</td>
<td>6.44</td>
<td>0.005</td>
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<tr>
<td>Compounds/Abbreviations</td>
<td>Chemical structure</td>
<td>Molecular mass (g mol(^{-1}))</td>
<td>Melting/Boiling points (°C)</td>
<td>Vapour Pressure (Pa at 25°C)</td>
<td>Log K(_{ow})</td>
<td>Solubility in water at 25°C (mg L(^{-1}))</td>
<td>K(_{H}) at 25°C (Pa.m(^3) mol(^{-1}))</td>
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<td>Perylene PER</td>
<td><img src="image" alt="Perylene structure" /></td>
<td>252.32</td>
<td>277.5 / 503</td>
<td>-</td>
<td>5.3</td>
<td>0.0004</td>
<td>-</td>
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<tr>
<td>Benzo[g,h,i] Perylene*</td>
<td><img src="image" alt="Benzo[g,h,i] Perylene structure" /></td>
<td>276.34</td>
<td>278.3 / 545</td>
<td>1.4 × 10(^{-8})</td>
<td>7.10</td>
<td>0.00026</td>
<td>0.027 (20°C)</td>
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<tr>
<td>Indeno[1,2,3-cd] Pyrene*</td>
<td><img src="image" alt="Indeno[1,2,3-cd] Pyrene structure" /></td>
<td>276.34</td>
<td>163.6 / -</td>
<td>-</td>
<td>-</td>
<td>0.00019</td>
<td>0.029 (20°C)</td>
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<tr>
<td>Dibenz[a,h] Anthracene*</td>
<td><img src="image" alt="Dibenz[a,h] Anthracene structure" /></td>
<td>278.35</td>
<td>266.6 / -</td>
<td>6.75</td>
<td>0.00050</td>
<td>-</td>
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<tr>
<td>Coronene COR</td>
<td><img src="image" alt="Coronene structure" /></td>
<td>300.36</td>
<td>439 / 525</td>
<td>2 × 10(^{-10})</td>
<td>5.4</td>
<td>0.00014</td>
<td>-</td>
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<tr>
<td>2-nitronaphthalene</td>
<td><img src="image" alt="2-nitronaphthalene structure" /></td>
<td>173.17</td>
<td>74 / 304</td>
<td>3.2 × 10(^{-2})</td>
<td>2.78</td>
<td>26</td>
<td>610</td>
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<tr>
<td>2- nitrofluorene</td>
<td><img src="image" alt="2-nitrofluorene structure" /></td>
<td>211.22</td>
<td>154 / 326</td>
<td>9.7 × 10(^{-5})</td>
<td>3.37</td>
<td>0.216</td>
<td>95</td>
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<tr>
<td>9-nitroanthracene</td>
<td><img src="image" alt="9-nitroanthracene structure" /></td>
<td>223.23</td>
<td>146 / -</td>
<td>-</td>
<td>4.16</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2- nitrophenanthrene</td>
<td><img src="image" alt="2-nitrophenanthrene structure" /></td>
<td>223.23</td>
<td>120 / -</td>
<td>-</td>
<td>4.23</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2- nitrofluoranthrene</td>
<td><img src="image" alt="2-nitrofluoranthrene structure" /></td>
<td>247.25</td>
<td>- / 420</td>
<td>9.9 × 10(^{-7})</td>
<td>-</td>
<td>0.019</td>
<td>13</td>
</tr>
<tr>
<td>1-nitropyrene</td>
<td><img src="image" alt="1-nitropyrene structure" /></td>
<td>247.25</td>
<td>152 / 472</td>
<td>4.4 × 10(^{6})</td>
<td>5.29</td>
<td>0.017</td>
<td>64</td>
</tr>
<tr>
<td>2-nitropyrene</td>
<td><img src="image" alt="2-nitropyrene structure" /></td>
<td>247.25</td>
<td>199 / 472</td>
<td>4.4 × 10(^{6})</td>
<td>-</td>
<td>0.021</td>
<td>64</td>
</tr>
<tr>
<td>7-nitrobenz[a] anthracene</td>
<td><img src="image" alt="7-nitrobenz[a] anthracene structure" /></td>
<td>273.29</td>
<td>162 / -</td>
<td>-</td>
<td>5.34</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6-nitrobenzo[a] pyrene</td>
<td><img src="image" alt="6-nitrobenzo[a] pyrene structure" /></td>
<td>297.31</td>
<td>260 / 567</td>
<td>-</td>
<td>6.13</td>
<td>-</td>
<td>12</td>
</tr>
</tbody>
</table>

* 16 priority PAHs defined by the US-EPA

**Table 1.** Physical and chemical properties of some PAHs and nitro-PAHs [8, 9].
2.2. Toxicity of PAHs and nitroPAHs

Over 100 chemical compounds formed during the incomplete combustion of organic matter are classified as PAHs. These ubiquitous environmental pollutants are human carcinogens and mutagens; therefore, they are toxic to all living organisms. There are various pathways for human exposure to PAHs. For the general population, the major routes of exposure are from food and inhaled air; however, in smokers, the exposure from smoking and food may be of a similar magnitude. Extensive reviews and guidelines concerning PAHs contamination in food and air have been performed, and they have questioned the correct marker capable of following the risk assessment for the population [10].

