

## Heat-Reflux extraction (HRE) and GC/MS Analysis of Polycyclic Aromatic Hydrocarbons and Their Nitro Derivatives Adsorbed on Diesel Combustion Engine Particles

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This study aims at the identification and quantitative determination of polycyclic aromatic hydrocarbons (PAHs) adsorbed on soot particles emitted by diesel engines, but also of their nitro derivatives "nitro-PAHs". The challenge is double: develop a Heat-reflux extraction (HRE) technique to selectively and quantitatively extract the targeted pollutants adsorbed on soot, and analyze them at trace amounts. Extraction results using dichloromethane showed a modest improvement in the extraction of volatile PAHs (more than 80%) and heavy PAHs (10 to 20%). Among the other solvents tested, pyridine proved to be the best extractant, with 50% extraction of the heaviest PAHs. Combined with diethylamine, the extraction efficiency of heavy PAHs reached 90%, which proves the ability of the pyridine-diethylamine mixture to extract quantitatively all PAHs, alkanes, and nitro-PAHs. Moreover, pyridine associated with 1% acetic acid allowed the quantitative extraction of heavy nitro-PAHs, which were only partially desorbed with previous solvents. In comparison, when extracting real soot directly from a diesel engine test bench, very high amounts of linear alkanes from C<sub>14</sub> to C<sub>32</sub> were obtained, but few PAHs: naphthalene, biphenyl, phenanthrene, anthracene, and fluorine (0.31-4.84 μg g<sup>-1</sup>) and nitrated derivatives: 1-nitronaphthalene, 2-nitrofluorene, and 1-nitropyrene (0.97-1.78 μg g<sup>-1</sup>).

**Keywords:** PAHs, Diesel exhaust particles, Nitro-PAHs, Soot, Alkanes

### INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are an important group of organic micropollutants, due to their distribution in the environment (water, atmosphere, soil, and marine sediments) [1], entering nature directly from mainly anthropogenic sources such as industrial effluents or accidental petroleum spills [2], but also from mobile activities such as road, river and air traffic [1,3]. Polycyclic Aromatic Hydrocarbons (PAHs) are organic compounds composed of several juxtaposed aromatic rings, which result essentially from incomplete combustion of organic materials or pyrolytic processes at high temperature, using

fossil fuels or more generally compounds containing carbon and hydrogen [4,5].

One of the most important environmental problems is the analysis of contaminants (air, soil, water, *etc.*), which requires rather heavy and tedious processes of sample preparation, extraction, purification, and reconcentration before separation and detection [2,6]. Consequently, various materials have been synthesized [7-9] and techniques developed (adsorption [10], membranes [11], coagulation and flocculation [12] and biological treatment [13]). Therefore, it is necessary to have sufficiently efficient, routine, and sensitive methods that also provide reliable results.

Due to the diversity of PAHs pollution sources, a complex mixture containing more than a hundred chemical

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compounds, including PAHs, nitro-PAHs, alkyl-PAHs, and their oxygen and/or sulphur derivatives, are found in different environmental matrices [5,14-16]. In addition, these substances are present in the gaseous or particulate phase of diesel engine emissions depending on their vapour pressure, which requires their assessment and quantification. Many researchers have focused on sixteen so-called priority PAHs (benz[a]pyrene...), whose harmful effects are well known and/or which found in high abundance (see the list of priority pollutants of the International Agency for Research on Cancer or the US Environmental Protection Agency) [17,18].

Published statistical data suggest that these PAHs and their derivatives, due to their relatively high toxicity and low biodegradability, could have an extremely negative impact on human health (cancer) [19]. Therefore, many researches are focused on this field, with the aim of finding remedies for the reduction of these emissions [20] and the cure of cancer [13,21,22]. Many studies have focused on the identification and quantification of organic pollutants, not only PAHs adsorbed on soot particles, but also their nitro derivatives (which are more carcinogenic and mutagenic than native PAHs [23-25]). Some researchers have shown that PAHs and their nitro derivatives are generally adsorbed on particulate matter (PM) present in diesel exhaust, and the adsorption of mainly carbonaceous and aromatic compounds on a carbon surface is very energetic [14,26,27]. PAHs and their derivatives are therefore very resistant to conventional extractions, which has led us to develop drastic extraction methods coupled with very sensitive chromatographic analysis techniques [28-30]. Among the extraction methods that have been used to extract organic substances is supercritical fluid extraction [31], pressurized solvent extraction [32], microwave solvent extraction [33], and ultrasonic extraction [34]. However, some extraction approaches have some disadvantages, including high cost, complex operation, and a long separation process.

The main objective is to develop a high-performance analytical method for the quantitative and selective extraction of PAHs, nitro-PHs, and heavy alkanes from particulate matter (PM) from diesel exhaust. Reflux extraction (HRE) was adopted as extraction technique by using appropriate solvent mixtures (pyridine, diethylamine, toluene...), due to its robustness, simplicity and efficiency,

and gas chromatography/mass spectrometry (GC/MS) as analytical technique due to its repeatability, linearity, detection and quantification limits, and also due to the complex nature of the analyzed samples.

## MATERIALS AND METHODS

### Solvents and Samples

Chloroform ( $\text{CHCl}_3$ , 99.8%), acetonitrile ( $\text{CH}_3\text{CN}$ , 99.8%), tetrahydrofuran ( $\text{C}_4\text{H}_8\text{O}$ , 99%), diethylamine ( $\text{C}_4\text{H}_{11}\text{N}$ , 99.5%), methylene chloride ( $\text{CH}_2\text{Cl}_2$ , 99.5%) pyridine ( $\text{C}_5\text{H}_5\text{N}$ , 99%) and toluene ( $\text{C}_7\text{H}_8$ , 99%) were obtained from Acros Organics. Acetic acid ( $\text{CH}_3\text{COOH}$   $\geq 99.8\%$ ) was supplied by Fluka. A solution of sixteen priority PAHs, six nitro-PAHs and three alkanes was prepared at a concentration of  $100 \mu\text{g ml}^{-1}$  for each component diluted in toluene : Anthracene (ANT,  $\geq 99\%$ ), Acenaphthene (ACE,  $\geq 99\%$ ), Benzo(k)fluoranthene (B(k)FLT,  $\geq 99\%$ ), benzo(a)pyrene (B(a)PYR,  $\geq 96\%$ ), dibenzo(a,h)anthracene (DB(a,h)ANT, analytical grade), 2-nitrofluorene (2N-FLUO, 98%), heneicosane (HENEI, 98%), naphthalene (NAPH, 99%), phenanthrene (PHEN, 98%), fluorene (FLUO, 98%), fluoranthene (FLT, 98%), pyrene (PYR, 98%), tetracosane (TETRACO, 99%), Triacontane (TRIACON, 98%), 1-nitronaphthalene (1N-NAPH, 99%), 1,5-dinitronaphthalene (1,5N-NAPH,  $\geq 97\%$ ), 2,7-dinitrofluorene (2,7N-FL, 97%), Acenaphthylene (ACTY, 99%), chrysene (CHRY, analytical grade) and indeno(1,2,3,cd) pyrene (I(1,2,3,cd)PYR, analytical grade) and 3-nitrofluoranthene (3N-FLT, 93%) were all supplied by Sigma-Aldrich. Benzo(b)fluoranthene (B(b)FLT, analytical grade), 9-nitroanthracene (9N-ANT,  $\geq 98.5\%$ ), benzo(a)anthracene (B(a)ANT, analytical grade) and benzo(g,h,i)perylene (B(g,h,i)PER, 98%) were procured from Supelco. During the entire duration of these studies, no degradation of the stock solutions was observed: they were regularly checked and reconstituted. Helium and nitrogen were delivered by Air Liquid (Alpha gas1 quality).

