

Optimisation of the extraction of polycyclic aromatic hydrocarbons and their nitrated derivatives from diesel particulate matter using microwave-assisted extraction

F. Portet-Koltalo · K. Oukebdane · F. Dionnet ·
P. L. Desbène

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Abstract Pressurised microwave-assisted extraction was used to extract a complex mixture containing polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs and heavy *n*-alkanes from a particularly refractory carbonaceous material resulting from the combustion in a diesel engine. A second-order central composite design was used to determine the optimal conditions of extraction in terms of time, temperature, volume and nature of extracting solvent from spiked diesel soots. To begin, methylene chloride, tetrahydrofuran and chloroform were tested for extracting the spiked diesel particulates; however, the nature of these solvents was not really an influential factor. Volume was the most influential factor and was kept at a medium level to enhance the extraction of heavy PAHs without introducing an important dilution factor. Temperature and time were not influential as main factors but interacted with the other factors. Finally, high temperature and duration associated with a medium volume of methylene chloride were better for the extractions. After this optimisation, five-ring and six-ring PAHs were nevertheless not satisfactorily desorbed. Other solvents were therefore tested. Only aromatic ones, and particularly heterocyclic aromatic solvents, managed to desorb the heaviest PAHs. Pyridine, with its both aromatic

and its basic character, was the most successful solvent. Desorption was even complete with an addition of 17% of diethylamine into pyridine. So, using MAE, we succeeded in extracting quantitatively, from the spiked refractory diesel soot surface, two-ring to six-ring PAHs, heavy *n*-alkanes and short nitrated PAHs. However, heavy nitrated PAHs were better extracted with a small addition of acetic acid (1%) into pyridine instead of a basic cosolvent.

Keywords Polycyclic aromatic hydrocarbons · Diesel particulate matter · Microwave-assisted extraction · Factorial design

Introduction

Diesel particulates which consist of soot spheres occur during combustion processes [1]. They can adsorb complex mixtures usually containing thousands of organic components, such as polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs (nitroPAHs) and aliphatic hydrocarbons. Fuel PAHs may survive intact the combustion process of diesel engines, with the same carbon skeleton, but can also recombine with other fuel fragments to produce other PAHs and even nitroPAHs, by reaction of PAHs with oxides of nitrogen [2, 3]. In fact, PAHs are mutagenic after metabolic activation, whereas nitroPAHs are powerful direct-acting mutagens. For example, 1-nitropyrene is one of the most active mutagenic compound as well as 6-nitrochrysene or some dinitroPAHs [4]. They can have higher carcinogen potentials than benzo[*a*]pyrene or dibenzo[*a,l*]pyrene, which have the highest toxic equivalent factors among all the native PAHs [5]. Consequently it is obviously of major interest to analyse PAHs and their nitrated derivatives. Analytical schemes used to identify

F. Portet-Koltalo · K. Oukebdane · P. L. Desbène (✉)
Laboratoire d'Analyse des Systèmes Organiques Complexes,
UPRES 3233-IRCOF et IFRMP, Université de Rouen,
55 rue Saint Germain,
27000 Evreux, France
e-mail: paul-louis.desbene@univ-rouen.fr

F. Dionnet
CERTAM, Technopole du Madrillet,
1 rue Joseph Fourier,
76800 Saint Etienne du Rouvray, France

and quantify these pollutants are typically performed not only by gas chromatography (GC) with a mass spectrometry (MS) detector [6, 7] or a flame ionisation detector [8], but also by liquid chromatography with ultraviolet, fluorescence detections [9, 10] or MS [11]. However, the limiting step in quantitative analysis is essentially the extraction process with the aim of removing rapidly and quantitatively the analytes from a more or less complex matrix. Several authors have compared a range of extraction techniques, including Soxhlet extraction, ultrasonic extraction, supercritical fluid extraction (SFE), accelerated solvent extraction (ASE) or microwave-assisted extraction (MAE) [12–14]. Extraction efficiency is particularly dependent on the nature of the sample matrix, that is to say the nature and the degree of analyte-matrix interactions, much more than on the amount of organic solvent, time, temperature or other experimental parameters. Among all environmental polluted matrixes studied, such as soils, marine sediments or urban dusts, carbonaceous matrixes and particularly diesel particulate matter are known to require very severe conditions in order to obtain good recovery yields of the higher molecular weight molecules [15, 16]. It was even suggested that among all the natural environmental matrixes, diesel particulate matter was the most refractory [17]. Some authors tried to extract PAHs or nitroPAHs from diesel soot by means of an ultrasonic bath [18], by Soxhlet extraction [19, 20], by ASE [21] or by SFE [17, 22]. But to our knowledge, MAE was not used to extract simultaneously PAHs and nitroPAHs from diesel particulates.

In the work reported here, pressurised MAE was optimised by using a factorial experimental design in order to attempt a simultaneous and quantitative extraction of PAHs, nitroPAHs and aliphatic hydrocarbons from spiked diesel particulate matter. The parameters studied included not only the temperature and the time of extraction but also the volume of three classic organic solvents (methylene chloride, tetrahydrofuran and chloroform). In addition, the effect of individual or combined aromatic solvents on the recovery yields of PAHs, nitroPAHs and *n*-alkanes was also investigated in order to understand the interactions between diesel soot and high molecular weight compounds and consequently the desorption mechanisms.