There have been concerns regarding the carcinogenic effects of these products for at least two centuries, following the report of a high incidence of scrotal cancer in soot workers in London by Sir P. Pottwatched. The association between cancer and a specific chemical compound, Benz[a]pyrene, was established when this compound was isolated from chimney soot. Several subsequent studies proved that, in addition to Benz[a]pyrene, other PAHs were also carcinogenic [11]. The United States Environmental Protection Agency (U.S. EPA) targeted sixteen specific PAHs for measurements in environmental samples (see Table 1), and Benz[a]pyrene (indicator of PAHs species) was classified as a 2B pollutant, which means that it is a probable human carcinogen based on sufficient evidence from animal studies, but there is inadequate evidence from human studies [12]. According to the International Agency for Research on Cancer Classification (IARC), it is Group 2A compound, which means that it is likely carcinogenic to humans [13]. The World Health Organization (WHO) also added PAHs to the list of priority pollutants in both air and water. France, Japan, Germany, Netherlands, Sweden, and Switzerland established emission standards for most of the hazardous air pollutants, including PAHs. The WHO and the Netherlands even established ambient air quality guidelines for PAHs (1.0 ng m⁻³ and 0.5 ng m⁻³, respectively). These limits are not legally binding, but the common consensus is that these pollutants require maximum reduction or “zero levels” in emissions.

The increased attention to nitro-PAHs is due to their persistence in the environment and the higher mutagenic (2x10⁵ times) and carcinogenic (10 times) properties of certain compounds compared to PAHs [14]. Studies have highlighted the important role of nitro compounds, and they emphasised the necessity of improving primary prevention methods to reduce nitrated molecule air pollution. Today, the known sources of these types of compounds are a variety of combustion processes, especially in diesel engines. It was reported that the main contributors to the direct-acting mutagenicity of diesel exhaust particulates were nitro-PAHs, including 1,3-, 1,6- and 1,8-dinitropyrenes, 1-nitropyrene, 4-nitropyrene, and 6-nitrochrysene [15-18]. Therefore, researchers have investigated the chemical and physical properties of particulate matter in diesel exhaust according to the development of diesel technology and emissions regulation; comparisons between the fuel and engine used, such as diesel versus gasoline, light-duty diesel, biodiesel and any so called “clean diesel” have also been reported [19-23].
2.3. Contribution of mobiles sources to atmospheric emissions.

PAHs primarily originate in heavily urbanised or industrialised regions; therefore, the majority of these compounds are anthropogenic. Different sources of PAHs were reviewed and classified according to five main categories (domestic, mobile, industrial, agricultural and natural) [24]. Domestic emissions are predominantly associated with the burning of coal, oil, gas, garbage, or other organic substances such as tobacco or char broiled meat. Mobile sources include the emission from vehicles such as aircraft, shipping vehicles, railways, automobiles, off-road vehicles, and machinery. Industrial sources of PAHs include primary aluminium production, coke production, creosote and wood preservation, waste incineration, cement manufacturing, petrochemical and related industries, bitumen and asphalt industries, rubber tire manufacturing, and commercial heat/power production. Agricultural sources include stubble burning, open burning of moorland heather for regeneration purposes, and open burning of brushwood and straw. With regard to the natural sources of PAHs from terrestrial sources (non-anthropogenic burning of forests, woodlands, and moorlands due to lightning strikes, volcanic eruptions) and cosmic origin,

<table>
<thead>
<tr>
<th>PAH ratio</th>
<th>Value range</th>
<th>Source</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Σ(low weight PAHs) / Σ(high weight PAHs)</td>
<td>&lt;1 &gt;1</td>
<td>Pyrogenic Petrogenic</td>
<td>[27]</td>
</tr>
<tr>
<td>FLT/(FLT+PYR)</td>
<td>&lt;0.5 &gt;0.5</td>
<td>Petrol emissions Diesel emission</td>
<td>[28]</td>
</tr>
<tr>
<td>ANT/(ANT+PHEN)</td>
<td>&lt;0.1 &gt;0.1</td>
<td>Petrogenic pyrogenic</td>
<td>[29]</td>
</tr>
<tr>
<td>FLT/(FLT+PYR)</td>
<td>&lt;0.4 0.4-0.5 &gt;0.5</td>
<td>Petrogenic Fossil fuel combustion Grass, wood, coal combustion</td>
<td>[30]</td>
</tr>
<tr>
<td>B(a)PYR/(B(a)PYR+CHRYS)</td>
<td>0.2-0.35 &gt;0.35</td>
<td>Coal combustion Vehicular emissions</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td>&lt;0.2 &gt;0.35</td>
<td>Petrogenic Combustion</td>
<td>[32]</td>
</tr>
<tr>
<td>B(a)PYR/(B(a)PYR+B(e)PYR)</td>
<td>&lt;0.2 &gt;0.5</td>
<td>Fresh particules Photolysis (ageing of particles)</td>
<td>[33]</td>
</tr>
<tr>
<td>InPYR/(InPYR+B(ghi)PER)</td>
<td>0.2-0.5 &gt;0.5</td>
<td>Petrogenic Petroleum combustion Grass, wood, coal combustion</td>
<td>[32]</td>
</tr>
<tr>
<td>2-MeNAPH/PHEN</td>
<td>&lt;1 2-6</td>
<td>Combustion Fossil fuels</td>
<td>[34]</td>
</tr>
<tr>
<td>Σ MePHE/PHEN</td>
<td>&lt;1 &gt;1</td>
<td>Petrol combustion Diesel combustion</td>
<td>[35]</td>
</tr>
<tr>
<td>B(b)FLT/B(k)FLT</td>
<td>2.5-2.9</td>
<td>Aluminium smelter emissions</td>
<td></td>
</tr>
<tr>
<td>B(a)PYR/B(ghi)PER</td>
<td>&lt;0.6 &gt;0.6</td>
<td>Non traffic emissions Traffic emissions</td>
<td>[36]</td>
</tr>
</tbody>
</table>