Diesel particulate matter was acquired from CERTAM (Centre d'Etudes et de Recherche Technologique en Aérothermique et Moteur, Rouen, France) at the outlet of a diesel engine. The soot was collected by using a commercial diesel particulate filter (DPF) made of cordierite located

between the oxidation catalyst (just after the diesel engine) and the exhaust pipe; after 24 h of high-temperature sampling, the soot material matter was blasted into glass bottles which were stored at low temperature.

### GC/MS Analysis

The gas chromatograph used was a Hewlett Packard Model HP 5890 Series II, was equipped with a mass spectrometer detector model HP 5972 (Hewlett Packard) with electronic impact. The chromatograph was equipped with a split/splitless injector with a J&W Scientific DB-5MS column (length: 50 m, diameter: 0.25 mm, film thickness: 0.25  $\mu\text{m}$ ), non-polar grafted phase (5% phenyl-95% methylpolysiloxane). The analysis was performed in the splitless mode (purge time: 2.3 minutes, with a leak rate of 50 ml  $\text{min}^{-1}$ ). The temperature of the spray chamber was maintained at 255  $^{\circ}\text{C}$ . The injector pressure was maintained for 1.7 min at 30 psi during splitless injection. The chromatograph was coupled to the mass spectrometer via a transfer line heated to 280  $^{\circ}\text{C}$ . The solvent delay was set at 5.5 min. The temperature programming thus optimized included a temperature increase from 50  $^{\circ}\text{C}$  to 180  $^{\circ}\text{C}$  at 35  $^{\circ}\text{C min}^{-1}$ , followed by a second temperature ramp at 4  $^{\circ}\text{C min}^{-1}$  up to 300  $^{\circ}\text{C}$ . The final temperature was held constant for 15 min. The carrier gas velocity was adjusted to 0.9 ml  $\text{min}^{-1}$ . The injections were made using a Hamilton syringe with a maximum capacity of 1  $\mu\text{l}$ .

### Extraction Process

The Buchi System B-811 automatic extractor was

applied in the standard solvent extraction and heating reflux extraction (HRE) of PAHs, nitro-PAHs, and heavy alkanes adsorbed on diesel particulate matter. Initially, extractions were performed from virgin soot ( $m = 100 \text{ mg}$ ) spiked with 100  $\mu\text{l}$  of 100  $\text{mg l}^{-1}$  of each component of the test mixture. The first standard extractions were performed with dichloromethane (a typical solvent in EPA protocols) [35], using 20, 40, or 60 cycles, with heating only of the lower compartment, this heating being able to go from level 1 (very low, about 30  $^{\circ}\text{C}$ ) to level 15 (very high, about 180  $^{\circ}\text{C}$ ). When HRE is applied, the upper part of the compartment is also heated. Table 1 shows the heating schedule used for some solvents (the heating levels were adapted to the vaporization temperature of these solvents). The matrix to be extracted was placed in a porous cellulose acetate cartridge (100 mm long and 32 mm in diameter).

After the extraction process, it was also necessary to evaluate the loss of analytes due to the evaporation of the solvent under reduced pressure. To do this, it was necessary to work under different pressures depending on the extraction solvent used, the aim being to obtain vaporization that is neither too slow (prohibitive time) nor too fast (loss of volatile compounds). So, depending on the solvent or solvent mixtures used, the procedure was carried out under different reduced pressures, as shown in Table 1. For binary mixtures, it was essential to work at decreasing pressures while observing several steps. Thus, for the pyridine/diethylamine and pyridine/acetic acid mixtures, pressures of 700 millibars were used initially and then gradually reduced to 50 millibars.

**Table 1.** Programming Heating of the Solvents Used in Heat Reflux Extraction (HRE)

Solvents	Vaporization temperature ( $^{\circ}\text{C}$ )	Heating programming		Vaporization conditions	
		Lower level	Upper level	Temperature of bath ( $^{\circ}\text{C}$ )	Pressure (millibars)
Dichloromethane	40	9	2	30	500
Acetone	56	11	3	35	300
Toluene	110	13	6	50	65
Diethylamine	57	11	3	35	290
Pyridine	115	13	6	50	50
Pyridine/Diethylamine	-	12	5	-	-
Pyridine/Acetic acid	-	13	6	-	-

## RESULTS AND DISCUSSION

In urban and metropolitan areas, PAHs are mainly produced by mobile sources. Particulate matter in diesel engine exhaust is composed of agglomerated solid carbonaceous material, oxygenated, hetero-atoms, and nitrated organic compounds [5,14,36]. These particles are mainly derived from unburned fuels and engine lubricating oils and depend on the type of diesel vehicle (light or heavy-duty diesel vehicles, ...*etc.*), the chemical composition of the fuel, the condition of the automobile (year, maintenance, ...*etc.*), the temperature and the sampling procedure of the diesel emissions, which is less well described.

The organic compounds adsorbed on the particulate matter are defined as the soluble organic fraction (SOF). The SOF fraction depends on the fuel and lubricating oil used as well as the engine and operating conditions [14,16]. It is generally agreed upon that soot forms in four stages (see Fig. 1) [14,36-40]: nucleation, particle surface growth, coagulation, and finally aggregation. In the exhaust line, the particle size also increases due to the condensation of the different constituents of the gas phase (hydrocarbons, metals, sulfur, and nitrate, *etc.*), which is allowed by the very high specific surface area of the particles, usually reaching  $220 \text{ m}^2 \text{ g}^{-1}$  [38,39].

The target PAHs were selected on the basis of their abundance or toxicity (PAHs belonging to the International

Agency for Research on Cancer “IARC” or the US Environmental Protection Agency “EPA” priority pollutant list), and their ability to be tracers of road pollution sources [6]. Also, the persistence of nitro-HAPs in the environment and the higher mutagenic and carcinogenic properties of some compounds compared to PAHs explain the increased attention given to these substances [23-25,41]. For this purpose, it was also envisaged to introduce nitrate and dinitratePAHs, as well as heavy linear alkanes that are also potentially present in diesel automobile emissions [38,41]. Figure 2 shows the list of compounds studied. Therefore, trace analysis of such a sample requires a sensitive and efficient analytical technique [4,10,14-15]. This is why we used gas chromatography coupled with mass spectrometry (GC/MS) [6,15].

### Optimization of the Analysis by “GC/MS”

In order to analyze these target pollutants (PAHs, nitro-PAHs, and heavy alkanes), several chromatographic columns were used and tested and in the end, we opted for a column with a stationary phase with 95% methyl and 5% phenyl (DB-5MS phase). This column with adapted programming allowed us to obtain a good resolution of the benzo(a)anthracene/chrysene and benzo(b)fluoranthene/benzo(k)fluoranthene couples, impossible on the conventional lengths of 30 meters or less used previously [42,43].

