

Pressurized liquid extraction and gas chromatography/mass spectrometry for determination of nitrated polycyclic aromatic hydrocarbons adsorbed on refractory diesel particles

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ABSTRACT

A pressurized liquid extraction (PLE) technique was evaluated in this study and optimized using response surface methodology (RSM) for the determination of polycyclic aromatic hydrocarbons and their nitro derivatives from diesel particulate matter. A central composite design (CCD) was applied for the study of three parameters (temperature, nature of solvent and static time) and the optimal conditions were determined for a time of 9 min and a temperature of 145 °C and dichloromethane as extraction solvent. With the GC/MS analytical technique, the limits of detection (LOD) obtained range from 0.3 to 1.5 µg.L⁻¹ for PAHs and from 4.6 to 8 µg.L⁻¹ for nitrated PAHs. Also, this method allowed excellent recoveries of NPAH adsorbed on diesel soot particles (R ≥ 90%) using a mixture of solvents (1% acetic acid in pyridine). The PLE process developed in this research is quantitative and reproducible while using much less solvent than conventional extraction methods.

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1. Introduction

The development of industrial activities and road transport has profoundly altered the perception of pollution, both in terms of the composition and content of pollutants and their dispersion.¹⁻⁴ The chemical composition of the particles emitted by the means of transport reveals the presence of high concentrations of polycyclic aromatic hydrocarbons (PAHs) and their derivatives nitrated oxygenated, etc.⁴⁻⁶ A number of PAHs present in the atmosphere exist simultaneously in gaseous and particulate form.⁶ The particle phase includes many types of particles that can be classified according to their size or composition. Exposure to diesel particulate matter (DPM) is a serious problem, as it contains toxic compounds, leading to widespread risks, and its concentration can be very high, leading to adverse, even toxic, effects on human health.^{2,5} In this context, in recent years, many publications have focused on particulate matter from diesel engines, but also on diesel itself, revealing the existence of PAHs and nitro-PAHs in such emissions.⁵⁻⁷ Nitrated PAHs (NPAHs) are responsible for more than 40% of the mutagenic activity determined in diesel particles.^{6,7} Their determination is of increasing interest since they are directly mutagenic, whereas PAHs are only mutagenic after enzymatic activation.^{7,8} NPAHs can be formed alternatively by reaction between PAHs and reactive species found in the air such as dinitrogen pentoxide N₂O₅ and oxygen radicals in the presence of NOx.^{6,9} The most abundant PAHs in the atmosphere are 1-nitropyrene, 2-nitrofluorene and 2-Naphthalene, which have already been identified in diesel particulates.¹⁰⁻¹² Also, it should be noted that dinitroPAHs have a higher mutagenic activity, but their abundance is however much lower than that of all nitroPAHs.^{12,13} The most accurate individual search for pollutants such as aromatic hydrocarbons,¹⁴ metals¹⁵ and dyes¹⁶⁻¹⁸ in complex matrices therefore requires an extraction method that specifically recovers the compounds of interest. Although many studies have focused on the analysis of PAHs in the environment in terms of air quality, few studies have presented as objective the characterization of adsorbed

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nitro-aromatic pollutants on diesel particles, whose carcinogenic properties are not to be demonstrated.^{1,4,9,11} Indeed, the main difficulties associated with the analysis of aromatic hydrocarbons stem from their physical properties (volatility), their low concentrations and the complexity of the environmental matrix in which they are present.^{19,20}

In general, in many studies, these organic compounds are extracted by conventional methods, using a wide variety of solvents such as acetone, toluene, hexane, dichloromethane or mixtures of solvents, with varying extraction times.^{13,18} However, analyses of PAHs and NPAHs in diesel PM have shown that it is more difficult to extract these compounds, with extraction recoveries decreasing with increasing PAHs molecular weight.^{19,20} These pollutants were strongly adsorbed onto the partially graphitic surface and absorbed into the condensation layer around the carbonaceous core, which can explain the difficulty of extracting using classical techniques.²¹⁻²² The alternatives to this technique are various and included the extraction by PLE (under pressure and temperature) which will be developed in this study. Operation at high temperatures results in greater solubility of analytes, faster diffusion rates, lower solvent viscosities and weakened solute-matrix interactions.²³⁻²⁵ In addition, pressurization allows working with solvents as liquids above their boiling point by accelerating the entire extraction process, which allows for greater automation and yields, as well as faster recovery, compared to conventional extraction methods.²³⁻²⁵ For this reason, PLE was the chosen method for this study. Among the parameters that can influence the extraction yield, temperature, static time and solvent nature are the main ones and will be studied here using the response surface methodology (RSM). In addition, a central composite design for the extraction of PAHs and NPAHs adsorbed in DPM was used to understand the impact of key parameters on extraction performance and eventual interactions.