Table 2. Diagnostic ratios reviewed from [26].
their contributions have been estimated as being negligible to the overall emission of PAHs. However, it is rather difficult to make accurate estimations of PAH emissions because some PAHs are common to a number of these sources, and it is not easy to quantitatively determine how much of a particular PAH comes from a specific source [25]. Additionally, understanding the impact of particular emission sources on the different environmental compartments is crucial for proper risk assessment and risk management. PAHs are always emitted as a mixture, and the relative molecular concentration ratios are considered (often only as an assumption) to be characteristic of a given emission source. Table 2 lists typical diagnostic ratios taken from the literature that show the wide diversity of approaches [26].

Diagnostic ratios should be used with caution; the reactivity of some PAH species with other atmospheric species, such as ozone and/or oxides of nitrogen can change the diagnostic ratio [36-40]. The difference in chemical reactivity, volatility and solubility of PAH species may also introduce bias but to minimise this error, diagnostic ratios obtained from PAHs that have similar physico-chemical properties is mainly used [28]. Regardless, vehicular emissions were shown to be a major source of PAHs, whether the diagnostic ratios were coupled or not with principle component analysis, and irrespective of the region or season involved; moreover, studies indicated that diesel exhausts were the largest source of PAHs and nitro-PAHs, compared with the emissions of the other vehicles [39-42].

3. Diesel exhaust collection, extraction and chemical analysis

Diesel exhaust contains not only volatile species, which constitute the gaseous phase, but also solid agglomerates of spherical primary particles of approximately 15-30 nm diameter. These agglomerates are larger particles, in the range 60-200 nm (with a lognormal size distribution), which are produced by an accumulation mode corresponding to a coagulation of the primary particles. The agglomerates are made of solids (elemental carbon and metallic ashes) mixed with condensates and adsorbed material (including organic hydrocarbons). The accumulation mode can be accompanied by a nucleation mode, which consists of smaller particles (which are called ultra-fine particles of 10-20 nm) where the organic material is condensed on primary inorganic nuclei (sulphuric acid) [43]. It has been demonstrated that the ultra-fine particles are more easily volatilised, depending on temperature and dilution conditions, because they are mostly composed of volatile condensates and contain little solid material [44]. Therefore, discriminating between the gaseous species and the chemical species present in the solid state in diesel exhausts remains difficult because their formation processes depend on the sampling train design, sampling location, temperature, humidity and dilution rates of exhausts, and also on after-treatment devices.

3.1. Exhaust sampling and collection for PAHs analysis

Numerous instruments are used to monitor and characterise particle-bound or gas-phase PAHs in diesel tailpipe emissions. To obtain reliable and reproducible measurements, it is necessary to properly design the sampling system and to choose adequate materials for trapping the chemical substances to be measured (filters, sorbents, etc.). The majority of
experiments are performed on chassis dynamometers under predetermined engine load; a heated hose transfers the exhaust from the tailpipe to full flow exhaust dilution tunnels, and therefore, the exhaust gases are collected at low temperature after being mixed and homogenised with the ambient air (with moderate dilution ratios ranging from 6 to 14) in the dilution tunnel, which is connected to a constant volume sampling system (CVS technique) [45, 46]. Chassis dynamometers can also be equipped with dilution systems such as critical-flow Venturi dilution tunnels [47], ejection dilutors [48], or rotating disk diluters [49], but undiluted exhaust can also be directly collected through a sampling probe inserted inside the tailpipe, which is a less conventional method [50].

3.1.1. Collection of the gas phase

The supports used for trapping diesel gaseous exhaust are often the same as those used for air sampling; polyurethane foam plugs (PUF) of appropriate density can trap semivolatile contaminants in aerosols without creating excessive back pressure, and they are typically used to collect the atmospheric gaseous phase [51]; however, sorbents such as XAD-2 resins can also be used to trap the air gas fraction [52]. XAD resins are nonionic macroporous polystyrene-divinylbenzene beads with macroporous porosity and high surface areas, which give them their adsorptive characteristics for non-polar hydrophobic compounds such as PAHs or their derivatives. Therefore, we can also find these materials for the collection of semi-volatile PAHs and nitro-PAHs in the gas phase of diesel exhaust, because they are inexpensive and easy to handle, store and transport. Different adsorbent resins, such as XAD-2 or XAD-16, coupled to PUF cartridges (making “sandwiches” cartridges) can be used to collect PAHs in the gaseous phase [53-54]. The gaseous PAHs can also be collected using an annular denuder coated with different sorbents: the first stage is coated with XAD-4 resin, the second stage collects the particulate matter and the third stage is composed of a “sandwich” of polyurethane foam plugs and XAD-4 resin, to assess the volatilisation of PAHs from particles [55].