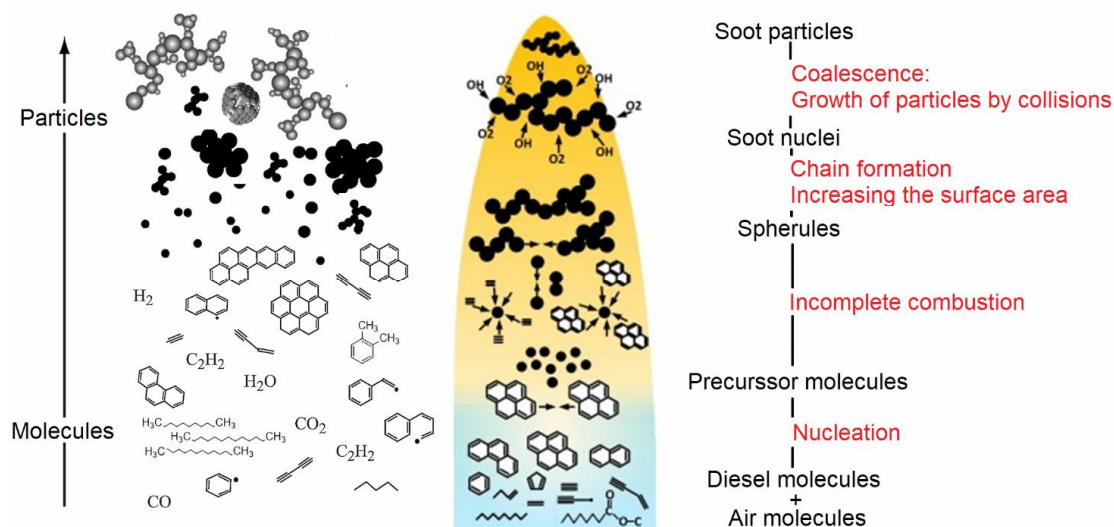


Fig. 1. Formation mechanisms of soot particulate from Diesel Engine.

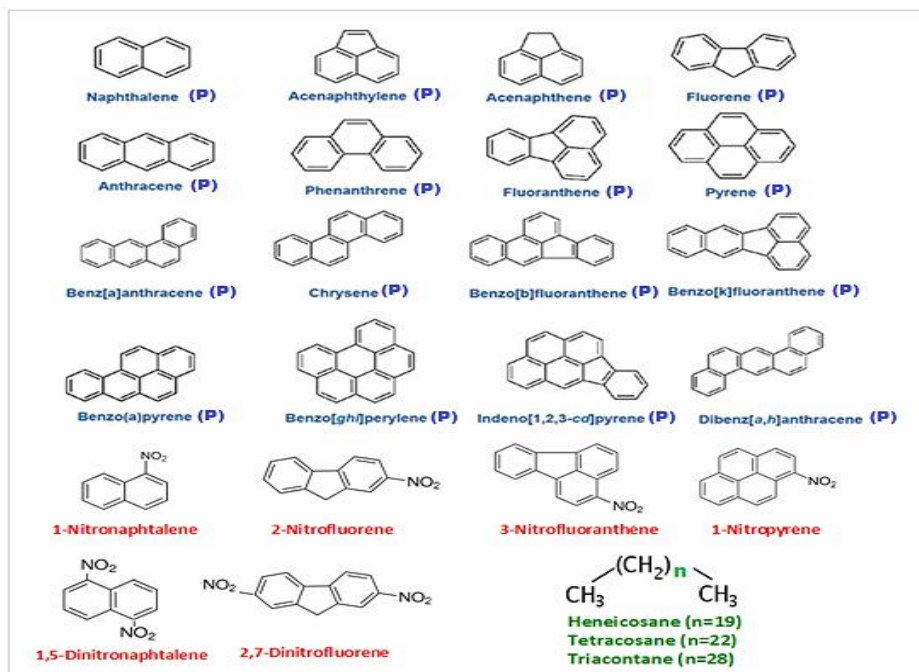


Fig. 2. List of PAHs, nitro-PAHs, and heavy n-alkanes studied (P: EPA priority).

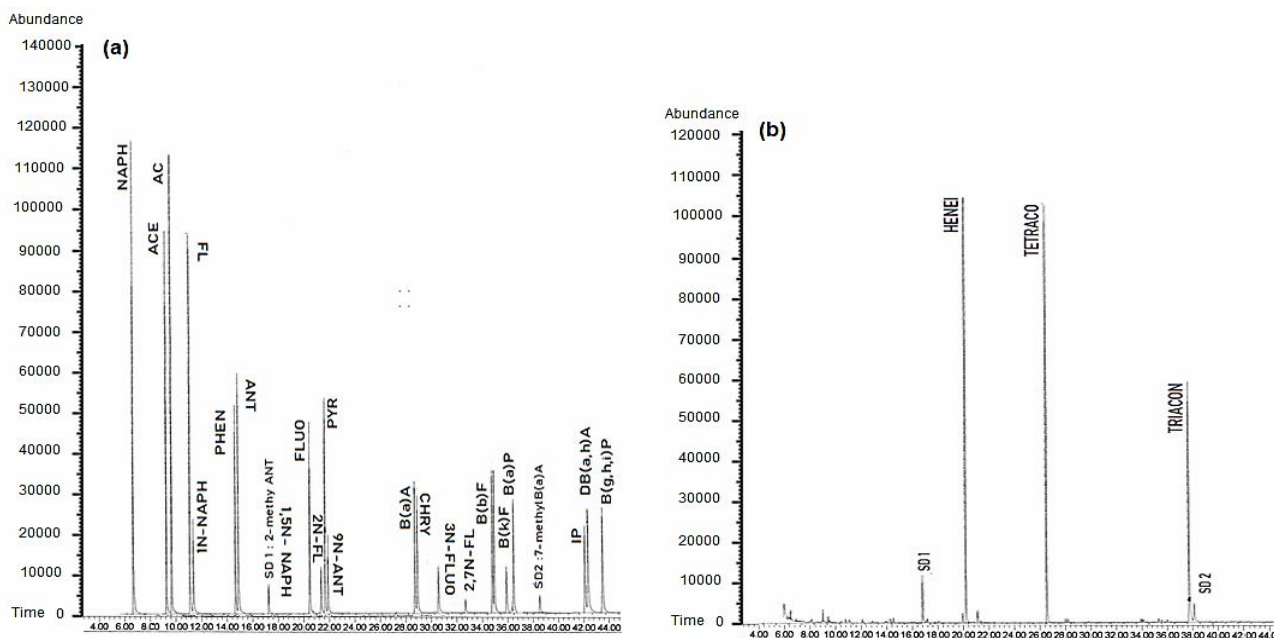


Fig. 3. GC/MS analysis chromatogram in SIM mode. (a): (PAHs and nitro-PAHs), (b): Alkanes.