2. Materials and method

2.1. Solvents and samples

Acetonitrile, toluene, pyridine, diethylamine, methylene chloride (all of HPLC grade) and acetic acid (purity 99.5%) were obtained from Fisher Scientific France. Phenanthrene (PHE, purity >96%), Anthracene (ANT, >99%), Fluoranthene (FLUO, >98%), Fluorene (FL, >96%) and Pyrene (PYR, > 96%) were from Sigma. Naphthalene (NAPH, > 99%) and 1-nitronaphthalene (1N-NAPH, > 99%) were supplied by Acros. Finally, Chrysene (CHRY, 98%), 9-nitroanthracene (9N-ANT, > 97%), 2-nitrofluorene (2N-FL > 98%), 3-nitrofluoranthene (3N-FLUO, > 90%), and 1,5-dinitronaphthalene (1,5N-NAPH, > 98%) were obtained from Sigma-Aldrich France.

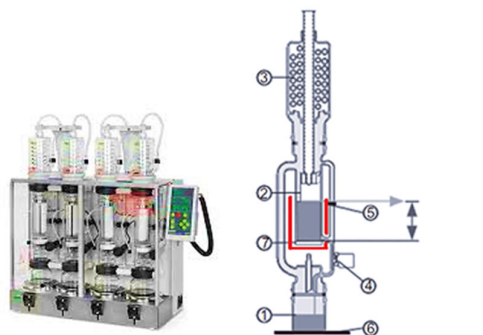
2.2. Diesel particulate matter

Soot from the combustion of a diesel engine was produced from CERTAM (Centre d' Etude et de Recherches Technologiques en Aréothermique et Moteur, France). The engine used is a turbocharged 2L turbo diesel engine running at 1500 rpm under an effective pressure of 8 bars (power 90 kW, torque 300 Nm). Exhaust emissions were collected directly from a diesel engine using a particulate filter and the measured sampling temperature was 300 °C. The exhaust has been filtered through a conventional cordierite filter (ceramic) with a volume of 1.7 litres, the diesel used being a standard fuel. Diesel particles were then stored at (-10 °C).

2.3. Extraction

2.3.1. Soxhlet purification process

Hot Soxhlet extractions were carried out with a Büchi B-811 Soxhlet extractor acquired from IMLAB (Lille, France) (**Fig. 1**).



1: distillation flask; 2: sampling tube; 3: condenser; 4: glass valve; 5: optical sensor; 6: lower heating level; 7: upper heating level.

Fig. 1. Scheme of the Hot soxhlet Extractor (HSE).

The objectives of this extraction are to clean the soot to obtain a virgin soot of alkanes and PAHs and their derivatives, in order to be able to spike it with known amounts of standard compounds, and consequently to evaluate the performance of extraction techniques other than the Soxhlet extraction. A 100 mg sample of collected diesel soot was extracted using 150 ml of a solvent at a reflux of 60 cycles. The extract was then evaporated at approximately 2 mL and analysed by GC/MS. Finally, the washed soot was finely ground to obtain a homogeneous matrix and stored at a temperature of 4 °C. Once the test solution was deposited, we waited several hours for the soot to permeate, before proceeding with the extraction. The matrices to be extracted were first brought into contact for 24 hours with the spiking solution, i.e. 100 μL of a toluene solution containing the standards mentioned above, with a concentration of 100 $\mu\text{g}\cdot\text{mL}^{-1}$.