As previously mentioned, the vast majority of diesel exhaust is sampled in a dilution tunnel at low temperatures, where the condensation of the gaseous phase on solid particles is dominant. Additionally, operating at dilution ratios of approximately 10 is far from perfect because typical atmospheric dilution ratios are between 500 and 1000. A consequence is that the nucleation mode is favoured in the dilution tunnels where the saturation ratios are higher than those during atmospheric dilution, and the gaseous species coming out of the tailpipe are generally impoverished. However, one can be interested in the analysis of the gaseous exhaust at high temperature before the appearance of nucleation or condensation. A sampling method that differs from conventional collection methods was developed for this purpose and consists of trapping PAHs in an aqueous solution by gas bubbling and not on a solid sorbent. Therefore, when a particulate filter is incorporated after the diesel engine, the original method for trapping vapour-phase PAHs present in the hot undiluted gaseous exhaust is to absorb them inside an aqueous solution containing various additives, including a cationic surfactant as a solubilising agent [56].
3.1.2. Collection of the particulate phase

Diesel particulate matter (PM) is frequently defined from the material collected on a filter at a temperature of 52°C (or less) after dilution of the diesel exhaust with air. Even if the experiments conducted inside a dilution tunnel do not represent the full range of atmospheric conditions, these sampling conditions are far more common.

With regard to determining particulate PAHs in atmospheric aerosols, many different types of filters can be used and compared for retaining them; filters made of quartz, glass fibres, Teflon coated and nylon can be used [57]. For diesel exhaust, collection systems are also generally composed of glass fibre filters to trap the particulate matter, e.g., Pallflex systems. However Teflon-coated glass fibre filters are preferred over glass fibre filters, because they are more inert to catalysing chemical transformations and are less moisture-sensitive [46].

The sampling procedure using filters to collect particle bound PAHs provides no information about the size of the particulate matter; therefore, a high-flow cascade impactor can be used to replace single filters, which collects particles based on size [58]. Many cascade impactors can separate the particulate matter using different quartz filters placed in each stages into eight size ranges, from particles smaller than 0.4 µm to sizes in the range of 6.6-10.5 µm [21]. Aluminium filters that have silicon grease sprayed onto their surfaces can also be used in each stage of the impactors to prevent the bouncing of the particles during the collection; therefore, the distribution of PAHs based on the particulate sizes can be evaluated [59].

Finally, many studies have focused on particles directly collected inside of a diesel particulate filter (DPF) to understand the effects that an exhaust after-treatment device may have on the formation of particle-bound PAHs; once the DPF filter is weighed for total mass emission control, the particles can be blown-off and recovered for subsequent chemical analysis [60].

3.2. Extraction of PAHs from the trapping media

3.2.1. Extraction and purification of trapped gaseous PAHs

Vapour-phase PAHs and nitro-PAHs present in the trapped phase are often solvent-extracted using conventional techniques such as an ultrasonic bath or Soxhlet apparatus. A large number of polyurethane foams are Soxhlet extracted with 10% diethyl ether in hexane, as described in US EPA method TO-13.

XAD-2 resins are also often Soxhlet extracted over the course of 8 hours with 120 mL of methylene chloride [53], whereas mixtures of PAHs and nitro-PAHs can be better extracted from XAD-16 resins using 300 mL of methylene chloride:acetonitrile 3:1 (v:v) for 16 hours [21]; the extracts are then concentrated to 1-2 mL using rotary evaporators or under nitrogen flow, and they must be purified before analysis to eliminate matrix interferences. For the cleanup process, the concentrated solutions can be introduced into a silica column that contains anhydrous sodium sulphate to exclude water, and then eluted with 20 mL of
methylene chloride:hexane 1:2 (to recover PAHs) and 30 mL of acetone:hexane 1:2 (to better recover nitro-PAHs). Finally, after purification, another concentration step by evaporation is necessary to enhance the concentration of solutes to be analysed. Each of these steps (desorption, evaporation, purification, and evaporation) is time consuming, and large volumes of organic solvents are consumed; additionally, the evaporation concentration steps can be critical for obtaining quantitative results for the most volatile PAHs.

Another method for concentrating and cleaning PAHs (in one step) after their absorption in an aqueous medium is the use of a solid phase extraction process (SPE), which consists of percolating the PAHs solubilising aqueous medium through a short column containing hydrophobic packing material and eluting them directly inside of the analytical apparatus without any losses. This method is less time and solvent consuming [56].

3.2.2. Extraction of PAHs from diesel particles

Among all of the solid environmental polluted matrices studied, such as soils, sediments or urban dusts, carbonaceous diesel particulate matter is known to require severe conditions to obtain good recovery yields of the higher molecular weight PAHs [61]. It was even suggested that among all of the natural environmental matrices, diesel PM was the most refractory [62]. Despite this observation, only a few studies have a reliable optimisation of the PAHs extraction step from the carbonaceous matrix.