GC/MS was applied in two modes: Total Ion Current (TIC) with a complete mass scan and for high sensitivity, the SIM mode (Single Ion Monitoring) was used (Fig. 3).

For this analytical approach by GC/MS, a study of the reproducibility of retention times and the concentration of the solute to be analyzed was carried out, it discovered that

the intermediate precision is excellent: the precision for retention times being between 0.03 and 0.09% and for concentrations around 0.04%. The detection limits established in SIM mode were between 0.14 and 2.3  $\mu\text{g l}^{-1}$  for PAHs, 35 and 65  $\mu\text{g l}^{-1}$  for heavy alkanes and 5 and 90  $\mu\text{g l}^{-1}$  for nitro-PAHs and dinitro-PAHs respectively. With a sensitive and reliable analytical method (GC/MS), it was necessary to develop and optimize the process (HRE) for the extraction of PAHs and their nitro derivatives from diesel soot.

### Standard Solvent Extraction

Significant advances have been made in the treatment of contaminated waters [10,12], soils, and particulate matter such as physico-chemical, thermal, and biological processes, with the aim of increasing efficiency at a lower cost. With such a variety of methods, the selection of an appropriate extraction method requires a thorough evaluation. Due to the complexity of the chemical composition of diesel soot, there is no universally accepted method to extract all adsorbed compounds. Despite the modernization of extraction techniques, the soxhlet is still considered the most robust method for diesel particulate matter (reference method), although it does not always provide the best extraction rate [15,44,45]. It is important for this type of study to perform extractions from a matrix

with a known and monitored the composition of the target pollutants and as close as possible to the real matrix. Soot particles cleaned and then doped are obviously more representative than sand or glass beads used in the first approach and which do not present the same types of potential interaction sites with PAHs, nitro-PAHs, or alkanes. Initially, extractions with dichloromethane (the solvent recommended by the EPA) [35] were applied for different numbers of cycles (20, 40, and 60), as shown in Fig. 4.

As shown in Fig. 4, extraction efficiency increases with the number of cycles. At least 60 cycles, *i.e.* more than 8 hours of extraction, are essential to obtain relatively satisfactory yields. Furthermore, it appears from these results that the extraction yields of PAHs and their nitrated derivatives decrease as a function of their molecular weight. In fact, after 60 extraction cycles volatiles, PAHs are extracted with an average yield of 50 to 70%, while this yield decreases to 40 to 50% for semi-volatile PAHs; the rate is much lower for heavy PAHs: only 10% to 20%. On the other hand, heavy alkanes yields were satisfactory: exceeding 82% for 60 cycles, their extraction can be described as quantitative. Five experiments were conducted to evaluate the relative standard deviations (RSD) corresponding to these extraction yields. The RSDs obtained ranged from 2% to 5% for volatiles PAHs, 3% to

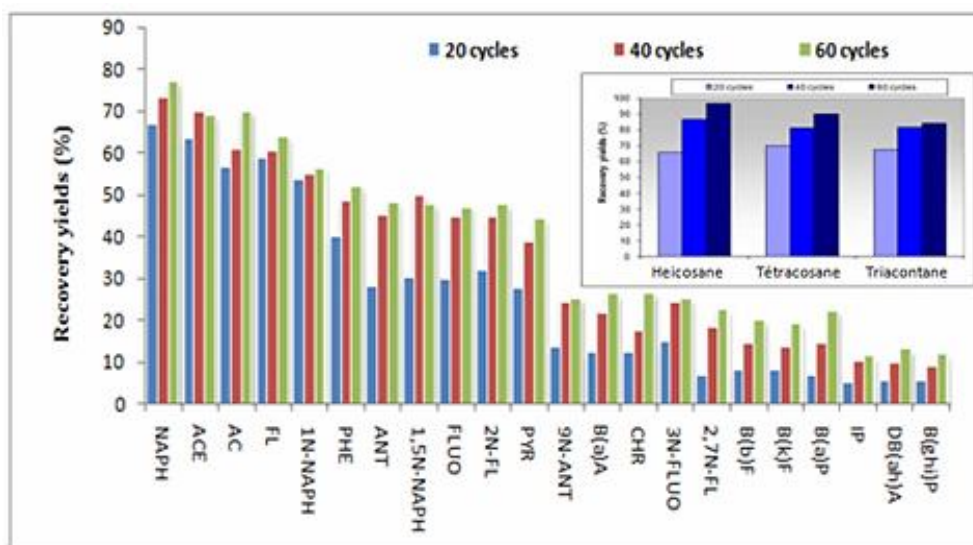


Fig. 4. Evolution of extraction yields by standard solvent extraction, as a function of the number of cycles.



8% for heavy PAHs, 7% to 10% for nitro-PAHs, and 2% to 8% for alkanes. As the quantitative extraction capacity was far from being reached under these conditions, it was necessary to test other solvents also used in the literature (acetone and toluene) [46]. Under the same extraction conditions (60 cycles), a modest increase in extraction yields was observed when using toluene compared to extractions with acetone or dichloromethane (see Fig. 5).

From these results, it appears that the extraction of PAHs was significantly enhanced in the presence of an aromatic solvent. On the other hand, heavy PAHs were not perfectly extracted (yields not exceeding 15-30%) thus nitro-PHAs extraction was not really improved when toluene is used as extraction solvent compared to extractions with dichloromethane or acetone. The extraction of alkanes remains quantitative whatever the solvents are used.

In view of these results, it appeared that standard solvent extraction was not sufficiently efficient for the extraction of semi-volatile PAHs, heavy PAHs, and nitro-PAHs unless the number of extraction cycles and thus the extraction time (more than 8 h) were significantly increased. For this reason, it was decided to improve one of the key elements

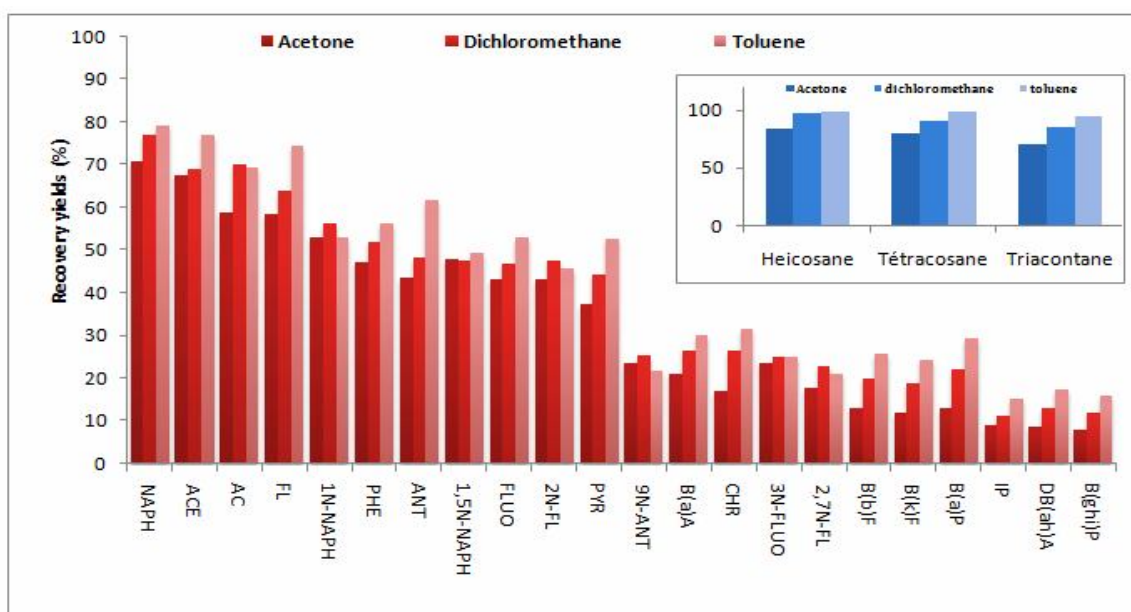
of the process, namely reflux extraction by heating (HRE).