2.3.2. Pressurized liquid extraction (PLE)

The Pressurized liquid Extractor is an automated system for the extraction of organic compounds from solid or semi-solid samples. It accelerates traditional extraction processes by using solvents at high temperatures maintained under high pressure. This pressure, applied to the extraction cell containing the filter, maintains the hot solvent in a liquid state throughout the extraction process. After the heating phase, the extract was transferred from the cell containing the sample to the recovery flask. An ASE100 extractor supplied by Dionex (see Fig. 2) was used for this purpose. It operates at high temperature and maintains the extraction solvent under pressure (100 bars). The extraction cell for this apparatus is placed in a heated chamber and can contain a maximum of 10 ml of solvent. After the heating phase, the extract was pumped from the cell to the recovery bottle.

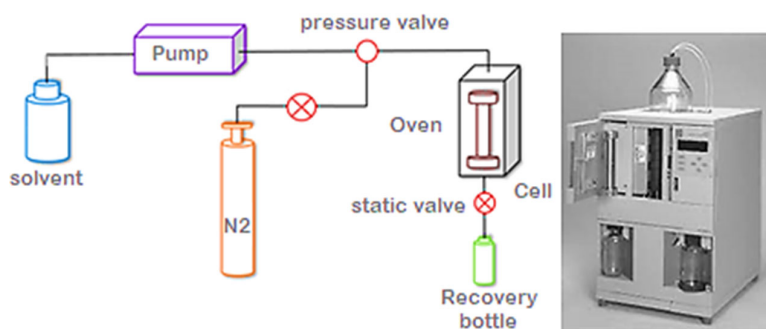


Fig. 2. Schematic diagram of the operating principle of the ASE100 extractor.

2.4. Chromatographic analysis GC/MS

All analyses were carried out using a Hewlett-Packard HP 5980 Series II gas chromatograph (Palo Alto, CA, USA) equipped with a splitless injector (purge time: 2.5 min, purge flow rate: 65 $\text{mL}\cdot\text{min}^{-1}$). An injection volume of 1 μL was set and the injector temperature was maintained at 255 °C. The temperature was programmed as follows: 65 °C for 4 min, followed by a temperature rise at a rate of 50 $^{\circ}\text{C}\cdot\text{min}^{-1}$ to 175 °C, then a second temperature ramp at a rate of 4.5 $^{\circ}\text{C}\cdot\text{min}^{-1}$ to 330 °C, and finally this temperature was maintained for 15 minutes. A DB5-MS capillary column (stationary phase: (5%-phenyl)-methylpolysiloxane, dimensions (50 m x 0.25 mm internal diameter, film thickness: 0.25 μm) was acquired from J&W Scientific (Folsom, CA, USA) and was operated under a helium flow rate equal to 0.9 $\text{mL}\cdot\text{min}^{-1}$. The chromatograph was coupled to an HP 5972 mass spectrometer (Hewlett Packard). Ionisation was carried out by electronic impact at an energy equal to 70 eV, and the solvent delay was fixed at 6.4 min. From different calibration curves, comprising 8 points, established from the injection of standard solutions of concentrations between 0.1 and 5 $\text{mg}\cdot\text{L}^{-1}$, the response factors of the 12 compounds studied were obtained.

2.5. Statistical data analysis

The optimisation of the PLE extraction process of PAHs and NPAHs adsorbed on diesel particles was performed using a CCD approach coupled with response surface methodology (RSM) and some related calculations, such as analysis of variance (ANOVA), were performed using JMP software (SAS Institute).

3. Results and discussion

3.1. Collection of virgin soot

In the context of our study, CERTAM provides us with soot from the combustion of diesel engines obtained under very rigorous experimental conditions. Tests on an engine test bench to check a large number of parameters: engine speed, load, fuel and filters (see Fig. 3).

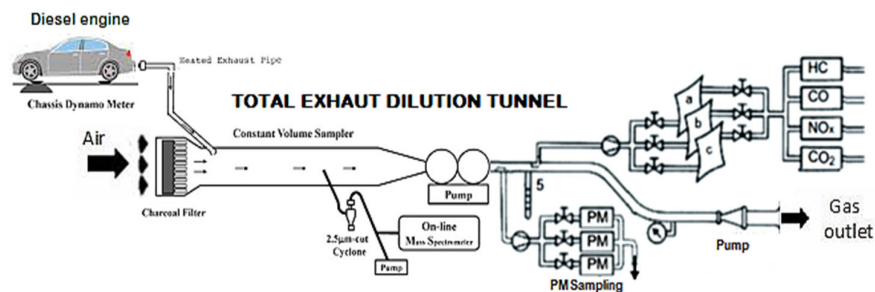


Fig. 3. Diesel engine exhaust emissions (dilution tunnel).