3.2.2.1. Conventional solvent extraction methods

In a significant number of studies, PAHs are extracted from PM trapped in glass-fibre filters in ultrasonic baths; for example, Karavakalis et al. used methylene chloride to extract three times the PAHs, with a total of 80 mL of solvent [45]. Riddle et al. used a 1:1 mixture of methylene chloride:hexane for 15 minutes, three times [63]. Fernandes et al. mentioned that using an ultrasonic bath for 1 hour with 70 mL of hexane was not as efficient as the Soxhlet extraction of PM with methylene chloride or a 3:1 mixture of methylene chloride:methanol [64]. However, Soxhlet extractions, even if they are more efficient than ultrasonic extractions, are longer; it can take 18 h to 24 h to extract PAHs using Soxhlet extractions [59, 65]. In many cases, even a long Soxhlet extraction does not result in the complete extraction of high weight PAHs and nitrated PAHs from diesel soot. Figure 1 shows that increasing the number of Soxhlet extraction cycles, using a classical extraction solvent for PAHs, does not permit the extraction of strongly adsorbed PAHs and nitro-PAHs from diesel soot; however, the aliphatic hydrocarbons are quantitatively extracted. In this example, the studied soot was very poor in the soluble organic fraction (SOF) and the pollutants were strongly adsorbed onto the partially graphitic surface and not absorbed into the condensation layer around the carbonaceous core, which can explain the difficulty of extracting high weight PAHs using classical techniques and solvents. However, more and more engines equipped with DPF result in the production of soot with very few condensed SOF, where the PAHs can be very difficult to extract; therefore, it seems risky to neglect the optimisation of the extraction step.
Soxhlet extraction can be enhanced with hot Soxhlet, where heating is also applied to the extraction cavity (unlike conventional Soxhlet), but the temperature must be kept lower than the boiling point of the extracting solvent mixture to keep it in the liquid state; therefore, temperatures are not high, and even if the recoveries are slightly better than using conventional Soxhlet, it remains difficult to quantitatively extract high weight PAHs from poor SOF diesel particles [60].

Finally, before the analytical step, columns containing a mixture of silica gel and deactivated alumina can be used for the fractionation and purification of extracts; the elution with $n$-hexane permits the elimination of aliphatic hydrocarbons and a second elution using 25 mL of a 3:1 mixture of cyclohexane:methylene chloride permits the elution of PAHs and nitro-PAHs [40]. As previously mentioned, all of these extraction and cleanup steps are time and solvent consuming.

3.2.2.2. Recent rapid solvent extraction methods

Other extraction procedures, such as microwave-assisted extraction (MAE), supercritical fluid extraction (SFE) or assisted solvent extraction (ASE) can favourably replace Soxhlet or sonication extractions and yields cleaner extracts with minimal loss of volatile compounds and minimal use of solvents. Although these recent and more effective extraction methods are employed to extract PAHs or nitro-PAHs from solid matrices such as soils, sediments, plants or atmospheric dusts [66-70], they are only little used for the extraction of PAHs from collected diesel soot.

**Figure 1.** Soxhlet extraction of a mixture of spiked PAHs, nitro-PAHs and $n$-alkanes from 100 mg of diesel particulate matter, blown-off from a diesel particulate filter after an European NEDC driving cycle test. Extraction conditions: reflux of 120 mL methylene chloride, each cycle representing approximately 8 minutes.
Microwave-assisted extraction uses closed inert vessels that contain the solid matrix and the organic solvents subjected to microwave irradiation (see Figure 2a). An important advantage of the MAE technique is the extraction rate acceleration due to microwave irradiation, resulting in an immediate heating to 120-140°C; therefore, extraction times on the order of a few minutes (approximately 30 minutes) can be obtained compared to a few hours when Soxhlet is used. Solvent volumes are low and range between 15 and 40 mL, depending on the quantity of matrix to be extracted. The solvent mixtures may have a dielectrical constant that is large enough to permit the heating transfer, and typical solvents such as acetonitrile or mixtures of toluene:acetone are employed to extract PAHs from atmospheric particles [71, 72]. In fact, the choice of the nature and the volume of the extracting solvents is especially important for the quantitative extraction of PAHs from diesel particles. Additionally, in the case of diesel soot with a very little SOF fraction, mixtures of drastic solvents such as pyridine:diethylamine or pyridine:acetic acid must be employed to quantitatively extract high weight PAHs or nitro-PAHs [73].

Supercritical fluid extraction exploits the unique properties of a supercritical fluid to more rapidly extract organic analytes from solid matrices, because the supercritical state imparts a great diffusion rate (like in the gaseous state) and a good solvating power (like in the liquid state). Carbon dioxide is the most used supercritical fluid because its critical temperature of 31°C and critical pressure of 74 bar are easily obtained. Supercritical fluids offer the opportunity to control the solvating power of the extraction fluid by varying the temperature (50 to 150 °C) and the pressure (100 to 400 bars), but also by adding minimal organic modifier (Figure 2b). In fact, the addition of small amounts of cosolvent into the CO₂ is absolutely necessary, not only to increase the PAH solubility in the extractant fluid but also to break the strong interactions between the aromatic retention sites of soot surface and the PAHs and nitro-PAHs: cosolvent mixtures of methylene chloride and toluene can be added to better extract PAHs from diesel soot [74], but other less conventional cosolvent mixtures, containing pyridine, are sometimes required [75]. SFE is an attractive method, as it leads to rapid extractions (less than 45 minutes, combining static and dynamic steps) and generates extracts ready for analysis without the need for additional concentration by means of solvent evaporation, because the extracted solutes are recovered into a very small volume of solvent. Moreover, SFE provides clean extracts because of its higher selectivity when compared to liquid solvent extraction techniques. Consequently, time consuming clean-up steps, which are also a source of analytical error, are not absolutely necessary after SFE extractions [76].