### Heating Reflux Extraction (HRE)

The thermal reflux extraction method has been used in the study of PAHs due to its higher sensitivity, good stability, low-cost equipment, simple operation, and wide dynamic range [47-49]. The choice of extraction solvent is the most important variable in the extraction process, as the yield and rate of extraction of PAHs are related to the characteristics of the solvent.

### Use of Conventional Solvents

As extraction yields are generally unsatisfactory with standard extraction, a new approach to extraction has recently been developed: heating reflux extraction (HRE). This new technique differs from the classical approach by heating the upper compartment of the standard solvent extraction containing the matrix to be extracted, soot in our case. The matrix/solvent exchanges are thus accelerated, resulting in more efficient desorption of the solutes, thus obtaining better extraction yields in a short time. However, this additional heating remains slight as the solvent must remain in a liquid phase in the upper compartment. As



**Fig. 5.** Extraction yields of PAHs, nitro-PAHs, and heavy alkanes as a function of the nature of the solvent extraction (number of cycles: 60).

shown in Fig. 6, in our case the heating reflux extraction with toluene as extractant led to a slight improvement in the extraction yields of volatile PAHs, with yields now reaching 80%.

A strong increase in the extraction of semi-volatile PAHs was also observed, with yields going from 30-50% to 70-80%, and finally a very significant improvement in the extraction of heavier PAHs, with yields now between 30-50%. However, it was noted that while the majority of the compounds in the tested mixture were almost quantitatively extracted, the nitro-HAPs and the heaviest PAHs remained refractory to this extraction.

With no intention of increasing the extraction time and therefore the number of cycles, it was considered to attempt to extract the doped soot by trying to use different types of solute/adsorption site/solvent interactions. For this purpose, a range of solvents (tetrahydrofuran, dichloromethane, acetone, hexane, chloroform, and diethylamine...) was evaluated, without finding any improvement in yields for heavy PAHs.

In view of this observation, it was then envisaged to use pyridine, a solvent with an electron-donating character in addition to its aromatic character, apparently favourable to the extraction of heavier PAHs. As shown in Fig. 6, this solvent shows a very significant improvement in the extraction yields of heavy PAHs, with extraction rates above 50%. As the extraction of volatile PAHs, semi-volatile PAHs, and heavy alkanes can be described as quantitative with this solvent, it was unambiguously stated that pyridine has the best extraction capacity of "diesel particles". As of nitro-PAHs no real improvement in desorption yields was observed compared to toluene.

### Use of Binary Solvents

Although dichloromethane has been reported to be more efficient for the extraction of low molecular weight PAHs, mixing solvents is often considered for the extraction of very heavy PAHs and PAHs [50]. In order to improve the extraction efficiency of heavier PAHs and even nitro-PAHs, binary mixtures have been used [28,51]. Indeed, we have

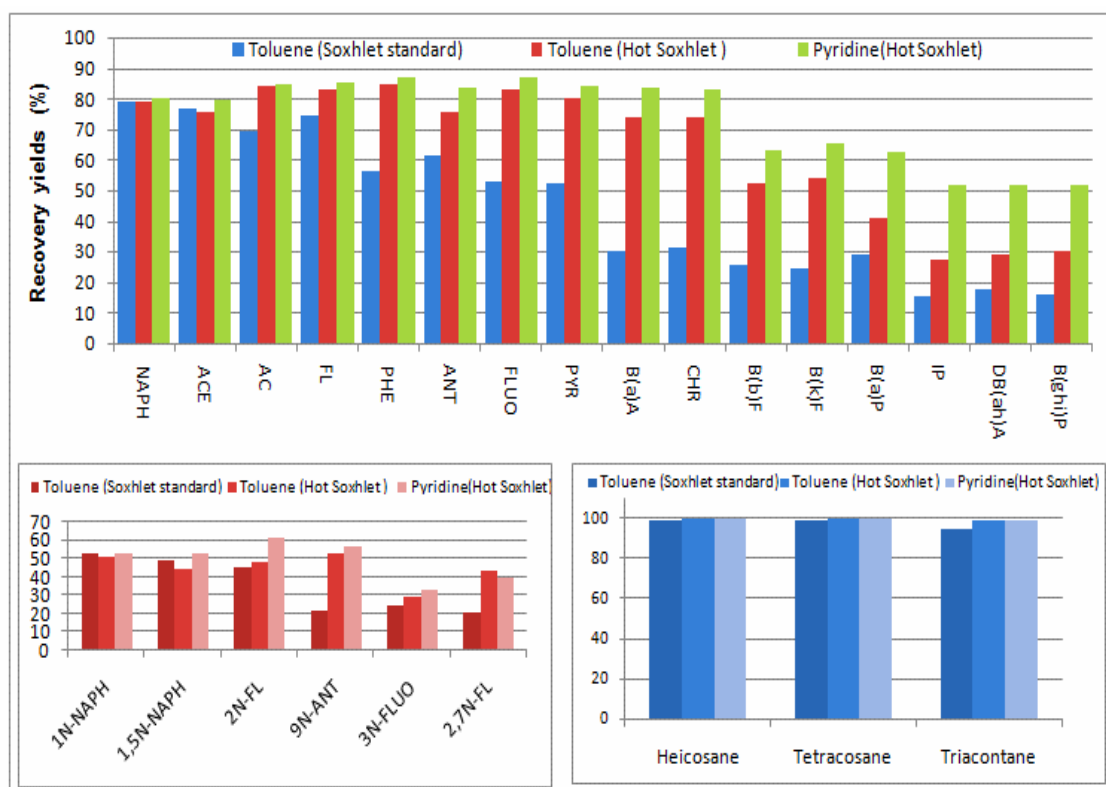


Fig. 6. Extraction yields using Heating reflux extraction (HRE).

