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Comparison of hot Soxhlet and accelerated solvent extractions with microwave and supercritical fluid extractions for the determination of polycyclic aromatic hydrocarbons and nitrated derivatives strongly adsorbed on soot collected inside a diesel particulate filter

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ABSTRACT

Several methods of extraction were optimized to extract polycyclic aromatic hydrocarbons (PAHs), their nitrated derivatives and heavy *n*-alkanes from a highly adsorptive particulate matter resulting from the combustion of diesel fuel in a diesel engine. This particular carbonaceous particulate matter, collected at high temperatures in cordierite diesel particulate filters (DPF), which are optimized for removing diesel particles from diesel engine exhaust emissions, appeared extremely refractory to extractions using the classical extracting conditions for these pollutants. In particular, the method of accelerated solvent extraction (ASE) is described in detail here. Optimization was performed through experimental design to understand the impact of each factor studied and the factors' possible interactions on the recovery yields. The conventional extraction technique, i.e., Soxhlet extraction, was also carried out, but the lack of quantitative extractions led us to use a more effective approach: hot Soxhlet. It appeared that the extraction of the heaviest PAHs and nitroPAHs by either the optimized ASE or hot Soxhlet processes was far from complete. To enhance recovery yields, we tested original solvent mixtures of aromatic and heteroaromatic solvents. Thereafter, these two extraction techniques were compared to microwave-assisted extraction (MAE) and supercritical fluid extraction (SFE). In every case, the only solvent mixture that permitted quantitative extraction of the heaviest PAHs from the diesel soot was composed of pyridine and diethylamine, which has a strong electron-donor character. Conversely, the extraction of the nitrated PAHs was significantly improved by the use of an electron-acceptor solvent or by introducing a small amount of acetic acid into the pyridine. It was demonstrated that, for many desirable features, no single extraction technique stound out as the best: ASE, MAE or SFE could all challenge hot Soxhlet for favourable extractions. Consequently, the four optimized extraction techniques were performed to extract the naturally polluted diesel soot collected inside the DPF. Comparisons with the NIST standard reference material SRM 1650b showed that the soot collected from the DPF contained 50% fewer *n*-alkanes, and also markedly lower levels of PAHs (44 less concentrated) than SRM 1650b, and that the ratio of nitroPAHs to PAHs was increased. These results were attributed to the high temperatures reached inside the particulate filter during sampling runs and to the contribution of the catalytic DPF to aromatic and aliphatic hydrocarbons abatement.

1. Introduction

Among all the extraction processes used to extract polycyclic aromatic hydrocarbons (PAHs) from solid environmental matrices, some are far more frequently used, despite being time-consuming and requiring large amounts of organic solvents. The most common of these methods are Soxhlet extraction and ultrasonic treatments [1,2]. Nevertheless, alternative extraction techniques have been developed and applied to environmental solids for many years. Supercritical fluid extraction (SFE) appeared almost 25 years ago and exploits the unique properties of a supercritical fluid to extract organic analytes more rapidly [3]. The second method developed was microwave-assisted extraction (MAE), where the solid matrix is subjected to microwave irradiation, leading to an accelerated extraction rate [4]. More recently, assisted solvent extraction (ASE), a method that uses an organic solvent at a relatively high pressure and temperature to achieve more rapid extractions, is increasingly performed in laboratories [5,6]. Independent of the

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time-consumption problem, these latter instrumental extraction methods allowed an important reduction of the solvent usage over the classical Soxhlet or ultrasonic methods, reducing solvent exposure in laboratories. It must be mentioned that new perspectives on the use of micro-focused sonication or focused microwave-assisted Soxhlet extraction were recently developed to suit US EPA recommendations concerning the reduction of time input and solvent consumption [7–9].

A reason to select a very powerful technique to extract PAHs from soot particulates emitted from diesel engines is that these carbonaceous matrices can be considered as "super sorbents" and are more refractory to conventional extractions than other environmental matrices, such as soils or sediments [10]. It must be added that our studied diesel soot matrix was a contaminated environmental material, which was obtained from engine tests by direct collection, under hot conditions, from a particulate filter placed downstream of the diesel engine. Soot collected this way does not have the same surface properties and retention behaviour as commonly studied soots (these latter ones are collected at the exhaust pipe without a particulate filter, under cold conditions). Consequently, the hydrophobic organic contaminants might be more strongly adsorbed on this specific diesel particulate material.

It is particularly important to determine the chemical composition of diesel particulates because of their important health effects, due not only to the ultra-fine particles that can penetrate cell membranes [11], but also to the nature of some of the adsorbed pollutants. PAHs, which are generated by the incomplete combustion of organic compounds, are known to be indirect mutagens, while their nitrated derivatives (nitroPAHs), formed by secondary reactions of PAHs with oxides of nitrogen, are directly active mutagens [12].

In this context, the present work reports on the applicability of three extraction processes (ASE, SFE and MAE) for the simultaneous extraction of PAHs, nitroPAHs and *n*-alkanes spiked onto our specific diesel particulate matter, and it reports also on their comparison with an improved Soxhlet extraction technique, called hot Soxhlet. Extracts were analyzed by gas chromatography coupled to mass spectrometry. Extractions by SFE and MAE were described in two previous papers [13,14] and here we describe the optimization of the ASE method in detail. Optimization was performed through experimental design for better understanding the influence and the interdependence of different operating variables, such as temperature or duration, on the extraction yields. Different extracting solvents were also investigated in this chemometric approach because their capacity to break the analyte–matrix interactions seemed to be particularly crucial. All four optimized extraction techniques were then compared in order to evaluate which of them could be the most advantageous according to different performance criteria. They were also applied to the native and naturally polluted diesel soot, which was collected inside a diesel particulate filter (DPF) during engine tests.