More recently, a method named accelerated solvent extraction (ASE) or pressurised fluid extraction (PFE) was developed. This method uses an organic solvent at a relatively high pressure and temperature to achieve more rapid extractions from solid matrices (Figure 2c) [77]. Elevated temperatures (150-200°C) permit to disrupt the strong solute-matrix interactions, and a high pressure (100-150 bars) forces the extraction solvent into the matrix pores. Less than 20 mL of solvent can be used to extract PAHs and nitro-PAHs from diesel PM; extractions with toluene [61], methylene chloride [16] or less conventional solvents based on pyridine [60] were performed.
Analytical Methodologies for the Control of Particle-Phase Polycyclic Aromatic Compounds from Diesel Engine Exhaust

Figure 2. Extraction apparatus (a) Microwave-Assisted Extraction: MAE extraction vessels are placed on a turntable inside an oven and are subjected to microwave irradiations generated by a magnetron. A programmable microcomputer controls and monitors the power, temperature and pressure within the vessel (b) Supercritical Fluid Extraction: SFE incorporates pumps which produce the high pressures required for supercritical CO₂ work. An organic cosolvent can be added to the extraction fluid by a separate module. The extraction cell is placed in an oven which maintains a precise fluid temperature. A static mode (equilibration) and a dynamic mode (with a controlled flow-rate) can be performed successively. A restrictor valve (changing the CO₂ from condensed to gaseous phase) provides precise control over flow-rates (c) Assisted-Solvent Extraction: ASE operates by moving the extraction solvent through an extraction cell which is heated by direct contact of the oven. Extractions can be performed first in static mode; when the extraction is complete, compressed nitrogen moves the heated extracting solvent to the collection bottle.
Finally, we stress the importance of optimising the PAH extraction step from soot; a chemometric approach can be useful because the influence of several operating variables must be understood. Indeed, the use of an experimental design fully permits the evaluation of not only the effects of each variable but also the interaction effects between the studied parameters, and at last permits the construction of a mathematical model that relates the observed response (PAH recovery yields in %) to the various factors and to their combinations (Figure 3).

**Figure 3.** Modelisation of the extraction of benz[a]pyrene from 100 mg of spiked diesel soot, as a function of several influent factors (a) SFE recoveries as a function of pressure and percentage of co-solvent (methylene chloride, chloroform or tetrahydrofuran) added into supercritical CO2, the temperature being fixed at 75°C and the extraction time at 10 minutes (static phase) and 20 minutes (dynamic phase) (b) ASE recoveries as a function of temperature, extraction time, and nature of the extraction solvent, the pressure being fixed at 100 bars.
3.2.2.3. **Extractions without solvent**

To avoid the use of organic solvents, other extraction techniques for chemical substances from particulate matter are proposed. Solid phase micro-extraction (SPME) seems to provide an alternative to solvent extraction methods [78]. Head-space SPME methods using polydimethylsiloxane fibres were tested on certified diesel particulate matter; it consisted in equilibrating PAHs sorbed on PM between a saline aqueous phase and the SPME fibre, and then the fibre was thermally desorbed inside the injection port of a gas chromatographer. However, this method was acceptable only for two to four PAHs congeners and was long (4 hours) [79]. Another method is to thermally desorb PAHs from filters or PM at 550°C in a thermogravimetric analyser, then recover them in a sampling bag where the vaporised phase is in equilibrium with a SPME fibre. Thereafter, PAHs are desorbed from the SPME fibre into a gas chromatographer [80]. However, for the quantitative analysis of high weight PAHs, the time necessary to establish the equilibrium (especially at higher concentration levels) is very long and can exceed 15h.

Direct thermal desorption (TD) can also be used for the desorption of PAHs from PM and this technique is generally hyphenated to a gas chromatographer for subsequent analysis. However, this fast extraction technique, which overcomes the main drawbacks of solvent extractions, is more often performed for PAHs sorbed on airborne particulate matter [81-83]; therefore, PAHs are desorbed from air dusts at 300-340°C (without pyrolytic degradation), cryogenically trapped and afterwards released in the gas chromatographer injection port at 325-400°C with a helium flow. Thermal desorption of PAHs from diesel exhaust particles seems to be more difficult and less reproducible, especially for high molecular weight PAHs [84].

Laser desorption-ionisation has also been studied to characterise pollutants immobilised on solid particles, and it offers the advantages of being orders of magnitude more sensitive for the analysis of PAHs and more rapid than solvent extraction. As will be discussed later, laser desorption systems are directly hyphenated to mass spectrometer analysers. Particulate PAHs and nitro-PAHs sorbed on soot particles are generally desorbed at an ionisation wavelength of 193 nm or 266 nm by an UV laser, mixed to a nebulised aerosol and transferred to the ion source region of the mass spectrometer [85]; solid samples to be desorbed can also be directly introduced with a probe into the ion source chamber [86, 87]. It has been described that this energetic UV laser desorption technology is vulnerable to matrix effects, and absolute quantification of PAHs seems to be difficult [88]. Therefore, new methods have appeared where particulate PAHs are deposited onto a probe, are irradiated with a less energetic pulsed Infra-Red laser beam (1064 nm) and the vapourised molecules are photoionised with UV radiation at 118 nm, so fragmentations are minimised and the sensitivity is higher [89].