Soot particles are mostly composed of carbon (about 90%). Hydrogen (about 10%), oxygen and nitrogen can be found in smaller proportions.^{7,26,27} Diesel particles consist of a carbonaceous material (soot: carbon core), generated during combustion, on which are adsorbed various organic species, consisting of molecules condensed, called SOF (Soluble Organic Fraction).^{2,7,13} It contains unburned hydrocarbons, oxygenated derivatives (ketones, esters, aldehydes, lactones, ethers, organic acids) and polycyclic aromatic hydrocarbons (the famous PAHs) together with their nitrated and oxygenated derivatives, etc. There are also minerals (SO₂, sulphates, etc.) and metallic derivatives.¹³ Moreover, diesel particles do not have a particular structure as can be explained in crystallography, for example. They are essentially concentric clusters of carbon atoms linked by covalent bonds. This random arrangement creates sites of various shapes and sizes, which favour the adsorption of a large number of molecules on their surface (see Fig. 4).

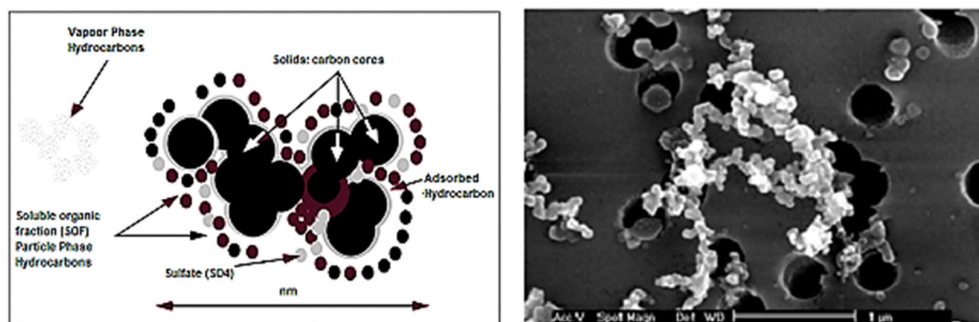


Fig. 4. Morphology of diesel aggregates.

Vehicle traffic is one of the most significant sources of PAHs in the environment. The majority of polycyclic aromatic hydrocarbons are classified as probable carcinogens.^{7,12} Due to their toxicity and/or mutagenicity/carcinogenicity, 16 PAHs identified by the U.S. Environmental Protection Agency (EPA) merit specific characterization to the extent possible.^{9,13,29} In this study, the following compounds were used: 6 condensed polyaromatic hydrocarbons (naphthalene, fluorene, anthracene, phenanthrene, pyrene, fluoranthene and chrysene), 4 mono-nitrated condensed polyaromatic hydrocarbons (1-nitronaphthalene, 2-nitrofluorene, 9-nitroanthracene, 3-nitrofluoranthene) and di-nitrated condensed polyaromatic compounds (1,5-dinitronaphthalene). However, it is important to note that the most common, but also the oldest, technique is soxhlet extraction, which is easy to perform and is also used as a reference in many European norms.^{30,31} In order to ensure that the soot was as completely free as possible of all compounds (i.e. the apolar fraction of the pollutants adsorbed on the particles), three successive extractions, each lasting eight hours, were performed on 10 grams of soot, using dichloromethane (150 ml for each extraction) as the extractant. At the end of the last extraction, an analysis of the extract was performed and no PAHs or alkanes could be detected. According to the GC/MS analytical technique, the detection limits (LOD) are between 0.3 and 1.5 µg.L⁻¹ for PAHs and between 4.6 and 8 µg.L⁻¹ for nitrated PAHs. In this paper, the LOD is defined as the signal required producing a signal-to-noise ratio (S/N) of 3. This analytical method should therefore be able to determine traces of PAHs and NPAHs. After developing a sufficiently sensitive and reliable analytical method, the method for the extraction of PAHs and their nitro derivatives from diesel exhaust soot was optimized.