2. Materials and methods

2.1. Chemicals

Methylene chloride, acetone and toluene, of HPLC grade, were purchased from Sigma–Aldrich (St Quentin Fallavier, France). Tetrahydrofuran, chloroform, pyridine, diethylamine, all of HPLC grade, and acetic acid (purity 99.5%) came from Acros Organics (Noisy le Grand, France).

A working stock solution was prepared from individual standards containing 100 μg mL^{-1} of 19 PAHs, 5 nitroPAHs and 3 heavy *n*-alkanes diluted into toluene. This solution was used for further dilutions and for spiking cleaned diesel soot. Naphthalene, biphenyl, acenaphtene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*k*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, dibenz[*a*,*h*]anthracene, 1-nitronaphthalene, 1,5-dinitronaphthalene, 2-nitrofluorene, 9-nitroanthracene, 3-nitrofluoranthene, heneicosane, tetracosane and triacontane were all obtained from Sigma–Aldrich–Fluka. Acenaphtylene, chrysene and indeno[1,2,3-*c*,*d*]pyrene were provided by Interchim (Montluçon, France). Benz[*a*]anthracene, benzo[*b*]fluoranthene and benzo[*g*,*h*,*i*]perylene were purchased from Supelco (Bellefonte, PA, USA).

Deuterated phenanthrene, purchased from Sigma–Aldrich, was used as an internal standard (100 μg mL^{-1} in toluene) for the chromatographic analysis.

Diesel particulate matter was obtained from the CERTAM (St Etienne du Rouvray, France). This material was produced by a recent-model, light-duty four cylinder direct-injection engine (Euro 4 standard), operating in steady-state conditions (torque: 220 N m, power: 80 kW, regime: 1500 rpm). Soot material was trapped by means of a commercial diesel particulate filter (DPF) made of cordierite situated between the oxidation catalyst (just after the diesel engine) and the exhaust pipe; after few hours of sampling at high temperatures (>300 °C), the accumulated particulate matter was blown into glass flasks which were stored at −20 °C.

The NIST standard reference material, SRM 1650b diesel particulate matter, was purchased from LGC Standards (Molsheim, France).

Sand, washed with sulfuric acid, also used as a laboratory test material for extraction methods, was purchased from VWR International (Fontenay sous bois, France).

Gaseous nitrogen (Alphagaz 1 quality) was purchased from Air Liquide (Honfleur, France).

2.2. Extractions

2.2.1. Soxhlet and hot Soxhlet extraction procedures

Soxhlet extractions were performed with a Büchi B-811 automated Soxhlet extractor purchased from IMLAB (Lille, France). 100 mg of cleaned diesel particulates or washed sand were spiked with 100 μL of the standard mixture described earlier (see chemicals), leaving 30 min for the standard mixture to contact with the solid matrix. Two modes of extraction were performed: conventional Soxhlet and hot Soxhlet. In conventional Soxhlet mode, the solid matrix was placed in the thimble holder but not heated, unlike the distillation flask which initially contained 150 mL of the extracting solvent to be refluxed. In contrast, heating was applied to the extraction cavity in hot Soxhlet mode, but the temperature had to be lower than the boiling point of the extracting solvent mixture to keep it in the liquid state. Consequently heating levels (level 1: 25 °C to level 15: 150 °C) were adapted to the vaporization temperatures of the various extracting solvents tested (see Table 1).

2.2.2. Soot cleanup procedure

10 g of crude diesel particulate material was cleaned by means of a conventional Soxhlet apparatus: three successive extractions were performed using fresh methylene chloride refluxed for eight hours each time. The cleaned soot was ground and stored at 4 °C. At first, blank extractions were performed (before optimization) at harsh conditions to be sure that all aromatic or aliphatic pollutants were removed. Blanks were then performed again, identical to a sample run, after the optimization of the extraction technique.

2.2.3. Accelerated solvent extraction procedure

An ASE 100 from Dionex Corporation France (Voisins le Bretonneux, France) was used for the pressurized-fluid extraction. A 10 mL stainless-steel cell was used for the extractions. Glass fiber

Table 1
Heating levels of the distillation flask and of the thimble holder according to the different solvents used for Soxhlet and hot Soxhlet extractions.

Extraction solvents or solvent mixtures	Solvents boiling temperatures (°C, P = 1 atm.)	Heating level of distillation flask	Heating level of thimble holder (only hot Soxhlet)
Methylene chloride	39.9	9 (≈100 °C)	2 (≈35 °C)
Acetone	56.3	11 (≈115 °C)	3 (≈40 °C)
Toluene	110.6	13 (≈130 °C)	6 (≈70 °C)
Diethylamine	55.5	11	3
Pyridine	115.2	13	7 (≈80 °C)
Pyridine/diethylamine	–	12 (≈125 °C)	5 (≈60 °C)
Pyridine/acetic acid	–	13	6

filters were placed at the outlet of the cell prior to being loaded with 100 mg of the solid matrix. Cleaned diesel soot, or washed sand, was then spiked with 100 μL of the standard mixture containing 27 pollutants (see chemicals) and left for 30 min before starting the extraction. Extraction pressure was 100 bars and static time was 10 min. After ASE extractions, extracts were flushed into a collection bottle. The cell was then rinsed with a 50% volume of the same extracting solvent, flushed into the same collection bottle and finally purged with gaseous nitrogen for 80 s. An additional rinse with the extracting solvent between samples was necessary to clean the extraction system.