Experimental

Solvents and samples

Acetonitrile, methanol, tetrahydrofuran, pyridine, diethylamine and chloroform, all of high-performance liquid chromatography (HPLC) grade, were purchased from Acros Organics France (Noisy le Grand, France). Acetic acid

(chemically pure quality, purity 99.5%) also came from Acros Organics. Methylene chloride, *n*-hexane and toluene, of HPLC grade, were provided by Sigma-Aldrich France (St. Quentin-Fallavier, France). Pyrrole (98% purity), *N*-methyl-2-pyrrolidinone (99%), fluorobenzene (99%), chlorobenzene (99%) and metaxylene (99%) were also purchased from Sigma-Aldrich. Finally, propan-2-ol, acetone and butan-1-ol, of HPLC grade, were provided by SDS (Peypin, France).

A mixture of 28 PAHs, nitroPAHs and *n*-alkanes was prepared at a concentration of 100 $\mu\text{g mL}^{-1}$ for each component diluted in toluene. This mixture included: naphthalene (purity 99%), biphenyl (99%), acenaphthene (99%), fluorene (99%), phenanthrene (96%), anthracene (99%), fluoranthene (98%), pyrene (98%), benzo[*k*]fluoranthene (99%), benzo[*e*]pyrene (99%), benzo[*a*]pyrene (97%), perylene (99%) and dibenzo[*a,h*]anthracene (98%), all provided by Sigma-Aldrich-Fluka. Acenaphthylene (98%), chrysene (98%) and indeno[1,2,3,cd]pyrene (98%) were purchased from Interchim (Monluçon, France). Benzo[*a*]anthracene (99%), benzo[*b*]fluoranthene (99%) and benzo[*g,h,i*]perylene (99%) were obtained from Supelco (Bellefonte, PA, USA). Lastly, 1-nitronaphthalene (99%), 1,5-dinitronaphthalene (98%), 2-nitrofluorene (98%), 9-nitroanthracene (97%), 3-nitrofluoranthene (90%), 2,7-dinitrofluorene (97%), heneicosane (99.5%), tetracosane (99.5%) and triacontane (99.5%) were purchased from Sigma-Aldrich-Fluka.

Two internal standards were used for quantisation (see “GC-MS analysis”): 2-methylanthracene (purity 97%) and 7-methylbenzo[*a*]pyrene (purity 98%), both purchased from Sigma-Aldrich.

Diesel particulate matter used for the optimisation of MAE operating conditions was provided by CERTAM (St. Etienne du Rouvray, France). Exhausts were directly sampled at the outlet of a diesel engine by means of a particulate filter. There was no partial-flow dilution tunnel between the engine and the ceramic filter and the measured sampling temperature was 300 °C. After a few hours of sampling, accumulated particulate matter was immediately blown into glass flasks. The four-cylinder direct-injection engine (power 80 kW, torque 250 N m) was operating in steady-state conditions (regime 1,500 rpm, mid-load conditions). Soot particles were then stored at -20 °C.

Sand, washed with sulphuric acid, was purchased from VWR (Strasbourg, France).

Extractions

Soot cleanup procedure by means of a Soxhlet apparatus

Diesel particulate matter (10 g) was cleaned by means of a Soxhlet apparatus, by using methylene chloride which was refluxed for 8 h. Three successive extractions were

performed in the same conditions. Cleaned soot was then tested as a blank, after microwave extraction, to ensure that all aliphatic and aromatic pollutants were removed. Cleaned soot was then stored at 4 °C.

Microwave-assisted extractions

Extractions were performed by using the Mars X microwave accelerated extraction system (CEM Corporation, Matthews, NC, USA) from spiked solid matrixes like sand or cleaned diesel soot. Before extraction, these spiked matrixes were left for 30 min in contact with 100 µL of a standard mixture of 28 PAHs, nitroPAHs and *n*-alkanes (see “Solvents and samples”). A known volume of extracting solvent was then added and MAE was started. Then, extracts were filtered using PTFE filters purchased from Millipore (Bedford, MA, USA) or centrifuged prior to analysis (4K15 Sigma model, Fisher Bioblock Scientific, Illkirsh, France).

GC-MS analysis

Analyses were performed with an HP 5890 gas chromatograph (Hewlett-Packard, Palo Alto, CA, USA) fitted with a splitless injector. The carrier gas (helium) was set at a constant flow rate of 0.9 mL min⁻¹. The injector was maintained at 250 °C and the injection volume was 1 µL. The temperature programme was 55 °C for 2.05 min, then the temperature was increased to 167 °C at 40 °C min⁻¹, then to 300 °C at 3.9 °C min⁻¹ and finally isothermal for 7 min. The DB5-MS capillary column used (50 m × 0.25-mm inner diameter, film thickness 0.25 µm; J & W Scientific, Folsom, CA, USA) was coated with a (5% phenyl) methylpolysiloxane stationary phase. The gas chromatograph was coupled with an HP 5972 mass detector (electron impact ionisation 70 eV, electron multiplier voltage 2,200 V) operating in the selected ion monitoring (SIM) mode for quantisation. The temperature of the transfer line was 290 °C.

All PAHs, nitroPAHs and *n*-alkanes were quantised in relation to two internal standards (2-methyl anthracene and 7-methylbenzo[*a*]pyrene). These methylated PAHs were used in the case of the analyses of cleaned soots spiked with known target PAHs or nitroPAHs and after verification that there was no coelution with these compounds. The response factors of the 28 compounds studied were calculated by using eight-point calibration plots, by injecting various pure standard mixtures ranging from 0.1 to 8 mg L⁻¹. The detection thresholds in SIM mode, calculated as three times the standard deviation of blank sample noise, ranged from 0.15 to 2.5 µg L⁻¹ for PAHs, from 40 to 60 µg L⁻¹ for alkanes and from 5 to 100 µg L⁻¹ for nitroPAHs and dinitroPAHs.