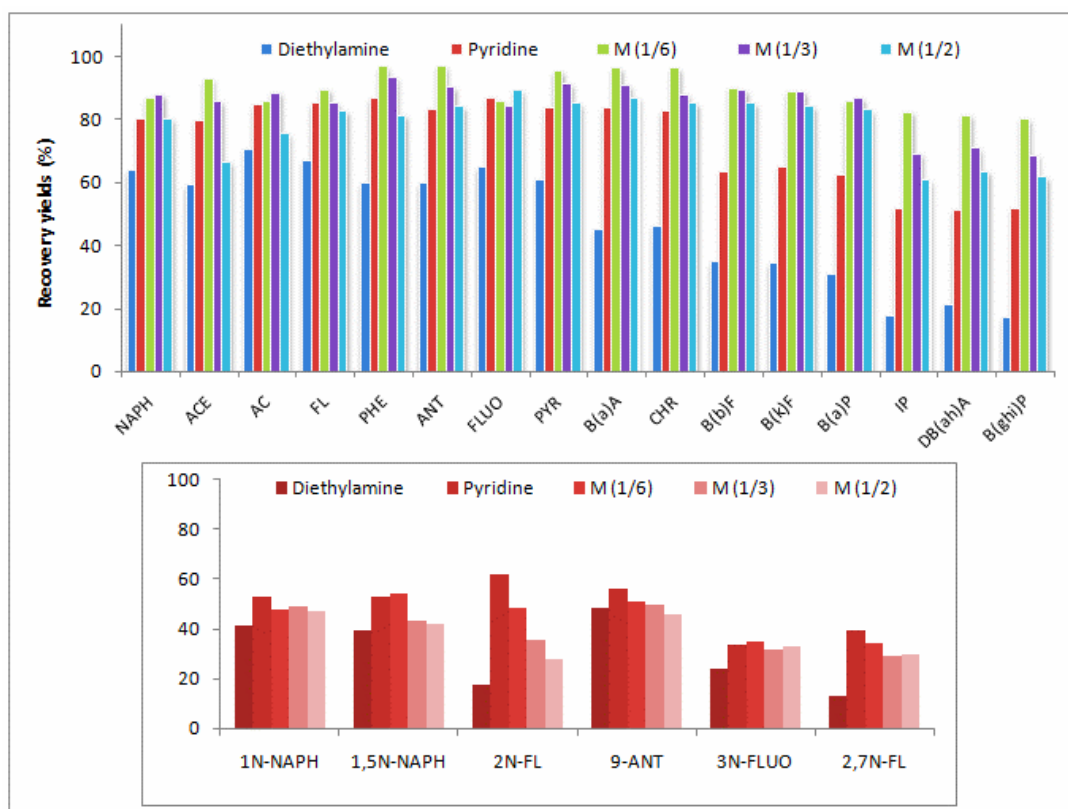


previously found that pyridine, which is both aromatic and basic, had a better extraction capacity than toluene, which has only an aromatic character. Following this approach, it was opted to combine diethylamine (which has a strong basic character) with pyridine. The extraction rates of the heavier PAHs such as indeno (1, 2, 3-c, d) pyrene or benzo (g, h, i) perylene, which were previously the most difficult to extract, reached 85% when a pyridine/diethylamine (M) mixture was used as shown in Fig. 7.

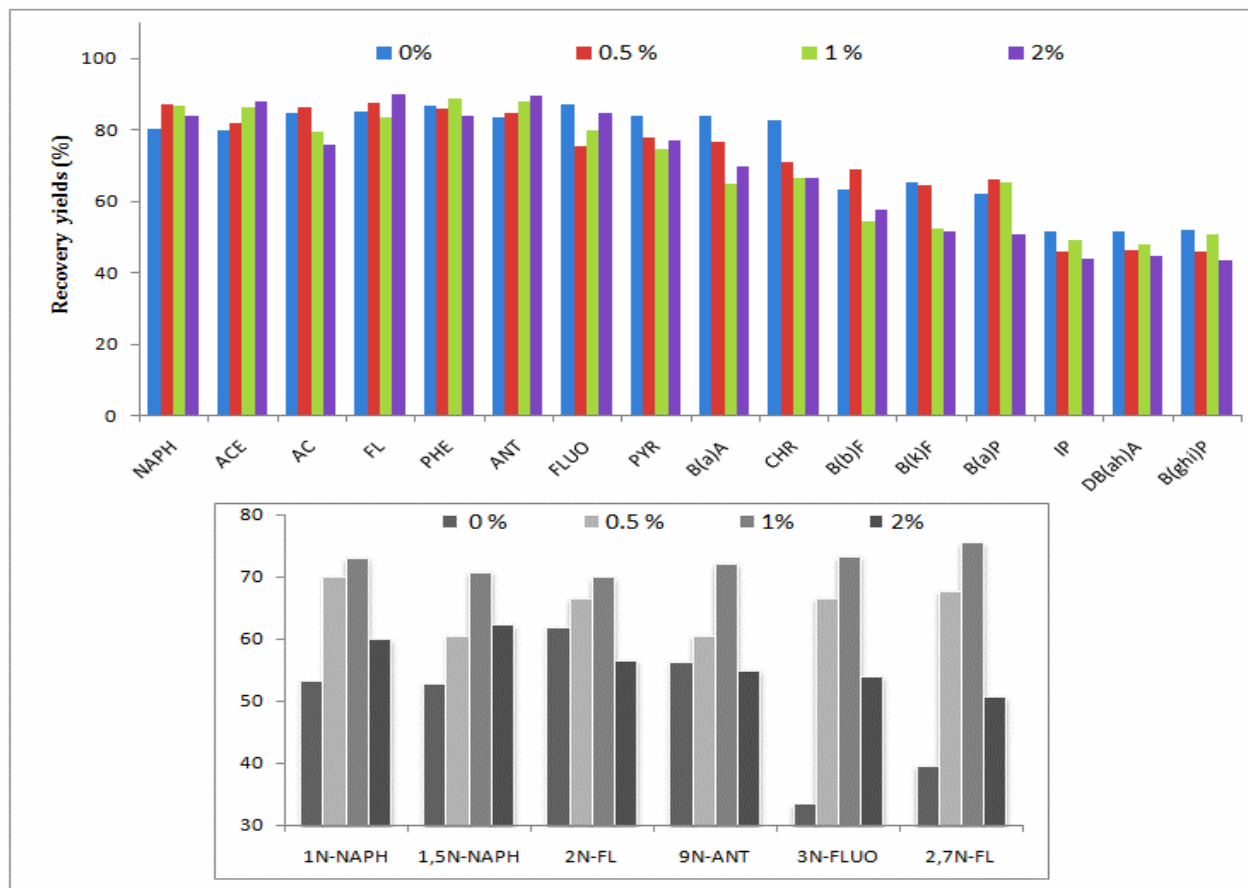
However, for important proportions of diethylamine (higher than 16% of pyridine) the PAHs recovery yields decreased which could be explained by a significant decrease in the aromatic character of the extractant mixture in favor of the basic character. Finally, it was also observed that the addition of diethylamine (enhancing the electron donor character), on the contrary, the extraction of nitro-PAHs was significantly deteriorated. Therefore, adding a small amount of diethylamine to the pyridine can

significantly improve the extraction of the heavier PAHs. Subsequently, it was envisaged to evaluate the effect of decreasing the basic character of pyridine on the extraction yield of nitrated PAHs. For this purpose, a mixture of acetic acid and pyridine was selected. The effect of adding acetic acid to pyridine, ranging from 0 and 2% on the extraction yield of PAHs and their nitrated derivatives was reported in Fig. 8.