3.2. Pressurized liquid extraction process

Pressurized liquid extraction methods are relatively recent and use solvents that are heated above their boiling point and kept under pressure. The high temperature and pressure have several advantages. Indeed, the temperature plays an important role on the viscosity of the solvent and thus on its molecular diffusion coefficient: the latter increases when the temperature rises, thus allowing a better penetration of the solvent molecules in the pores of the matrix on which the compounds of interest are adsorbed.²²⁻²⁵ Generally, diffusion rates are multiplied by a factor of between 2 and 10 when the temperature rises from 25 to 150 °C.³² In order to assess the factors influencing the PLE extraction efficiency of compounds such as

PAHs and NPAHs, a design-of-experiment study was carried out. The study was conducted in three stages: research into the influencing factors, modelling and optimization. Depending on the equipment or the operating conditions, different parameters are fixed, so all that remains is to study the influence of three factors: temperature, the solvent to be added in the extraction cell and the extraction time (static time). The extraction yield of each of our 12 compounds will be chosen as the analytical response. It should be noted that the yield was determined by GC/MS analysis of the extracted amount.

3.2.1 Modelling: central composite design (CCD)

Response surface methodology (RSM) is a statistical method that exploits quantitative data from appropriate experiments to determine the regression model equations and operating conditions.^{13,33} RSM is a combination of mathematical and statistical techniques for the modelling and analysis of systems in which a response of interest is influenced by several variables.^{33,34} A central composite design named CCD was used in the present study to investigate the independent variables allowing maximum extraction of adsorbed PAHs and NPAHs from diesel particulate matter and to obtain information on the significant effects and interactions between the selected factors that positively influence the extraction process and to identify the optimal value of each variable. Consequently, a 3-factor composite design was developed. The three factors selected for further optimization were temperature (°C), static time (min) and nature of solvent (%), which were denoted by A, B and C, respectively. This modelling then consists of studying the evolution of the response (extraction efficiency of PAHs and NPAHs in %) as a function of these factors. The study of the effects on the Y response is based on the responses obtained for two levels of this factor (a higher level noted +1 and a lower level noted -1). The experimental domain can be represented in k-dimensional space with experimental points are located at the 8 vertices of a cube, the central points in the center, necessary for the evaluation of the residual variance and axial points located at the origin of the orthonormal axes with coordinates $-\alpha$ and $+\alpha$, with $\alpha = 1.68$ for $k = 3$. It is therefore a design of experiments (Central Composite Design) with three factors. A quadratic model was applied (Eq. (1)):

$$Y = h_0 + h_A A + h_B B + h_C C + h_{AB} AB + h_{BC} BC + h_{AC} AC + h_{AA} A^2 + h_{BB} B^2 + h_{CC} C^2 + h_{ABC} ABC \quad (1)$$

where: Y is the predicted response, h_0 the constant, h_A , h_B , and h_C the linear coefficients, h_{AB} , h_{AC} , and h_{BC} the cross-product coefficients, and h_{AA} , h_{BB} , and h_{CC} are the quadratic coefficients.

The modeling was performed adjusting polynomial equation obtained by analysis of variance (ANOVA). Before developing the study using the RSM method, a first series of tests was carried out to select the relevant factors in the extraction of PAHs and NPAHs and the experimental ranges for the independent variables (see **Table 1**). Once the parameters have been defined, the limits of the experimental field need to be fixed. These limits are imposed on the one hand by the instrumental constraints and on the other hand by the field of study which must remain within the realism of an analytical study (short time, temperature, etc). Three factors will be studied: temperature (T), extraction time (t) and the nature of the solvent (S). The volume of the solvent is fixed at 10 mL by the size of the extraction cell.