Recovery yields obtained from GC-MS quantisation were handled by using JMP 5.1 software (SAS Institute, Cary, NC, USA) for statistical calculations and modelling.

Results and discussion

Preliminary tests before optimisation

In this work, MAE was based upon closed inert vessels which contained the solid matrix and the organic solvents subjected to microwave irradiation. An important advantage of MAE is the rate acceleration due to microwave irradiation; thus, extraction times of the order of a few minutes can be obtained in contrast to a few hours when conventional methods are used. Some authors have claimed that pressurised MAE could be disadvantageous in relation to focused MAE in an open system under atmospheric pressure [23], because the sample must be sealed inside a compatible vessel and cooled to room temperature before it can be opened. However, sealing requires a few seconds using a special wrench, and cooling requires only a few minutes using an effective ventilation system located within the microwave cavity. Moreover, 14 extractions could be simultaneously realised and closed vessels are a real advantage for the extraction of volatile compounds. The main drawback of MAE is that the solvent needs to be physically removed from the solid matrix after completion of the extraction except if the GC analyser is fitted with a programmable temperature Vaporisation system [24]. In other cases, papers have reported that extracts can be filtered through a hydrophobic membrane or through open columns filled with silica gel [23, 25, 26]. So, before starting the optimisation study of the MAE process, we tried to evaluate two processes of particulate elimination from the extracting solvent. A mixture of 28 components was spiked on 100 mg of cleaned diesel soot (see “Experimental”) and their extraction was performed by means of an acetone/toluene mixture (1:1). These extraction conditions were not optimised, but acetone and toluene are known to be good solvents for PAH extractions and in this study this mixture was more effective than the commonly used acetone/hexane mixture [27]. Then, extracts were filtered using PTFE filters or centrifuged prior to analysis. Table 1 shows that the recovery yields were not significantly different for both filtered and centrifuged extracts. However the relative standard deviations were significantly larger in the case of the centrifugation process and, moreover, this process was more time consuming. So filtration through an inert filter was chosen prior to GC-MS analysis.

It is relevant to note from the results shown in Table 1 that the recovery yields were not quantitative, not only for

Table 1 Influence of the sample preparation and the nature of the solid matrix on polycyclic aromatic hydrocarbon (PAH) recovery yields (%) after microwave-assisted extraction using 6 mL of 1:1 (v/v) acetone/toluene, 30 min at 125 °C

Compounds	Diesel soot matrix		Sand matrix
	Filtration Average + (RSD) (%) (n=5)	Centrifugation Average + (RSD) (%) (n=5)	Filtration Average (%) (n=2)
Naphthalene	106 (5.1)	99 (18.0)	101
Biphenyl	102 (5.6)	94 (15.2)	102
Acenaphthylene	79 (5.7)	74 (15.4)	81
Acenaphthene	99 (6.2)	93 (15.1)	100
Fluorene	98 (6.8)	92 (14.4)	100
1-Nitronaphthalene	65 (9.9)	65 (15.1)	56
Phenanthrene	92 (6.2)	86 (15.1)	98
Anthracene	77 (6.6)	73 (15.6)	86
1,5-Dinitronaphthalene	47 (13.1)	46 (15.0)	35
Fluoranthene	69 (6.4)	68 (16.3)	98
Heneicosane	100 (13.7)	99 (21.3)	103
2-Nitrofluorene	38 (13.6)	40 (21.9)	38
Pyrene	67 (7.1)	67 (16.1)	101
9-Nitroanthracene	69 (18.4)	73 (18.7)	64
Tetracosane	95 (17.2)	95 (20.9)	97
Benzo[a]anthracene	30 (13.5)	33 (20.9)	89
Chrysene	37 (11.8)	38 (18.3)	100
3-Nitrofluoranthene	30 (16.2)	34 (18.0)	64
2,7-Dinitrofluorene	20 (14.3)	21 (16.0)	21
Benzo[b]fluoranthene	11 (11.2)	13 (26.3)	87
Benzo[k]fluoranthene	10 (11.5)	12 (27.1)	89
Benzo[e]pyrene	10 (10.5)	11 (28.8)	92
Benzo[a]pyrene	5 (13.3)	6 (31.8)	79
Perylene	6 (13.0)	9 (57.2)	85
Triacotane	93 (7.3)	86 (13.5)	90
Indeno[1,2,3,cd]pyrene	1 (11.8)	2 (47.8)	82
Dibenzo[a,h]anthracene	2 (14.7)	2 (40.4)	87
Benzo[g,h,i]perylene	1 (15.1)	2 (46.5)	89

the heaviest PAHs, especially for five-ring and six-ring ones, but also for nitroPAHs and dinitroPAHs. Although spiked solid matrixes are known to be more easily extractable than real environmental matrixes, these first results indicated that it could be very difficult to quantitatively extract heavy native PAHs strongly adsorbed on a carbon surface (diesel particulate matter). To prove that strong solute-matrix interactions were responsible for these low recovery yields we spiked the same sample mixture, in the same conditions, on sand. It was clear from the results shown in Table 1 that the recovery yields were now quantitative for PAHs and alkanes extracted from sand, even for the heaviest ones, the recovery yields being increased from 1.5% (extraction from diesel soot) to 89% (extraction from sand) for benzo[g,h,i]perylene as an example. In view of these results, it could be concluded that the carbon content was predominantly responsible for the strong interactions between PAHs and diesel particulate matter. Nevertheless the recovery yields for nitroPAHs and dinitroPAHs remained poor in the case of extractions from

sand, suggesting that the nature of solute-matrix interactions was not the same for nitroaromatics and/or that the extracting solvent used was not adequate for nitroPAHs.