### 3.3. Identification and quantitation of PAHs and their derivatives

#### 3.3.1. **On-line mass spectrometry analysis**

To avoid time consuming sample preparation, we previously mentioned that PAHs can be desorbed from soot particles by IR or UV lasers, and after an ionisation step, they can be directly analysed by mass spectrometry. Generally, time-of-flight (TOF) mass spectrometers...
are used, and mass peaks ranging from 1 to 5000 g mol\(^{-1}\) are displayed. The advantages of this on-line analysis are that very small amounts of PM are required (as small as 10\(^{-12}\) to 10\(^{-11}\) g) and that the mass range is virtually unlimited [90]. Moreover, even if multiple mass spectra are required to yield a representative spectrum for each chemical species present in the particulate effluent, high acquisition rates allow a significant increase in time resolution and measurements can be performed within minutes [85]. The drawbacks are that only qualitative analyses are assured (identification of compound classes), due to effects of species variations in the small irradiated sample area and to the variability of the laser intensity [87]. Moreover, there is not any selectivity on PAHs isomers on mass spectra, and interferences due to alkylated compounds, carbon clusters, polyyne compounds and photofragments of nitro-PAHs are inevitable in spectra because of the complexity of diesel soot particles. On-line carbon speciation of diesel exhaust particles can also be performed by near-edge X-ray absorption spectroscopy (NEXAFS), but the same drawbacks can be underlined: only fingerprints can be established because PAHs isomers cannot be resolved and quantitative information cannot be proposed [91]. Consequently, a separation technique before the detection instrument seems essential to obtain isomer resolution and quantitation.

3.3.2. Chromatographic analysis

3.3.2.1. Gas chromatography (GC)

The vast majority of chromatographic separations of PAHs and nitro-PAHs in gas chromatography were obtained using classical columns with a length of 30 m, and an internal diameter of 0.25 mm; the open tube is generally coated with a stationary phase composed of cross-linked phenyl (5%) methyl (95%) siloxane (film thickness of 0.25 µm). However, many researchers have used a less polar stationary phase for the separation of PAHs (100% methyl), and a more polar one for nitro-PAHs (50% phenyl) [92]. Original stationary phases sometimes have to be employed to obtain an isomer resolution of non-priority high weight PAHs, which are nevertheless of considerable interest because they have a high carcinogenicity; smectic-liquid crystalline polysiloxane phases permitted the separation of these PAHs [93]. Another method for a better isomer resolution was to use a longer column, which was 50-60 m long [16]. The most used detector for detecting PAHs or nitro-PAHs after their chromatographic separation is the mass spectrometer, which has the advantages of being more sensitive and providing information for identification, compared to the flame ionisation detector [65]. Quadrupole mass analysers are the most used for PAHs detection, with electron ionization energies of 70 eV. Ion traps can also be used, which provide more accurate structural information (for isomer identification) in the MS-MS mode [63]. With regard to nitro-PAHs, the electron-capture detector (ECD) can be employed, which is a sensitive and selective detector [21]. MS detectors can also be used for the detection of nitro-PAHs, but with different ionisation modes than those applied for PAHs; the most frequent mode is negative chemical ionisation (NICI) with methane as a reagent gas [92], but electron monochromator mass spectrometry (EM-MS) appears to be more selective and specific [94].
It must be noted that the use of programmable temperature vaporisation (PTV) injection systems may enhance the sensitivity by injecting up to 40 µL of samples instead of the 1 µL used for classical split-splitless injectors [69]. However, GC injection systems can also be directly hyphenated to thermodesorption units, which permits on-line PAH thermodesorption, GC separation and MS detection [95], as mentioned in a previous chapter. Finally, it will be necessary to count on comprehensive two dimensional GC techniques (GCxGC) in the future to obtain increased separation power and better sensitivity [96].

3.3.2.2. High performance liquid chromatography (HPLC)

As PAHs are lipophilic compounds, separations are generally achieved using reversed phase liquid chromatography with an apolar octadecyl (C₁₈) column and a mobile phase composed of acetonitrile and water. However, phenyl-modified stationary phases can also be employed for the separation of PAHs and their oxidised derivatives, with methanol and water used as a mobile phase [97]. Even if Ultra-Violet detectors can be used to detect PAHs and nitroPAHs [98], fluorescence detectors are more frequently employed for PAHs because of their greater sensitivity and selectivity, even if one of the sixteen priority PAHs cannot be detected (acenaphtylene) [56]. Nitro-PAHs must be derivatised to be fluorescent (reduction to the amine), and other more appropriate detectors can be employed for their detection, such as chemiluminescence or coulometric detectors [17]. Mass spectrometers have also proven to be useful detectors; PAHs can be analysed using an atmospheric pressure chemical ionisation interface (APCI) between the separation column and a single-quadrupole detection system [97]; atmospheric pressure photoionisation interfaces (APPI) can also be coupled to triple quadrupole mass spectrometers, permitting the analysis of PAHs in the positive ion mode, and nitro-PAHs in the negative ion mode, but also providing structural information about the metabolites [99]. Analytical systems were developed to improve the sensitivity of nitro-PAHs analysis (over chemiluminescence detection) using a two dimensional HPLC procedure (on-line derivatisation and separation), an electrospray ionisation source (ESI) and a triple quadrupole mass spectrometer [100]. Finally, a highly original approach consisting of a hyphenated HPLC and GC-MS resulted in the better analysis of isomers of high weight PAHs from diesel particulate matter [101].