Table 1. Description of the levels of the three studied parameters

	Coded Levels				
	$-\alpha$	-1	0	+1	$+\alpha$
Temperature (T) (°C)	83	100	125	150	167
Solvent (S)	CHCl ₃	CHCl ₃	THF	CH ₂ Cl ₂	CH ₂ Cl ₂
Extraction time (t) (min)	1.6	5	10	15	18.4

The temperature of the extraction was studied over a range from 83 to 167 °C, with the oven of the PLE extractor not exceeding 200 °C. The extraction time was estimated to be between 2.7 minutes and 18.4 minutes, based on literature data showing that the extractions did not exceed 20 minutes.²²⁻²⁵ Finally, the solvents chosen for the experiment were chloroform (CHCl₃), tetrahydrofuran (THF) and dichloromethane (CH₂Cl₂). These solvents in fact have the particularity of belonging to groups, listed in the Snyder selectivity triangle, which develop only one type of weak interaction force.^{13,35} Chloroform, from group VIII, is essentially a proton donor; THF, from group V, is mainly a proton attractor; and finally dichloromethane, from group V, essentially develops dipolar interactions.³⁶ These solvents will enable us to better determine which of these interactions are more likely to promote the extraction of PAHs and NPAHs. Thus, the statistical optimisation using CCD has a full factorial design ($2^3 = 8$: factor points) for the three variables, 6 axial points and 6 centre point replicates, indicating that a total of 20 experiments were required. These experiments were carried out randomly in order to avoid fluctuations due to uncontrolled factors that reveal a deviation in the responses.

3.2.2. Optimisation of PLE process

The experimental data were evaluated using ANOVA (analysis of variance) to determine which were significant and to obtain the interaction between the treated variables and the responses. The quality of the model was examined using a correlation coefficient (R^2) and the F-test was used to check statistical significance.³⁷ Once the experimental plan has been

completed, mathematical modelling was carried out using JMP software, after calculating the extraction yields of all the compounds present in the tested mixture. For all PAHs (naphthalene, phenanthrene, anthracene, fluorene, fluoranthene, chrysene and pyrene) and NPAHs (1-nitro naphthalene, 2-nitro fluorene, 9-nitro anthracene, 3-nitro fluoranthene and 1,5 dinitro naphthalene), the quadratic modelling was greater than 92%, which is considered good modelling and was in agreement with more than 95% of the observed experimental responses. Furthermore, to investigate the mathematical relationship between the response (% extraction) and the variables (time, temperature and nature of the solvent) for each compound studied, analyses (ANOVA) were carried out by judging according to the F- and p- values for the extraction of PAHs and NPAHs (a p value of less than 0.05 reveals the statistical significance of the variable at the 95% confidence level). This modelling permitted the assessment of the main factors and interactions affecting the responses (through an analysis of variance, based on the points in the centre). The significant effects of some PAHs and NPAHs and their coefficients was presented in the **Table 2**.

In this context, it is the temperature, whose rise is favourable for extraction. This demonstrates that a rise in temperature is accompanied by a change in the intrinsic properties of the solvent, resulting in a significant increase in the solubility of the compounds to be extracted in the solvent used. It appeared that the most suitable solvent for extracting PAHs was dichloromethane with a relatively low time and high temperature.

Table 2. Estimated effects of statistically significant factors and/or interactions for some representative compounds of the test mixture

factors	PAHs				NPAHs	
	PHEN	ANT	PYR	9N-ANT	2N-FL	1,5N-NAPH
S	9.12	9.56	6.54	4.98	6.54	5.86
t		2.92	3.89		2.56	
T	12.39	12.62	7.17	6.26	4.88	5.89
t × S		-8.30		-9.44		-3.56
T × S	12.52	11.06	9.54	5.64	6.58	7.25
t × T	-6.54	-10.07	-4.58	3.98	3.21	4.10
T²		7.73		12.46		
t × T × S	-10.51	-8.88	-9.87	10.63	14.75	12.36

(with *solv*: type of solvent, *t*: extraction time and *T*: extraction temperature)

Regarding the influencing factors for this class of compounds, the most important is the temperature (the increase in thermal energy facilitates desorption of solutes from active sites in the solid matrix of diesel soot), followed by the nature of the solvent and the extraction time, which are less significant. For most other compounds, the main factors do not have an influence alone, but they interact with each other: the double interactions that are most often found are between the nature of the solvent and temperature, and then between time and temperature. However, the triple interaction between the three factors is the most common for all compounds, demonstrating that each factor is interdependent on the other two factors in the pressurized liquid extraction.