In view of the difficulties encountered in extracting the heavy PAHs and nitroPAHs from a spiked diesel soot it was important to explore the critical variables of MAE and so to enhance the extraction efficiency for alkanes, polyaromatic compounds and nitroaromatic compounds.

MAE optimisation by means of experimental design

To fully understand the way in which MAE operating variables may affect extraction yields, three variables were firstly considered: temperature, extraction time and volume of solvent. Microwave power was kept constant at its highest value, namely 1,200 W. The amount of diesel soot (100 mg) and the quantity of spiked compounds were also kept constant. However, according to the literature, only a few studies were carried out on the influence of the nature of the solvent on extractability of PAHs by MAE. Most

MAE extractions (open or closed vessels) were performed with acetone, methylene chloride, hexane/acetone mixtures or toluene/acetone mixtures [26, 28, 29]. Although some results seemed to show that there was no significant difference between the recovery yields using these various solvents [30], other studies demonstrated that solvents like *N*-methyl-2-pyrrolidinone could be better [31]. So we chose to consider also the nature of the solvent in our chemometric approach. Indeed the use of an experimental design permits us to fully evaluate not only the effects of each operating variable but also the interaction effects between the parameters studied.

The second-order central composite design 2^4 involved sixteen runs at two coded levels -1 and +1, one 0 central point with six runs and required eight experiments at $-\alpha$ and $+\alpha$ levels to estimate the effects of squared terms if the response was not linear on the defined experimental space. The temperature, time and volume were chosen according to previous experiments and considering instrumental constraints (Table 2). In contrast the three solvents studied for this optimisation were chosen according to their classification by Snyder [32]. Indeed according to Snyder's approach, eight classes of solvents can be defined and among them group V (containing very dipolar solvents like methylene chloride), group VIII (containing proton-donor solvents like chloroform) and group I (containing proton-acceptor solvents like aliphatic ethers) correspond to solvents having mainly one specific interaction strength. The choice of one of these solvents could indicate which of these primary interactions could be favourable to desorb and to solubilise PAHs, nitroPAHs or *n*-alkanes. Nevertheless group I contains solvents that are too dangerous when used with MAE (aliphatic ethers, which have very low flash points, can explode). So we chose another group close to this latter one that also has large proton-acceptor interactions, namely group III, and in this case tetrahydrofuran. This cyclic ether has a higher flash point, but the formation of peroxides must be inhibited with butylated hydroxytoluene. So chloroform, tetrahydrofuran and methylene chloride were respectively coded at levels -1, 0 and +1 as a function to their dielectric constants (4.81, 7.60 and 9.08 at 20 °C, respectively). In fact, in MAE, the choice of the solvent depends also on its ability to absorb microwaves,

defined by its dielectric constant. Very apolar solvents such as aliphatic hydrocarbons (*n*-hexane for example) do not meet this requirement, whereas solvents with high dielectric constants can absorb microwaves and transform this energy into heat.

Experiments were carried out in a random order to minimise the bias effect. A mathematical model using multi-linear regression was then built which relates the observed response (PAH recovery yields in percent) to the various factors and to their combinations [33, 34]. The parametric equation contained the following terms:

$$Y_i = b_0 + \sum_i b_i X_i + \sum_{ij} b_{ij} X_i X_j + \sum_{ijk} b_{ijk} X_i X_j X_k + \sum_i b_{ii} X_i^2,$$

where Y_i is the experimental response, X_i are the studied factors, b_0 is the average response, b_i are the average effects (also named parameter estimates) of the different factors, b_{ij} and b_{ijk} are the average effects of, respectively, the second-order and the third-order interaction factors (the fourth-order one being neglected) and b_{ii} are the quadratic components.

Table 3 summarises the estimated effects that have a statistical significance at the 95% confidence level ($p \leq 0.05$). For the other factors or interactions, experimental error was greater than the effect, which signified that they were not influential. Only typical compounds were chosen here to illustrate the results of modelling. It can be seen from Table 3 that except for the volume of solvent, which is an influential factor for semivolatile and heavy PAHs, other main factors were not individually influential. Nevertheless some second-order and third-order interactions were significant, as were some squared terms. So the temperature, interacting with other factors (see Table 3, where the volume and temperature factors appear through numerous second-order or third-order interactions), seemed to be the most important factor after the solvent volume, unlike the extraction time and the nature of solvent, which were less influential factors. Moreover as can be seen in Table 3, volume had no effect on light PAHs but had a large positive effect on medium and heavy PAHs. Indeed the positive sign of the effect indicates that the extraction efficiency is enhanced when the volume of the extracting solvent is

Table 2 Description of the experimental domain as a function of the four factors studied and the coded levels of the factorial design

Factors	Levels				
	$-\alpha$	-1	0	+1	$+\alpha$
T (°C)	80	95	110	125	140
t (min)	5	13	21	29	37
V (mL)	6	12	18	24	30
Solvent	Chloroform	Chloroform	Tetrahydrofuran	Methylene chloride	Methylene chloride

Table 3 Estimated effects of the factors studied and/or the interactions statistically significant (*t*-test approach) for some typical compounds