2.3. *Analysis by gas chromatography–mass spectrometry*

Analysis (and quantitation) of PAHs, nitroPAHs and *n*-alkanes was performed by gas chromatography using a Hewlett Packard model 5980 (Palo Alto, CA, USA) equipped with a VF-5MS Factor Four capillary column (5% phenylmethylsiloxane, 40 m, 0.15 mm i.d., 0.15 μm film thickness) from Varian (Les Ulis, France). Splitless injections were performed at 250 °C and the injection volume was 1 μL. The oven temperature program was the following: 60 °C for 2.05 min, an increase up to 170 °C (at 40 °C min^{-1}), an increase up to 300 °C (at 3.7 °C min^{-1}), then isothermal for 7 min. The carrier gas (helium) was kept at a constant flow rate of 0.5 mL min^{-1}. The chromatograph was fitted to an HP 5972 mass detector operating with electron impact ionization (electron multiplier voltage: 2000 V) in the single-ion monitoring mode for quantitation. The interface was held at 290 °C. PAH quantitation was carried out using eight-point calibration plots obtained from pure standard mixtures from 0.1 to 5 μg mL^{-1}, each one containing 1 μg mL^{-1} of the internal standard (perdeuterated phenanthrene).

3. Results and discussion

3.1. *Optimization of ASE extractions by a chemometric approach*

ASE is now frequently used as an extraction procedure for a variety of environmental analyses, particularly to extract PAHs or hydrocarbons from soil or sediment samples [15–18]. However, some results have shown that, concerning extractions from diesel particulate matter, very drastic conditions are necessary to recover higher molecular weight PAHs, which are strongly adsorbed on soot particles [19]. Moreover, it appeared that the ASE conditions previously optimized for extractions from certified reference materials (diesel particulate matter SRM 1650 and 2975) would not be sufficiently severe to extract the heaviest PAHs from our particular material: indeed, preliminary experiments using extraction conditions described by Schantz et al. [20] or Perraudin et al. [21] showed a very poor recovery of the 4–6 aromatic-ring PAHs (data not shown). The particularity of our diesel soot material resulted from the way it was collected, i.e., inside a wall-flow diesel particulate filter (DPF). These devices are designed to remove diesel particulate matter from the exhaust gas of a diesel engine. An increasing number of powered vehicles are currently equipped with a functioning filter and will consequently emit no visible smoke from the exhaust pipe. In addition to collecting the soot particulates, a method exists to burn off the accumulated particulates during the filter regeneration step. Here it must be mentioned that our diesel particulate matter had a significantly lower soluble organic fraction (SOF) compared to certified diesel particulate materials. This low content (less than 10% versus 20.2% for SRM 1650b [22]) was certainly due to the high temperatures reached inside the particulate filter throughout the collecting process (approximately 300 °C), while certified materials were sampled at only 52 °C. Effectively, studies on soot thermal treatments have demonstrated an important release of the most volatile part of the SOF at high temperatures and also an increase in the specific surface area of the particulate matter, leading to an increase of highly energetic active adsorption sites [23]. Obviously, we can link this increase of high-energy adsorption sites to an important increase of the PAH adsorption strength, particularly concerning the heaviest PAHs. Moreover, it is known that organic soluble compounds can certainly help the extraction of PAHs. Consequently, we supposed that it would be not only difficult to extract heavy PAHs from our native diesel particulates but also from the cleaned soot used for the spiking experiments. ASE experiments performed on 500 mg of spiked sand (for comparison) or on 100 mg of spiked cleaned soot, with methylene chloride as the extracting solvent, at 100 °C, for an extraction time of 10 min, showed that all the PAHs were quantitatively removed from the sand matrix in these conditions, while only volatile PAHs (from naphthalene to fluorene) were totally extracted from the spiked diesel particulates. Recovery yields were dramatically decreased from phenanthrene (48% extracted) to the three heaviest PAHs (indeno[1,2,3-*c*,*d*]pyrene, dibenz[*a*,*h*]anthracene and benzo[*g*,*h*,*i*]perylene), these latter PAHs being very highly retained on the carbonaceous surface, with recovery yields not exceeding 5–10%. These results implied that if extractions were incomplete for a spiked matrix, they would be lower yet for a real soot sample. It was then obviously necessary to investigate all the factors which might influence the ASE extraction to enhance PAH recoveries.

The dependence of the extraction yields on the temperature and on the static extraction time was studied as well as the nature of the extracting solvent. The pressure and the volume of the solvent were kept constant (using 10 mL extraction cells) and we first considered only one cycle of extraction. Univariate investigations would have lead to numerous experiments which could not have revealed the interdependence between the different factors studied, so we chose a chemometric approach to investigate the three operating parameters mentioned earlier. The use of a full central composite design (2^3) allowed all the operating variables to be investigated individually, and their two and three component interaction effects, involving eight runs at two coded levels −1 and +1. Squared terms, required to evaluate the response curvature, could be estimated thanks to six other runs (axial or star points) at $-\alpha$ and $+\alpha$ levels ($\alpha = \pm 1.68$) and, finally, five runs at the zero central point permit-

Table 2
Central composite design used for the optimization of ASE extractions of PAHs, nitroPAHs and heavy *n*-alkanes from diesel particulates.