3.2.3. Response surface plotting

The response surface method was applied considering all significant interactions between the different design variables in order to find the most important effects. In order to interpret the results, it was therefore essential to represent the responses according to the three factors simultaneously: three-dimensional representations were required. **Fig. 5** shows an example of the three-dimensional representation of some compounds, representative of the PAHs and NPAHs studied, over the whole experimental field of the model.

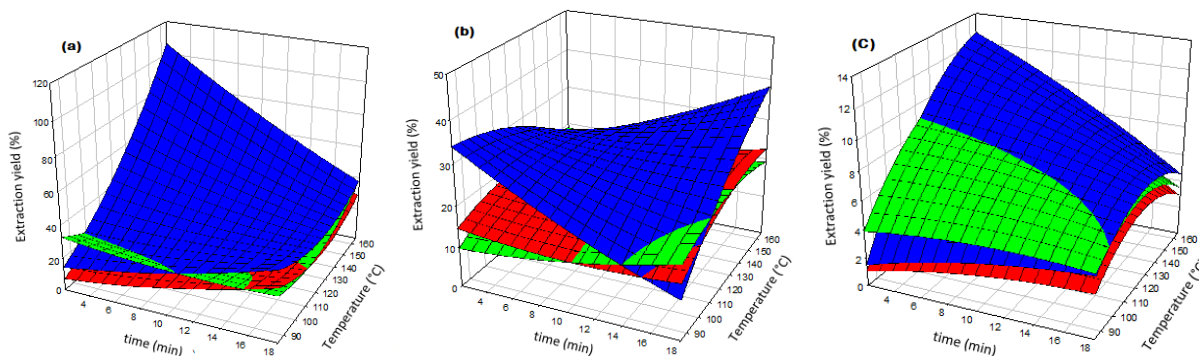


Fig. 5. 3-dimensional representation of PAH and nitro-PAH extraction.

(a: Phenanthrene, b: Pyrene, c) 2-nitro fluorene.

From these 3D representations reporting the evolution of extraction yield as a function of the influential factors (see Fig. 5), the main findings can be summarized as follows:

- i) Dichloromethane is the most suitable solvent for the extraction of PAHs and NPAHs but it is hardly satisfactory for the heaviest pollutants,
- ii) It should be noted that, for all groups of compounds, the extraction yields obtained are significantly better at higher temperatures.
- iii) On the other hand, the duration of the extraction of PAHs and NPAHs is favoured by short times.

Thus, the results of this first phase of PLE optimization are relatively positive, except for the extraction of heavy PAHs and NPAHs where relatively low yields were obtained for this class of compounds (below 30% with the best solvent tested). After validation of the quadratic model, the optimal conditions for the extraction process of PAHs and NPAHs from diesel soot were determined using the desirability function. The optimised values suggested by RSM are: time 9 min, temperature 145 °C using dichloromethane as a suitable solvent. However, it is also important to test another family of solvents, of an aromatic nature, which has a good possibility of facilitating extraction thanks to the electronic transfers between the π systems of the aromatic rings of the PAHs and the π electrons of the surface of the soot.

3.2.4. Aromatic solvents and binary mixtures

From the results of the PLE experimental design, it was unfortunately found that PAHs consisting of four aromatic rings, as well as NPAHs, were far from being extracted quantitatively, with extraction yields not exceeding 50% with conventional solvents (chloroform, THF and dichloromethane). To improve these results, we tried aromatic solvents (toluene, pyridine) in order to extract PAHs from soot, as shown in Fig. 6.