Influencing factors or interactions	Light PAHs		Medium PAHs		Heavy PAHs		Nitrated PAHs		<i>n</i> -Alkanes	
	Naphthalene	Phenanthrene	Pyrene	Chrysene	Benzo[<i>b</i>]fluoranthene	1-Nitronaphthalene	3-Nitrofluoranthene	Heneicosane	Triacotane	
<i>V</i>										
<i>T</i> /solvent	4.97			7.11	2.54	−4.49	4.72	−5.1		
<i>T</i> / <i>V</i>					1.68	2.29		−6.61	13.29	
<i>T</i> / <i>V</i> /solvent	−8.58	−3.2	−3.29	−2.59				8.51	7.14	
<i>T</i> / <i>t</i> /solvent	4.84	3.61	3.68			2.61	3.51			
<i>T</i> ²	5.29	2.78				3.83	3.77			
<i>f</i>						3.53	4.67			
Solvent ²										7.85

increased. This behaviour pattern is rather usual in MAE, low extraction volumes leading to a saturation of the solvent by the dominant extracted compounds. In contrast nitroPAHs and *n*-alkanes were at best rather insensitive to solvent volume and at the worst negatively influenced by a volume increase, probably because of a harmful dilution effect. Considering that heavy PAHs were a principal target in this study, we chose to keep a medium solvent volume (18 mL, i.e. the centre of the experimental domain) to enhance the extraction yields of the heaviest PAHs without inducing a decrease of the extraction yields of nitroPAHs and heavy alkanes.

Next it was necessary to plot response surfaces in order to understand the influence of the other factors on the whole experimental domain. Indeed main factors were not easy to interpret alone because they all interact more or less with each other (Table 3), meaning that both factors had to be studied together. Figure 1 shows the response surfaces drawn for chrysene, tetracosane and 9-nitroanthracene. Figure 1a shows that the effect of the nature of the solvent was generally poor for chrysene, knowing that it was also true for light and heavy PAHs. This result indicated that none of the primary interactions studied (proton donor, proton acceptor or dipolar) was more particularly favourable for extraction of PAHs from the carbonaceous surface. The same trend was observed for *n*-alkanes (Fig. 1b), whereas the nature of the solvent had a greater influence on the recovery yields of nitroaromatics (see the squared term in Table 3, Fig. 1c). In fact, within the whole experimental domain, tetrahydrofuran was never the best solvent. Chloroform and methylene chloride were slightly better extracting solvents, but not in the same experimental domain. Consequently it could be observed that the highest recovery yields could be reached for two local optima: one corresponding to extractions using 18 mL methylene chloride at 140 °C (highest level) for 37 min (highest level), the other one corresponding to extractions using 18 mL chloroform at 80 °C (lowest level) for 37 min (highest level).

To determine the accuracy of the extraction method, five independent extractions were carried out keeping these optimised experimental conditions (Table 4). Relative standard deviations ranged from approximately 5 to approximately 17% for light and medium PAHs, *n*-alkanes and nitroPAHs. However, they were higher for heavy PAHs, particularly for the three last ones. In fact, although quantitative extractions were obtained not only for light and medium PAHs (i.e. from naphthalene to pyrene) and also for *n*-alkanes, recovery yields decreased dramatically for four-ring to six-ring PAHs. So with the aim of completing quantitative extractions of heavy PAHs and nitroaromatics from diesel soot, we tried to find more appropriate extracting solvents.