Factors	Coded levels				
	$-\alpha$	-1	0	+1	$+\alpha$
Temperature: T (°C)	83	100	125	150	167
Extraction time: t (min)	1.6	5	10	15	18.4
Extraction solvent: Solv	$CHCl_3$	$CHCl_3$	C_4H_8O	CH_2Cl_2	CH_2Cl_2

ted the evaluation of the variance of prediction (uniform precision design). The total number of experiments was randomized to prevent the bias effect due to remaining extraneous sources. Table 2 shows the limits assigned to temperature and extraction time. In the case of temperature, it depended upon instrumental constraints ($T < 200$ °C), whereas for extraction time, we decided not to exceed 20 min, in accord with prior literature data. Concerning the selection of the organic extraction solvent, we chose to investigate three particular solvents which were selected from the Snyder selectivity triangle [24]. Solvents are grouped in this triangle according to their ability to either donate or accept protons or to induce dipole moments. Many solvents have been classified into eight groups, but group I (which includes aliphatic ethers), group V (which includes methylene chloride) and group VIII (which includes chloroform) may each mainly develop only one specific interaction strength, which are, respectively, proton acceptor, dipole–dipole and proton donor. We thought that it would be interesting to investigate which of these primary interaction strengths might be more favorable for desorbing and solubilizing PAHs, nitroPAHs or *n*-alkanes from a super-sorbent such as our soot particulates. It must be noted that tetrahydrofuran (group III) replaced ether solvents from group I, because this cyclic ether was less dangerous than non-cyclic ones when subjected to high temperatures and pressures.

The results from the experimental design were assessed using a multi-linear regression and equations relating the response (recovery yield of each target compound) to the estimated effects of the three factors studied and to their second-order or third-order interactions. Statistical treatment of the data for some typical compounds is shown in Table 3. It is apparent that all the three main factors influenced the extraction yields (except for heavy *n*-alkanes, for which the temperature was the only main factor that directly affected the recovery yields) and that second and third-order interactions cannot be neglected. These results are very different from those of Saim et al., who did not find any influence of the temperature, of the extraction time or of many solvents on the ASE extraction of PAHs from a contaminated soil [25]. Table 3 indicates that an increase of the temperature is favorable to the ASE extraction of all compounds (as the positive sign of the parameter estimate indicates) but that extremely elevated temperatures are not as favorable for heavy PAHs (see the negative sign of the squared term). As regards the extraction time, tendencies are contradictory if we compare the volatile PAHs and their nitrated derivatives, which are better extracted with a low extraction time, with the other PAHs, for which a longer extraction time is necessary. With the aim of fully understand the effects of each factor and their interactions on the various compounds, it was more informative to plot response surfaces over the whole experimental domain. As shown on Fig. 1, PAHs have a different behavior towards the studied factors: from naphthalene to benzo[*a*]pyrene (Fig. 1a and b), methylene chloride, which mainly develops a dipolar interaction strength, is the best extraction solvent for the polarizable PAHs, and a compromise must be found regarding the extraction time at elevated temperatures. The zero level of the domain (10 min) must then be selected. On the other hand, Fig. 1c shows that the three heaviest PAHs are better extracted by tetrahydrofuran, which possesses a basic character, and that extremely elevated temperatures are not as favorable: so level +1 (150 °C) is preferred to level $+\alpha$ (167 °C).

Table 3
Estimated effects statistically significant at the 95% confidence interval (*t*-test approach) for some typical studied compounds (naphthalene for volatile PAHs, benz[*a*]anthracene for semi-volatile PAHs, benzo[*g*,*h*,*i*]perylene for non volatile PAHs, 9-nitroanthracene for nitrated PAHs and tetracosane for heavy *n*-alkanes).

	NAPH	B(a)ANT	B(ghi)PER	9N-ANT	TETRA
Solv	9.12	3.11	−1.57	−4.98	
t	−5.45	2.91	1.58	−5.34	
T	12.39	2.11		6.26	13.88
$t \times$ Solv				−9.44	
$T \times$ Solv	12.52		2.23		
$t \times T$		−6.73			
$(T)^2$			−2.53	12.46	
$T \times t \times$ Solv	−10.51				−19.90

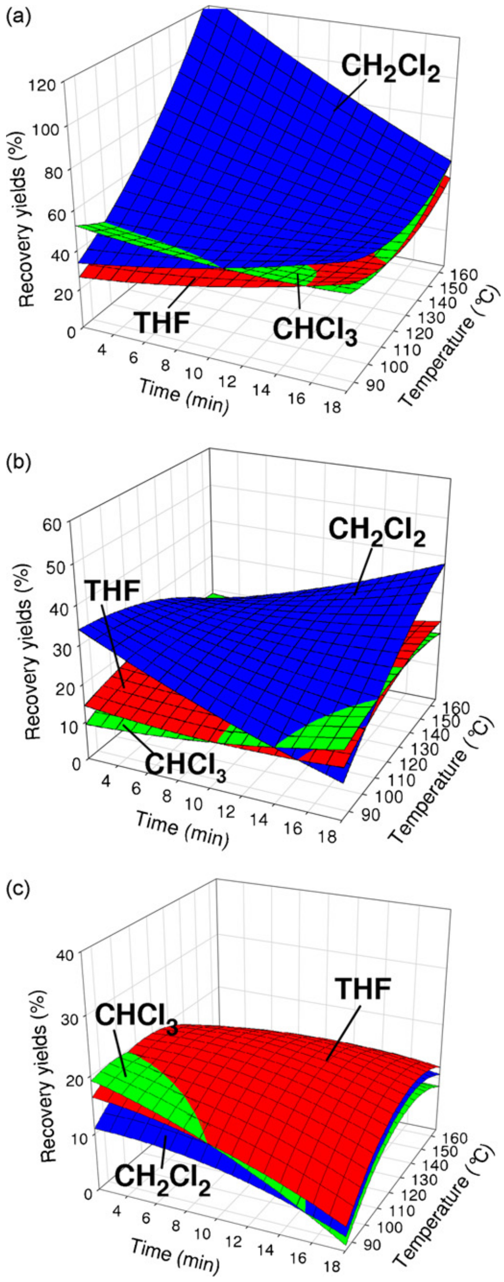

Fig. 1. Response surfaces (recovery yields in %) after ASE extractions, according to time, temperature and nature of extraction solvents: (a) naphthalene; (b) benzo[*a*]pyrene; (c) dibenz[*a*,*h*]anthracene.