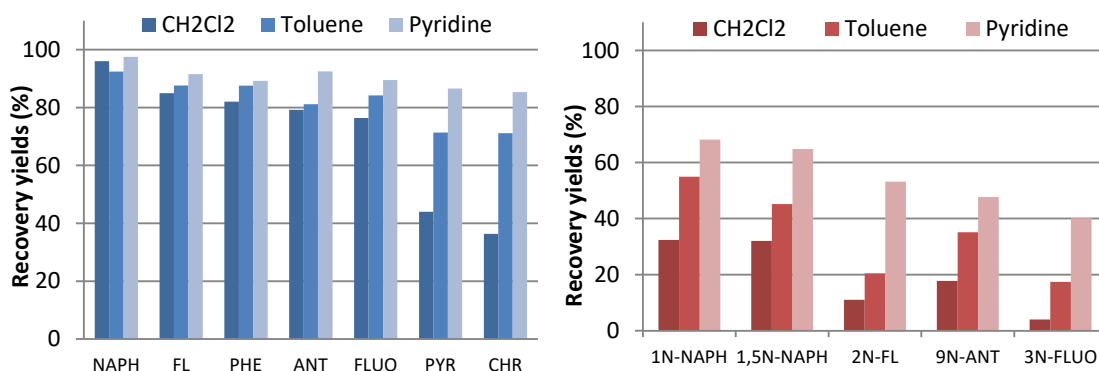


Fig. 6. Effect of different aromatic solvents on extraction yields (%) of PAHs and NPAHs. (P = 100 bars, T = 145 °C, time = 9 min).

It can be observed that toluene, which is only aromatic, is better than dichloromethane, but that pyridine, which is both aromatic and basic, has the best extraction capacity with yields above 85% for all PAHs (three to four rings) studied. However, Fig. 6 showed that this method is not very efficient for nitrated PAHs. Different studies have clearly confirmed that it is the proton-donor character of the solvent that improves the extraction of NPAHs. Indeed, it is pyridine combined with acetic acid that allows the quantitative extraction of NPAH, which were only imperfectly extracted with the previous solvents, even pyridine (see Fig. 7).

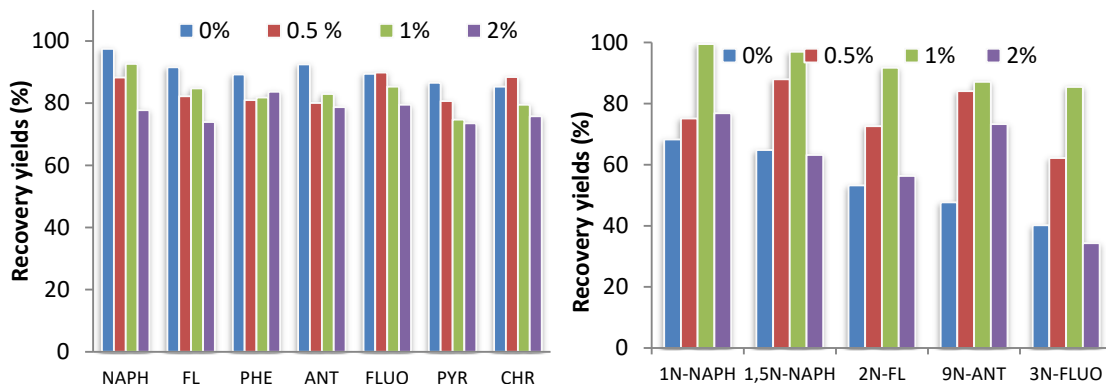


Fig. 7. Effect of the percentage of acetic acid in pyridine on the extraction of PAHs and NPAHs from diesel soot (P = 100 bars, time = 9 min, T = 145 °C).

According to the latter **Fig. 7**, a strong increase in extraction yields for NPAH can be observed using a binary mixture containing 1% acetic acid in pyridine. The extraction yields for 2N-FL increase from 52% to 91%, and 9N-ANT from 46% to 88%. Following these results, a better extraction of all nitro-PAHs was observed using 1% acetic acid in pyridine, with very satisfactory extraction yields and high promoters for this highly refractory matrix. Applied sciences are very important in different fields and this concept was reported before in a lot of papers.³⁸⁻⁴⁶

3. Conclusion

In the pressurized solvent extraction of PAHs and their nitro derivatives from diesel particles, temperature, static time and solvent type significantly influenced the pressurized liquid extraction. From all the results, the optimal conditions for extraction by PLE are: an extraction time of 9 minutes, a maximum temperature of 145 °C and the use of pyridine allow the quantitative extraction of all PAHs (with three to four cycles) and also remove the light NPAHs. Analysis by GC/MS in SIM mode made it possible to obtain very low detection limits for most of the compounds studied (PAHs and NPAHs). On the other hand, in the case of the extraction of all NPAHs, the binary mixture pyridine/acetic acid (1%) proved to be a very effective extractant, obtaining extraction yields all above 90% for the nitrated derivatives. Therefore, the developed PLE method is very fast, highly efficient, and reproducible compared to conventional extraction methods.

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