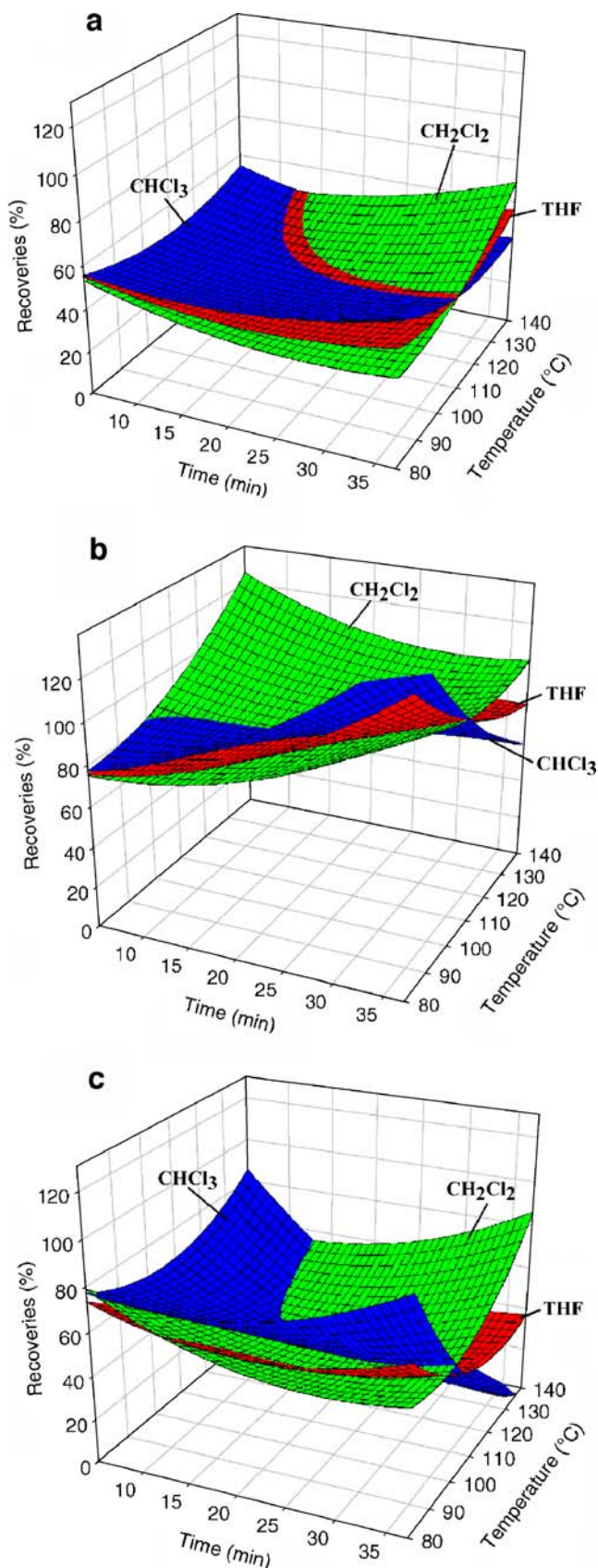


Fig. 1 Response surfaces (polycyclic aromatic hydrocarbon, PAH, recovery yields), after microwave-assisted extraction (MAE) using 18 mL of methylene chloride, tetrahydrofuran (THF) or chloroform, as a function of extraction time and temperature. **a** Chrysene, **b** tetracosane, **c** 9-nitroanthracene

Use of aromatic solvents and binary mixtures

It should be underlined that we chose now to work at the optimal extraction domain defined previously in the case of methylene chloride, namely a high extraction time associated with a high temperature, in order to be able to use extracting solvents with boiling temperatures higher than 80 °C. Nonaromatic solvents like a set of various alcohols (group II from Snyder's classification), namely methanol, propan-2-ol or butan-1-ol, did not give a noticeable increase in extraction rates of nitroPAHs and heavy PAHs. Acetonitrile and acetone (group VI according to Snyder's classification) were also tested but they were not better than alcohols.

As previously mentioned, *N*-methyl-2-pyrrolidinone was used to extract PAHs from contaminated soils and sediments [31]. *N*-Methyl-2-pyrrolidinone was the most effective solvent in that study. Consequently we decided to try also *N*-methyl-2-pyrrolidinone, which was indeed much better than the previously tested solvents, in the case of some medium and heavy PAHs, leading to recovery yields of about 30–40% for the three heaviest PAHs instead of 2–3% using methylene chloride or chloroform. However, this solvent was worse for acenaphthylene, 1-nitronaphthalene, 1,5-dinitronaphthalene, 2-nitrofluorene and 2,7-dinitrofluorene, which were completely degraded, while fluorene, anthracene, 9-nitroanthracene, benzo[*a*]anthracene, benzo[*a*]pyrene and perylene were only partially degraded.

Finally some aromatic solvents, belonging to group VII of Snyder's classification, were tested. They were effectively supposed to develop electron transfer interactions with the electron-rich soot surface and consequently with the retention sites, this type of interaction having not been studied during the first part of the optimisation. Among all available aromatic solvents, we chose to try toluene, metaxylene, chlorobenzene and fluorobenzene, the boiling points of which were below 140 °C (110.6, 139.3, 131 and 84.7 °C, respectively). As can be seen in Fig. 2, these solvents, which possess a delocalised π -electron system, are particularly more effective in desorbing the five-ring and six-ring PAHs. For example, the recovery yield of dibenzo[*a,h*]anthracene, which was approximately 3% with methylene chloride as the extracting solvent, reached 35% with chlorobenzene or metaxylene.

These results could be supplemented by the study of heterocyclic aromatic solvents. Pyrrole and pyridine have boiling temperatures compatible with the optimised temperature of MAE (130 and 115 °C, respectively). Although

the resonance energies of pyrrole and pyridine (88.6 and 94.9 kJ mol⁻¹, respectively) are less than those of the previously studied aromatic solvents (approximately 150 kJ·mol⁻¹), the capacity to desorb the heaviest PAHs for pyrrole and pyridine was greater than with chlorobenzene, as shown in Fig. 2. In fact, pyrrole and toluene had similar effects on two-ring to four-ring PAHs, but pyrrole was more effective on five-ring PAHs (see benzo[*b*]fluoranthene in Fig. 2). However, the best solvent (better than pyrrole) was in fact pyridine, which showed a very interesting capacity to desorb quantitatively all PAHs, even the three heaviest ones. The recovery yield of benzo[*b*]fluoranthene reached 61% (average value of five replicates), which was 20–120 times larger than when using nonaromatic solvents and approximately 2 times larger than when using metaxylene or chlorobenzene as extracting solvents. It is interesting to note that, in contrast to pyrrole, pyridine possesses a lone pair of electrons out of the

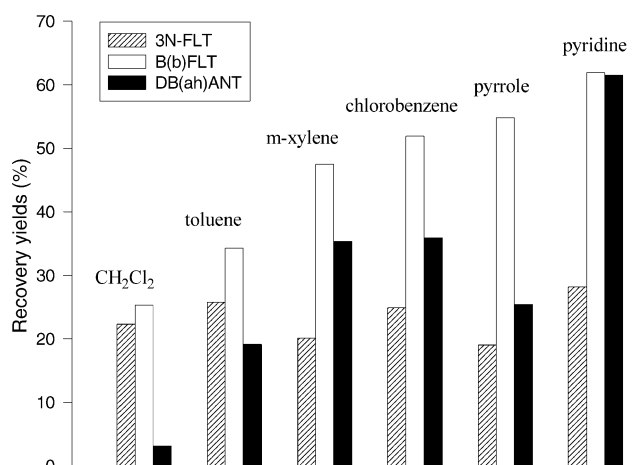


Fig. 2 Comparison of the influence of various aromatic solvents on the recovery yields of typical heavy PAHs and nitrated PAHs (methylene chloride is reported as a reference). MAE was carried out with 18 mL of solvent, for 37 min at 140 °C. *3N-FLT* 3-nitrofluoranthene, *B(b)FLT* benzo[*b*]fluoranthene, *DB(ah)ANT* dibenzo[*a,h*]anthracene