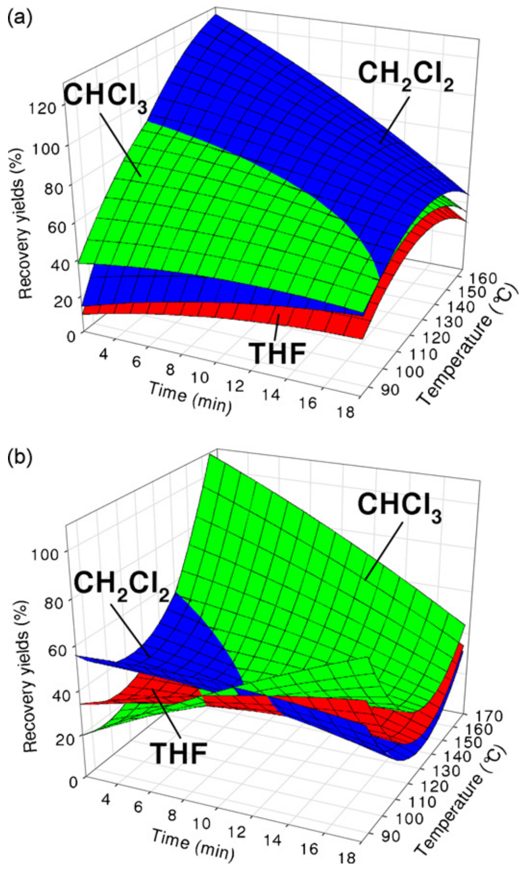

Fig. 2. Response surfaces (recovery yields in %) after ASE extractions, according to time, temperature and nature of extraction solvents: (a) heneicosane; (b) 9-nitroanthracene.

In all the cases no optimal operating conditions could be found to quantitatively extract PAHs having from four to six aromatic rings. Concerning heavy *n*-alkanes, Fig. 2a clearly shows that they can be quantitatively extracted using methylene chloride at 150 °C over 10 min, but as shown in Fig. 2b, nitroPAHs were somewhat better extracted using chloroform (which possesses a proton-donor character), at elevated temperatures and a relatively low extraction time. In view of all these results, we concluded that a relatively short extraction time (10 min) and a relatively high temperature (150 °C) had to be chosen to better extract our target pollutants from diesel particulates. Moreover methylene chloride seemed to be the best solvent to simultaneously extract the majority of the target compounds. However, for the heaviest PAHs and nitroPAHs not being quantitatively extracted even when using optimized extracting parameters, we also tested if a second extraction cycle could improve the low recovery yields, but no significant increase was seen. Consequently, it seemed more judicious to investigate new extraction solvents, which could develop other interaction strengths that had not been studied yet, such as electron transfer with the electron-rich soot surface. For this purpose we tried aromatic solvents such as toluene, pyridine and nitrobenzene. As can be seen in Fig. 3, toluene was better able than methylene chloride to extract all the compounds, but its single aromatic character was not sufficient to desorb the heaviest PAHs. The previous results, involving tetrahydrofuran (THF) as the best solvent to desorb the heaviest PAHs, led us to suppose that the basic character also had to be considered. Next, we noticed a significant increase in the PAH recovery yields when using pyridine (see Fig. 3). Indeed this solvent is not only an aromatic one but it has also a basic character because of its lone pair of electrons outside of the aromatic system. Ultimately, pyridine, which is a strong electron-donor solvent, was the best one to displace and desorb the PAHs from the highly sorptive soot surface. At the same time, we notice in Fig. 3 that pyridine was not the best solvent to disrupt the interactions between nitroPAHs and the carbonaceous surface: nitrobenzene, which is an electron-acceptor solvent, was more able to quantitatively desorb the nitrated PAHs. At this point of the discussion, it could be concluded that native PAHs and their nitrated derivatives are not adsorbed onto the same kind of energetic interaction sites. PAHs, which are electron-donor compounds, are greatly retained on electron-acceptor sites, whereas the nitroPAHs, which are electron-acceptor compounds because of the mesomeric attraction of the nitro moiety, are instead mainly adsorbed on electron-donor sites. In this context, it appeared that it was difficult to find a compromise to quantitatively and simultaneously extract the native PAHs, which are better extracted with a solvent possessing an aromatic character in addition to a basic one, and the nitroPAHs, which are certainly better extracted with a solvent possessing an electron-acceptor character or, to a lesser extent, a proton-donor character