4. Conclusion

It is a known fact that polyaromatic hydrocarbons in diesel exhaust are harmful. Therefore, it seems crucial to characterise them in both the gaseous and particulate phases, even if they are not yet regulated pollutants. It has been shown here that a variety of measurement protocols are available and that, even if many regulations in diesel exhaust sampling exist, it is not the case for the whole analytical process. And even for the first step of the measurement, the dilution factor and sampling temperature range are not strictly specified, which can induce great variability in diesel particle mass and composition. For that reason, various conclusions have been drawn about the influence of fuel composition, after-treatment devices, engine load, etc., on PAHs emissions; however, results from different research groups remain difficult to compare and all of the analytical artefacts were not...
resolved. For example, differentiating between gaseous and particle-bound PAHs is still a problem, because of the desorption or re-adsorption of volatile compounds during sampling. Additionally, neglecting the vapour-phase analysis (as suggested in some studies) also introduces significant error, because the toxic equivalent factors of exhaust are not correctly evaluated. The second step of the analytical process is also, without a doubt, an important source of analytical bias. There is not a universal technique for the extraction of every possible PAH or nitro-PAH from a solid matrix, and all of the described techniques have advantages and disadvantages; for example, high time resolution when coupling the laser desorption directly with the detection is not compatible with isomeric resolution, and thermal desorption remains less reproducible than solvent extraction. With regard to solvent extraction, which is the most employed method for the extraction of PAHs and nitro-PAHs from diesel soot, its optimisation is regrettably widely neglected. Conventional extraction methods such as Soxhlet or ultrasonic extractions, which are generally investigated on diesel PM extractions, and conventional solvents, such as methylene chloride or hexane, are in many cases not sufficient to quantitatively extract high weight PAHs and nitro-PAHs from carbonaceous diesel PM [102]. It is particularly the case for “dry” diesel soot, which has a reduced portion of soluble organic fraction. Indeed, in this case, the sorption is dominated by strong surface adsorption while a high amount of SOF attenuates PAHs adsorption, blocking the energetic sites, and thus a simple phase partitioning dominates [103]. Consequently, the presence on the particles of relevant amounts of SOF helps the solvent extraction process; however, it is now relevant to notice that recent diesel engines that are equipped with oxidation catalysts and particulate filters produce leaner particulates, and as it previously mentioned, more drastic extraction conditions are required [61]. Therefore, in the future, it will be important to pay more attention on the optimisation of the extraction step to obtain quantitative results, especially for the highest weight and more toxic PAHs and nitro-PAHs. Then, new standard reference materials with low SOF, issued from more recent diesel engines, should be produced, characterised and commercialised to validate this important analytical step. Finally, it can be emphasised that studies on PAHs other than the sixteen priority ones, as well as on other oxygenated or sulphured derivatives, could be another important task in the future, considering the fact that some of them are particularly more dangerous. For those studies, comprehensive chromatographic techniques (GCxGC) could help in enhancing the resolution of hundreds of aromatic compounds that can be found on diesel particles.

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Abbreviations and symbols
APCI Atmospheric Pressure Chemical ionisation
APPI Atmospheric Pressure PhotoIonisation

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Analytical Methodologies for the Control of Particle-Phase Polycyclic Aromatic Compounds from Diesel Engine Exhaust

ASE Assisted Solvent Extraction
CVS Constant Volume Sampling
DPF Diesel Particulate Filter
ECD Electron Capture Detector
EM-MS Electron Monochromator Mass Spectrometry
ESI Electro Spray Ionisation
GC Gas Chromatography
HPLC High Pressure Liquid Chromatography
IARC International Agency for Research on Cancer Classification
Kh Henry’s law constant
Kow \(n\)-octanol/water partition coefficient
MAE Microwave Assisted Extraction
MS Mass Spectrometry
NEDC New European Driving Cycle
NEXAFS Near Edge Xray Absorption Spectroscopy
NICI Negative Chemical Ionisation
PAH/PAHs Polycyclic Aromatic Hydrocarbon(s)
PM Particulate Matter
PTV Programmable Temperature Vaporisation
PUF PolyUrethane Foam
SFE Supercritical Fluid Extraction
SOF Soluble Organic Fraction
SPE Solid Phase Extraction
SPME Solid Phase Micro Extraction
TD Thermal Desorption
TOF Time of Flight
US-EPA United States Environmental Protection Agency
UV Ultra Violet
WHO World Health Organization
XAD/XAD-2/XAD-16 Resins with different macroreticular porosity

5. References


Particulate Filters: Conversion of PAHs versus Formation of Nitro-PAHs.