Table 4 Recovery yields (percent) and relative standard deviations calculated under optimal conditions of extraction of 100 mg of spiked diesel soot by using 18 mL of solvent, for 37 min, at 140 °C for methylene chloride and at 80 °C for chloroform

Compounds	CH ₂ Cl ₂ ^a	CHCl ₃ ^a	RSD (%) ^b
Naphthalene	125	122	5.9
Biphenyl	118	129	5.0
Acenaphthylene	95	114	5.2
Acenaphthene	114	128	10.5
Fluorene	117	129	4.6
1-Nitronaphthalene	93	101	10.6
Phenanthrene	114	118	6.3
Anthracene	91	98	6.9
1,5-Dinitronaphthalene	48	54	17.4
Fluoranthene	104	100	8.4
Heneicosane	121	116	11.0
2-Nitrofluorene	56	51	9.9
Pyrene	101	99	8.6
9-Nitroanthracene	80	78	13.8
Tetracosane	116	100	11.5
Benzo[<i>a</i>]anthracene	48	40	18.2
Chrysene	57	50	15.9
3-Nitrofluoranthene	22	24	27.4
2,7-Dinitrofluorene	17	14	14.8
Benzo[<i>b</i>]fluoranthene	25	17	20.4
Benzo[<i>k</i>]fluoranthene	22	15	21.0
Benzo[<i>e</i>]pyrene	24	18	22.4
Benzo[<i>a</i>]pyrene	11	10	25.7
Perylene	13	11	26.7
Triacotane	99	76	9.8
Indeno[1,2,3,cd]pyrene	2	2	45.0
Dibenzo[<i>a,h</i>]anthracene	3	2	48.0
Benzo[<i>g,h,i</i>]perylene	3	2	48.0

^a Average recovery yields calculated after five replicates

^b Relative standard deviations estimated using the variance deduced from the factorial design

aromatic system. Consequently, for pyrrole, aromaticity competes with basicity, while pyridine possesses a basic character independent of the aromatic one. For that reason pyridine is 105 times more basic than pyrrole. So pyridine is a strong π -electron donor which may have the capacity to disrupt the π - π^* interactions between the π -acceptor sites of the soot surface and PAHs (π -electron donors).

Considering the favourable effect of solvent basicity on the desorption of the heaviest PAHs from a diesel soot, we decided to test a pure basic solvent: diethylamine ($T_{\text{vap}} = 56.3$ °C). In fact diethylamine was only slightly less effective than toluene in desorbing light, medium and even heavy PAHs. Such a situation was clearly better than that mentioned for the other nonaromatic solvents studied; however, it was worse for nitroPAHs, the recovery yields falling below 10%. So it appeared more interesting to mix diethylamine with an aromatic solvent in order to test if synergy effects could happen. As reported in Fig. 3, positive effects were noticeable for mixtures having 17 or 33%, respectively, of diethylamine in pyridine or toluene. For example, extraction yields of dibenzo[*a,h*]anthracene were increased from 61 to 85% by using, respectively, pure pyridine and a 1:6 (v/v) diethylamine/pyridine mixture. It must be recalled that the recovery yield of dibenzo[*a,h*]anthracene did not exceed 3% when methylene chloride was used as an extracting solvent. So, to summarise, we succeeded in extracting quantitatively all PAHs from the spiked diesel soot surface, even the heaviest ones, using a 1:6 (v/v) diethylamine/pyridine mixture.

Concerning nitroPAHs, it is worth mentioning that although pyridine was the best solvent to extract all the native PAHs, it did not completely desorb heavy nitro-PAHs. Indeed Fig. 2 shows that in the case of the heaviest

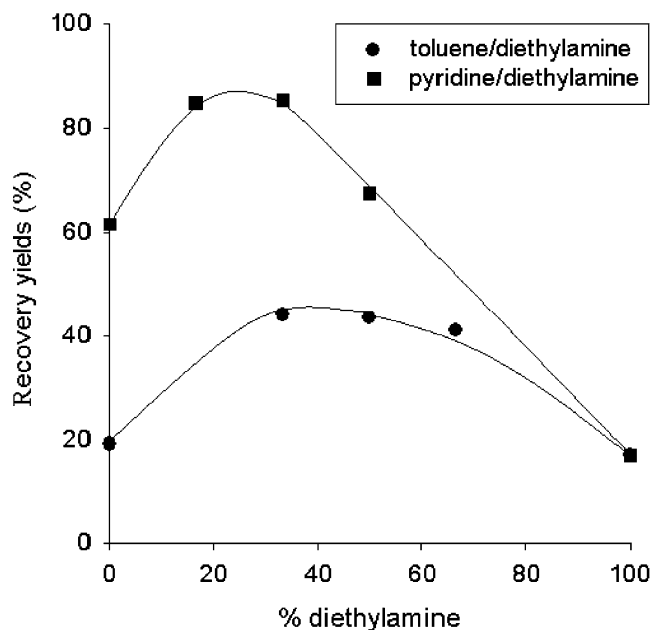


Fig. 3 Effect of the addition of diethylamine to toluene or pyridine on the recovery yields of DB(ah)ANT. MAE operating conditions as follows: 18 mL of the binary solvent mixture, for 37 min at 140 °C