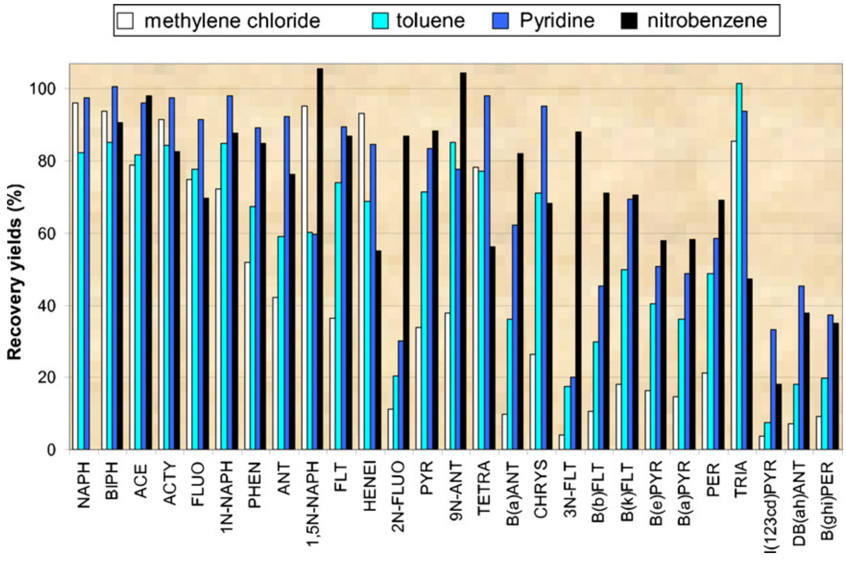

Fig. 3. Influence of the nature of many extraction solvents on the ASE recovery yields of target PAHs, nitroPAHs and *n*-alkanes. Experimental conditions: 10 min of static extraction (one cycle) using 10 mL of solvent at 150 °C and 100 bars.

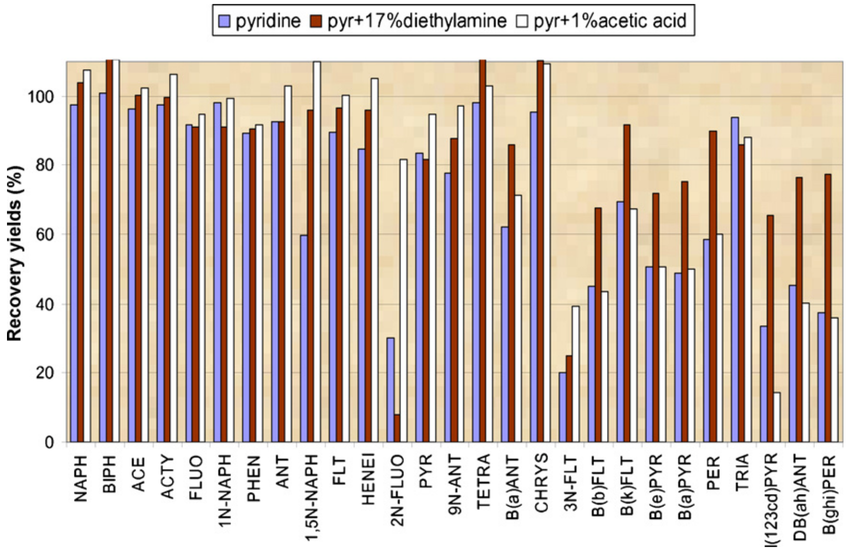

Fig. 4. Influence of the addition of diethylamine or acetic acid to pyridine on the ASE recovery yields of PAHs, nitroPAHs and *n*-alkanes. Experimental conditions: 10 min of static extraction (one cycle) using 10 mL of the solvent mixture at 150 °C and 100 bars.

(recall the favorable influence of the chloroform for this class of compounds). Indeed, Fig. 4 shows that addition of the basic diethylamine to pyridine enhanced the extraction of all the PAHs and particularly the heaviest ones, whereas the addition of acetic acid to pyridine enhanced the nitroPAH recovery yields. Consequently the best extraction conditions for extracting PAHs and heavy *n*-alkanes using ASE were: 150 °C for 10 min (one cycle) with a mixture of pyridine/diethylamine 83/17% (v/v) at 100 bars. Regarding the nitroPAHs, the best conditions were: 150 °C for 10 min (one cycle) at 100 bars with nitrobenzene as the solvent or with a mixture containing 99% pyridine and 1% acetic acid. We can notice from Figs. 3 and 4 that nitrobenzene was better for extracting the heaviest nitroPAH (3-nitrofluoranthene for example) but this solvent could not be easily vaporized, which is a major disadvantage compared to the pyridine/acetic acid mixture when traces have to be extracted and concentrated prior to analysis.

3.2. Optimization of hot Soxhlet extractions

Owing to the fact that even spiked diesel particulates were particularly refractive to conventional extractions, we quickly concluded that Soxhlet extraction conditions found in the literature were not sufficiently severe to obtain quantitative recovery yields. We first performed extractions using increased extraction cycles (20, 40 and 60 cycles) and classical extraction solvents such as acetone, methylene chloride or toluene. But these experiments showed that despite the use of an aromatic solvent, which is better than acetone or methylene chloride, and despite long extraction cycles (60 cycles, i.e., more than eight hours), only fair recovery yields were obtained for the lightest PAHs (less than 60%) and very poor ones for the heaviest PAHs (less than 25%) and nitroPAHs (20–52%). Further increasing the number of cycles being impractical because of the very long time consumption, so we rather chose to try a hot Soxh-