As shown in Fig. 8, the extraction yield of nitro-HAPs increased significantly with the addition of acetic acid, with a maximum of 1% acetic acid in pyridine. Under these conditions (1% acetic acid in pyridine), more than 78% of the heavy nitro-HAPs that were only very partially desorbed from the soot were extracted, regardless of the conditions used previously. For example, the extraction yield of 3-nitrofluorene increased from 32% with pyridine alone as the extraction solvent, to nearly 75% when pyridine/acetic acid (99/1%) was used as the extraction solvent. On the



**Fig. 7.** Extraction efficiency by Heating reflux extraction of PAHs and nitro-PAHs as a function of the proportion of mixture M (diethylamine in pyridine).



**Fig. 8.** Extraction efficiency by Heating reflux extraction of PAHs and nitro-PAHs as a function of the percentage of acetic acid in pyridine.

other hand, the addition of 1% acetic acid to pyridine seems to have little effect on the extraction yields of the native PAHs, including the heavy PAHs, with the exception of chrysene, whose extraction yield decreased from more than 80% in pyridine alone to about 60% when pyridine/1% acetic acid was used. This effect of acetic acid addition to pyridine can be explained simply by the reinforcement of the dipolar character of this extractant: strong dipole-dipole interactions are developed between the extracting solvent and nitro-PAHs that are strongly dipolar compounds, thus promoting their solubilization in the extracting solvent. Moreover, since the interactions  $\pi$  acceptor/ $\pi$  donor are always present, the extraction yields of the other aromatic compounds constituting the test sample (volatile to heavy PAHs) were minimally modified.

### Extraction of Particles from a Diesel Engine Bench

The CERTAM carries out engine bench tests during which it controls a large number of parameters: engine speed, load, fuel, supercharging, and filters (see Fig. 9). For our study, it provided us with soot from the combustion of diesel fuel used in a diesel engine.

Figure 9 shows a connection part inserted in the exhaust line and having two outlets: one directed to the gaseous analysis bay, the other to the particulate sampling system. Such a device allows both isokinetic particulate sampling and undisturbed flow of the particulate to the filter holder. In this case, variable dilution of the exhaust aerosol with filtered ambient air was performed to maintain a constant total flow (air+sample) under all operating conditions.

Sampling is performed isokinetically [14,38,52], with an

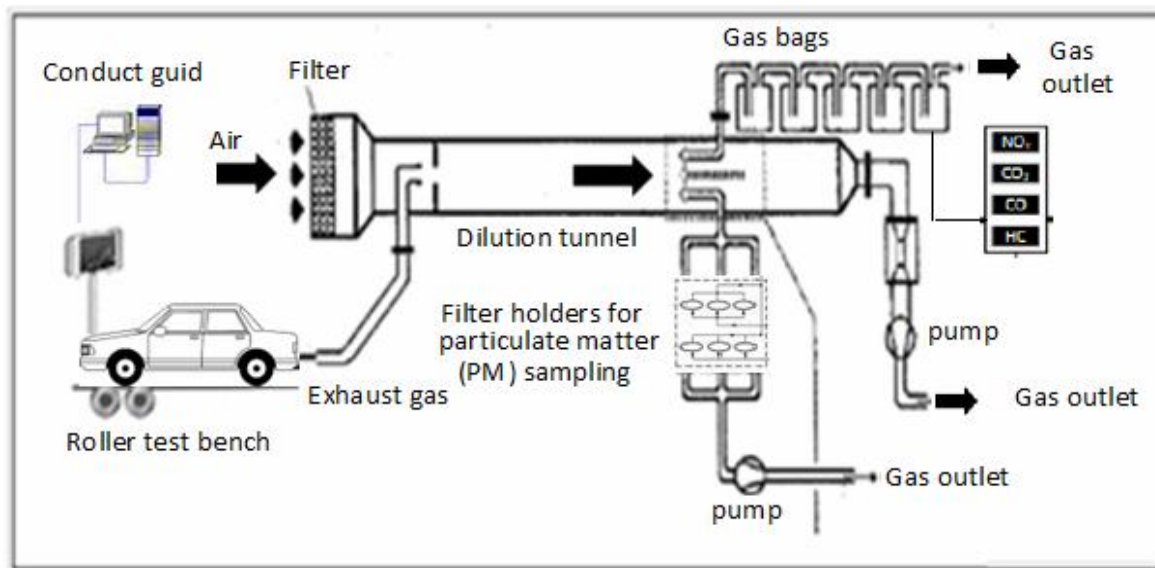


Fig. 9. Sampling system installed on Diesel engine bench (CERTAM).

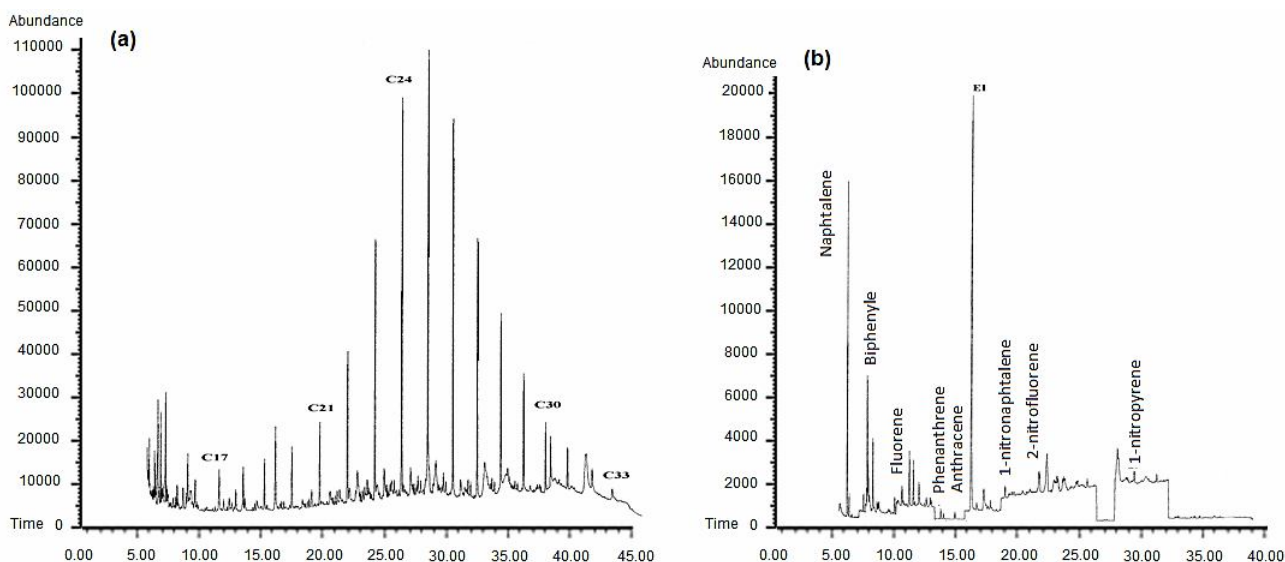
average velocity of the sampled gas equivalent to that of the exhaust gas flow. Soot was collected from the exhaust of a diesel engine by CERTAM. The engine used was a PSA "turbo-diesel" engine type DW20 ATED with 4 cylinders, for a maximum power of 80 KW at 4000 rpm. Diesel particles were collected during the operation of the engine far from extreme combustion conditions (operation of the engine at medium charge), without an oxidation catalyst, using fuel of the Elf 120 A type (sulphur content less than 8 ppm, cetane number equal to 52.1, composition of polyaromatics of 5% by mass) and a Total 5W40 type oil. The exhaust was filtered through a conventional cordierite particulate filter (FAP) ( $V = 2.5$  L,  $dp = 32$  nm). This was then counter-blown for soot recovery in glass bottles. The sampling temperature was measured at the inlet of the particulate filter and was approximately 280 °C, while the temperature during blowing was 120 °C. These diesel particulate matter extraction tests, were collected during engine tests resulting from the combustion of diesel fuel, showed interesting results. The analysis of the extract in TIC mode revealed, in fact, a very preponderant presence of alkane-type pollutants (linear and ramified) and a priori very few PAHs or nitro-PAHs, as shown in Fig. 10.