nitroPAHs (3-nitrofluoranthene for example), their recovery yields were not noticeably increased when an aromatic solvent was used, even pyridine. Moreover, all of other nonaromatic solvents tested did not noticeably improve the recovery yields of heavy nitroPAHs in relation to methylene chloride or chloroform. Concerning the diethylamine/pyridine mixture (1:6 v:v), the presence of a small proportion of diethylamine did not decrease the recovery

yields of nitroPAHs compared with those obtained with pure pyridine, but no positive synergy effect was noticed. Finally it should be mentioned that nitroPAHs were quantitatively extracted neither from the spiked soot particles nor from the spiked sand matrix (Table 1). So nitroPAHs may be particularly strongly retained on energetic sites which interact with the nitrated moiety of the molecule rather than with the aromatic ring. Now if sand possesses effectively very polar sites which are able to interact strongly with the nitrated moieties, diesel soot possesses undoubtedly strong π -electron donor sites that can interact with π -electron acceptor compounds such as nitroaromatics. Then we thought that it could be more interesting to add an acid to the pyridine rather than a basic cosolvent with the aim of increasing the extraction yields of the nitroPAHs. Figure 4 shows the evolution of the recovery yields of light and heavy nitroPAHs as a function of the addition of small quantities of acetic acid to pyridine. The extraction yields of heavy nitroPAHs could effectively be increased from around 20% to more than 60% when 1% of acetic acid was added to pyridine. So we observed for the first time a noticeable increase of the desorption yields of heavy nitroPAHs from the spiked diesel soot surface.

Conclusion

By using pressurised MAE, we managed to improve the difficult extraction of a complex mixture of PAHs, nitroPAHs and *n*-alkanes from a particularly refractory carbo-

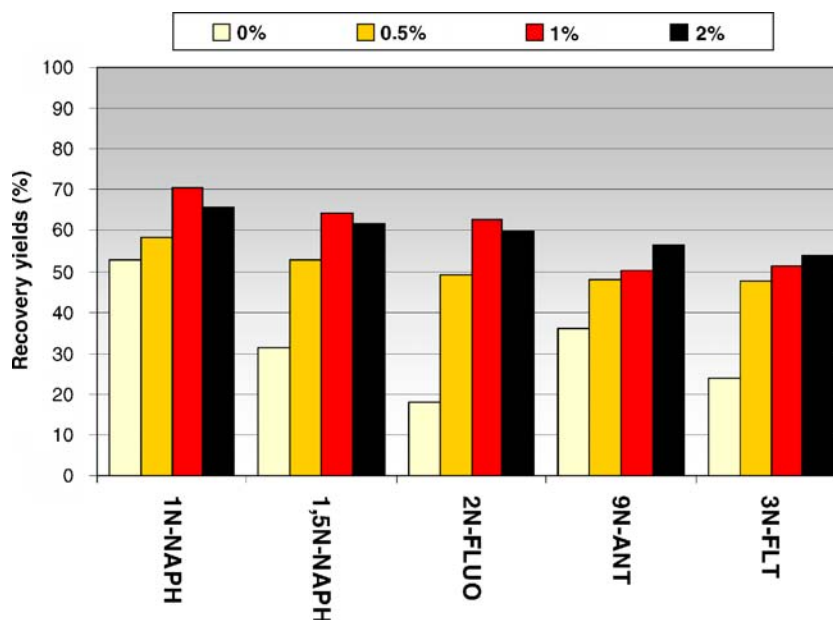


Fig. 4 Evolution of the recovery yields of light and heavy nitrated PAHs as a function of the addition of small quantities of acetic acid (percent) to pyridine. For the MAE operating conditions, see the legend

to Fig. 3. *1N-NAPH* 1-nitronaphthalene, *1,5N-NAPH* 1,5-dinitronaphthalene, *2N-FLO* 2-nitrofluorene, *9N-ANT* 9-nitroanthracene

naceous matrix, namely spiked diesel particulate matter. A second-order central composite design permitted us to localise two optimal extraction domains in the case of chloroform and methylene chloride as extracting solvents. Moreover, these results were supplemented by testing other nonconventional aromatic solvents which helped to extract heavy PAHs and nitroPAHs. Among heterocyclic aromatic solvents, pyridine was the best and an increase of the basic character of the extracting mixture (by the addition of 17% of diethylamine to pyridine) allowed the quantitative extraction of all of the PAHs studied, including the more retained ones, from the spiked diesel soot. The lightest nitroPAHs were also extracted by means of this solvent mixture, but the heaviest ones were not extracted quantitatively from a noncarbonaceous matrix such as sand. In fact, the nitroaromatic compounds were better extracted from the spiked diesel soot by means of pyridine containing 1% of acetic acid, leading to fair recovery yields. Consequently, heavy PAHs and heavy nitroPAHs could not be simultaneously and quantitatively extracted from spiked diesel soot by means of MAE. So, a choice must be made depending on the target pollutants. Finally, although very good results could be achieved in the case of the extraction of spiked heavy PAHs and nitroPAHs from a refractory carbonaceous material, it must be recalled that native matrixes are certainly more difficult to extract. So studies will have to be carried out on native diesel soots and, on the other hand, other extraction techniques will have to be compared with MAE.

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