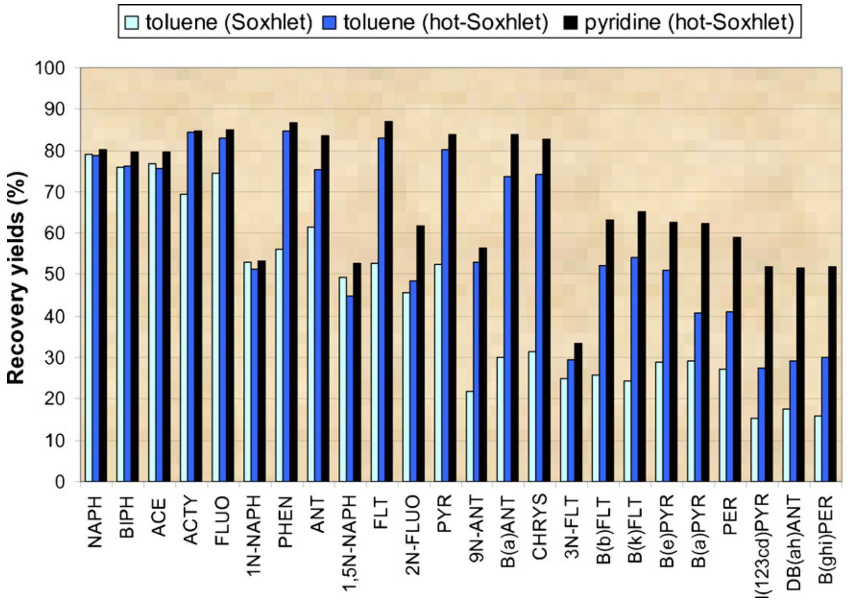

Fig. 5. Influence of the Soxhlet extraction compartment heating and of two aromatic solvents on recovery yields of PAHs, nitroPAHs and *n*-alkanes spiked on 0.1 g diesel particulates, using 150 mL of solvent.

Table 4
Comparison of various criteria of performance for the extraction of the target compounds using the four optimized extraction techniques.

Extraction technique	Extracted compounds	Better extraction solvents	Solvent volume (mL)	Time	Temperature (°C)	Pressure (bar)	Solvent evaporation prior to analysis
Hot Soxhlet	PAHs/heavy *n*-alkanes	Pyridine/diethylamine 83/17% (v/v)	>150 mL	60 cycles >8 h	<65	1	Yes
	Nitrated PAHs	Pyridine + 1% acetic acid	>150 mL	60 cycles >8 h	<70	1	Yes
MAE	PAHs/heavy *n*-alkanes	Pyridine/diethylamine 83/17% (v/v)	18 mL	37 min	140	Not measured	Yes
	Nitrated PAHs	Pyridine + 1% acetic acid	18 mL	37 min	140	Not measured	Yes
SFE	PAHs/heavy *n*-alkanes	CO_2 + 15% of a mixture pyridine/diethylamine 83/17% (v/v)	<3 mL	10 + 30 min	75	300	Not necessary
	Nitrated PAHs	CO_2 + 15% of a mixture pyridine + 1% acetic acid	<3 mL	10 + 30 min	75	300	Not necessary
ASE	PAHs/heavy *n*-alkanes	Pyridine/diethylamine 83/17% (v/v)	16–20 mL	1 cycle: 10 min	150	100	Yes
	Nitrated PAHs	Pyridine + 1% acetic acid	16–20 mL	1 cycle: 10 min	150	100	Yes

Table 5
Figures of merit of the four extraction methods for the determination of PAHs, nitroPAHs and *n*-alkanes from highly sorptive spiked diesel soot ($m = 0.1$ g), using optimal extraction conditions.

	NAPH	BIPH	ACE	ACTY	FLUO	1N-NAPH	PHEN	ANT	1,5N-NAPH	FLT	HENEI	2N-FLUO	PYR	9N-ANT
SFE [14]														
Mean recovery[a] (%)	89	91	90	97	96	63	84	83	60	92	98	61	85	66
RSD (%)	6	6	6	7	6	10	7	7	13	7	7	12	8	15
LOD (ng g^{-1})	0.09	0.05	0.06	0.05	0.19	1.8	0.1	0.1	7.6	0.2	10	3.7	0.21	2.2
LOQ (ng g^{-1})	0.30	0.17	0.20	0.17	0.63	6.0	0.33	0.33	25	0.67	33	12	0.70	7.3
MAE														
Mean recovery[a] (%)	86	83	103	107	109	71	102	104	65	99	100	64	96	55
RSD (%)	10	8	7	7	11	13	6	7	15	8	14	15	9	21
LOD[b] (ng g^{-1})	0.18	0.10	0.15	0.10	0.20	1.0	0.10	0.10	8.5	0.25	11	4.5	0.24	3.4
LOQ[b] (ng g^{-1})	0.60	0.33	0.50	0.33	0.67	3.3	0.33	0.33	28	0.83	37	15	0.80	11
ASE														
Mean recovery[a] (%)	84	88	100	100	91	99	91	93	98	97	95	82	99	97
RSD (%)	15	13	12	12	11	12	11	11	8	13	12	25	13	13
LOD[b] (ng g^{-1})	0.15	0.10	0.11	0.10	0.23	1.4	0.12	0.12	5.5	0.25	12	3.3	0.25	1.8
LOQ[b] (ng g^{-1})	0.50	0.33	0.37	0.33	0.77	4.7	0.40	4.0	18	0.83	40	11	0.83	6.0
Hot Soxhlet														
Mean recovery[a] (%)	87	83	93	86	90	73	97	97	71	86	99	70	95	72
RSD (%)	10	10	7	8	5	7	5	5	12	5	6	9	6	7
LOD[b] (ng g^{-1})	0.40	0.21	0.15	0.15	0.50	3.5	0.30	0.30	15	0.54	11	7.5	0.45	4.5
LOQ[b] (ng g^{-1})	1.3	0.70	0.50	0.50	1.7	12	1.0	1.0	50	1.8	37	25	1.5	15