It should be noted that the background noise of the analysis in TIC mode is very important and is mainly due to

the presence of ramified alkanes. The extract was then analyzed in SIM mode in order to visualize, by category, only PAHs and nitro PAHs on one hand and heavy alkanes on the other. As a result, heavy alkanes with 14 to 32 carbons are clearly adsorbed on this soot, in proportions ranging from 1.76  $\mu\text{g g}^{-1}$  for C<sub>14</sub>, the least abundant, to 44.18  $\mu\text{g g}^{-1}$  for C<sub>25</sub>, the most abundant.

In reality, the distribution of heavy alkanes adsorbed on diesel particles appears to be a Gaussian distribution [53-56], with a maximum concentration for alkanes with a carbon number between C<sub>24</sub> and C<sub>26</sub>. These results are in accordance with those found during the analysis of alkanes emitted during incomplete combustion of petroleum derivatives, for which the authors noted a majority concentration of the C<sub>27</sub> alkane on the collected soot [54]. On the other hand, Harrison *et al.* [57] reported that the profile of n-alkanes emitted from fossil fuel combustion showed a bimodal distribution with higher emission rates between C<sub>20</sub> and C<sub>22</sub> and C<sub>24</sub> and C<sub>26</sub>.

Regarding the analysis of PAHs and nitro-PAHs in SIM mode, very few PAHs are found, mainly Naphthalene, Biphenyl, Fluorene, Phenanthrene, and Anthracene, but in very small quantities, with concentrations ranging from 4.84  $\mu\text{g g}^{-1}$  for Naphthalene to 0.31  $\mu\text{g g}^{-1}$  for Anthracene (see Table 2). Three nitro-PAHs were also detected and



**Fig. 10.** Analysis by GC/MS in SIM mode of the extract after heating reflux extraction. (a): Alkanes (b): PAHs and nitro-PAHs.

**Table 2.** PAHs and Nitro-PAHs are Extracted from Diesel Soot by HRE

Compounds (PAHs) ( $\mu\text{g g}^{-1}$ )	Compounds (nitro-PAHs) ( $\mu\text{g g}^{-1}$ )
Naphtalene: 4.84	1-nitronaphtalene: 0.97
Biphenyle: 3.65	2-nitrofluorene: 1.22
Fluorene: 2.75	1-nitropyrene: 1.78
Phenanthrene: 0.31	
Anthracene: 0.31	

quantified, namely: 1-nitronaphtalene, 2-nitrofluorene, and 1-nitropyrene, the latter being presented, according to several studies, as the marker for diesel engine emissions [58]. Qualitatively, some of these findings are consistent with other studies in this domain.

Bamford *et al.* developed an analytical procedure to quantify nitro and dinitro-PAHs, present in SRMs of air and diesel particulate matter and noted the abundance of both nitro-PAHs: 2-nitrofluoranthene and 1-nitropyrene [59].

In the diesel particulate matter from an industrial forklift (reference material SRM 2975), it was detected 30-40  $\mu\text{g g}^{-1}$  of 1-nitropyrene, 3-4  $\mu\text{g g}^{-1}$  of 3-nitrofluoranthene, 3  $\mu\text{g g}^{-1}$  of 9-nitroanthracene and 5-7  $\mu\text{g g}^{-1}$  [60]. The diesel engines

emit 0.4 to 1.9  $\mu\text{g km}^{-1}$  of nitro-PAHs [25,61]. However, in the study by Karavalakis *et al.*, 1-nitropyrene and 6-nitrobenzo[a]pyrene were found to be the dominant nitro-PAHs while others such as 3-nitrofluoranthene and 7-nitrobenzo[a]anthracene were below the detection limit [61,62]. Also in recent studies, Li *et al.* [63] characterized the emissions of PAHs derivatives from a direct injection diesel engine of diesel, biodiesel, and their blends where it found the low molecular weight PAHs emitted clearly decreased with the addition of biodiesel to all engine loads, while 1-nitropyrene was the dominant compound in the exhaust particles for all fuels.

## CONCLUSIONS

Diesel particulate matter contains a variety of organic substances adsorbed on its surface, which are of great concern due to their high toxicity to human health. In this study, the heated reflux extraction approach (HRE) demonstrated a real breakthrough in the extraction of PAHs and their nitro derivatives from diesel particles, known to be among the most refractory:

\* Using binary mixtures (pyridine/diethylamine: 6/1), it is possible to extract quantitatively heavy alkanes and all PAHs, including the heaviest ones (with four to five rings) with yields above 85%.

\* For nitro-HAPs, virtually successful extraction can be obtained with a pyridine/acetic acid (1%) solvent mixture.

During the extraction of real soot directly from a diesel engine test bench, significant amounts of linear C<sub>14</sub> to C<sub>32</sub> alkanes and, to a lesser extent, branched saturated hydrocarbons were found, but few PAHs: naphthalene (4.84 µg g<sup>-1</sup>), biphenyl (3.65 µg g<sup>-1</sup>), phenanthrene (0.31 µg g<sup>-1</sup>), anthracene (0.31 µg g<sup>-1</sup>) and fluorene (2.75 µg g<sup>-1</sup>) and nitro derivatives: 1-nitronaphthalene (0.97 µg g<sup>-1</sup>), 2-nitrofluorene (1.22 µg g<sup>-1</sup>) and 1-nitropyrene (1.78 µg g<sup>-1</sup>). Under these conditions, it would appear that most PAHs and even very heavy alkanes are only slightly condensed on the soot, most of them remaining in the gas phase at high temperature, and would therefore be vaporised directly from the engine. Moreover, following the results obtained from this study, reflux extraction has remained one of the most widely used extraction processes for its efficiency, simplicity, ease of use, wide range of applications, and the possibility of integration with different analytical approaches.

For future research, other PAH derivatives (oxygenated, sulphurated, alkyl PAHs, heterocyclic PAHs, ...) will be studied and compared with other recent techniques.

### Highlights

- Optimization and validation of a GC/MS method for the analysis of PAHs and nitro-PAHs.
- The Heating reflux extraction (HRE) technique was evaluated
- Quantification of PAHs from diesel engine exhaust particles was developed.
- HRE gives reliable results for the extraction of PAH and nitro PAH from complex samples such as soot.

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