	TETRA	B(a)ANT	CHRYS	3N-FLT	B(b)FLT	B(k)FLT	B(e)PYR	B(a)PYR	PER	TRIA	I(1,2,3,cd)PYR	DB(ah)ANT	B(ghi)PER
SFE [14]													
Mean recovery[a] (%)	91	81	82	58	86	84	81	79	79	90	81	81	79
RSD (%)	13	9	10	14	11	11	9	9	12	13	15	14	15
LOD (ng g^{-1})	15	0.2	0.18	2.5	0.16	0.17	0.16	0.27	0.22	17	0.65	0.78	0.65
LOQ (ng g^{-1})	50	0.67	0.60	8.3	0.53	0.57	0.53	0.90	0.73	57	2.2	2.6	2.2
MAE													
Mean recovery[a] (%)	87	84	86	52	85	86	85	88	86	94	85	85	87
RSD (%)	10	14	13	20	14	14	13	14	15	16	15	16	15
LOD[b] (ng g^{-1})	15	0.28	0.25	3.5	0.22	0.22	0.25	0.30	0.28	18	0.85	0.91	0.83
LOQ[b] (ng g^{-1})	50	0.93	0.83	12	0.73	0.73	0.83	1.0	0.93	60	2.8	3.0	2.8
ASE													
Mean recovery[a] (%)	103	86	101	36	98	92	72	75	90	86	73	77	78
RSD (%)	14	24	19	26	11	20	19	17	17	17	25	23	15
LOD[b] (ng g^{-1})	17	0.25	0.20	4.7	0.20	0.21	0.25	0.34	0.25	21	1.0	1.0	0.80
LOQ[b] (ng g^{-1})	55	0.83	0.67	16	0.67	0.70	0.83	1.1	0.83	70	3.3	3.3	2.7
Hot Soxhlet													
Mean recovery[a] (%)	99	97	96	73	90	89	90	86	89	95	79	80	79
RSD (%)	6	6	6	14	5	6	7	7	7	6	8	9	9
LOD[b] (ng g^{-1})	17	0.44	0.40	4.7	0.40	0.40	0.38	0.60	0.49	19	1.6	2.0	1.6
LOQ[b] (ng g^{-1})	57	1.5	1.3	15.7	1.3	1.3	1.3	2.0	1.6	63	5.3	6.7	5.3

[a] Average recovery yields calculated on five replicates.

[b] LOD and LOQ evaluated from 0.25 μg of each target pollutant spiked on 0.1 g of cleaned soot and after concentration by solvent evaporation.

let procedure to improve the poorest recovery yields. In this case, heating was also applied to the extraction compartment containing the soot matrix (see experimental part) leading to extraction rate acceleration. As can be seen in Fig. 5, recovery yields were markedly increased when performing the hot Soxhlet procedure, but as discussed earlier, toluene was not the best extraction solvent despite its favorable aromatic character. For the reasons already mentioned, pyridine was better for extracting the heaviest PAHs from the diesel soot surface (see Fig. 5). When adding a percentage of diethylamine to the pyridine, as was done for the ASE procedure, the extraction of all the PAHs was quantitative. Indeed, indeno[1,2,3-*c*,*d*]pyrene, which is one of the most difficult PAHs to extract, was quantitatively desorbed (recovery yield: 79%) by using the pyridine/diethylamine mixture 83/17% (v/v), whereas the recovery yields of heavy nitroPAHs were unchanged. On the other hand, an addition of acetic acid to the pyridine markedly improved the extraction of the nitroPAHs: 1% acetic acid in pyridine permitted the quantitative extraction of all the nitroPAHs, even the heaviest one (recovery yield of 3-nitrofluoranthene being 73%), whereas the recovery yields of heavy PAHs were unchanged.

3.3. Comparisons between hot Soxhlet, ASE, SFE and MAE extractions

This part of the discussion aims at comparing all the extraction methods performed to quantitatively extract PAHs, nitroPAHs and heavy *n*-alkanes from the very sorptive soot collected inside the diesel particulate filter. MAE and SFE were also optimized by a chemometric approach, as described in two previous papers [13,14]. The same difficulties in extracting heavy PAHs and nitrated PAHs were encountered using SFE or MAE with classical extraction solvents. As was described for the ASE and hot Soxhlet procedures, the pyridine/diethylamine mixture was always the best extraction solvent (or co-solvent mixed with carbon dioxide in the case of SFE) to desorb all the PAHs from the highly retentive carbonaceous surface. Also as before, an addition of acetic acid to the pyridine was favorable in all the cases to extract nitroPAHs, although quantitative recovery yields (≥80%) were not reached. Table 4 summarizes the optimal extraction conditions for the four studied extraction techniques, and Table 5 shows many meritorious features of the four optimized methods. The mean recoveries and the precision (as relative standard deviations) were established from five replicates, with 10 μg of each pollutant spiked onto 0.1 g of cleaned soot. Detection limits (LOD) and quantification limits (LOQ) were calculated respectively as three times and ten times the standard deviation of the blank sample noise. They were estimated after a solvent evaporation step (solvent reduction to approximately 1–1.5 mL) in the case of hot Soxhlet, MAE and ASE. SFE did not require an evaporation step before GC–MS analysis. It must be added that these low detection limits were determined from spiked cleaned soot samples, with no interference appearing in the chromatographic analysis.

As can be seen in Tables 4 and 5, hot Soxhlet was particularly interesting in terms of recovery yields, for heavy PAHs (≥79%) as well as for nitroPAHs (≥70%), but the extraction time remained far too long, even though it was certainly reduced compared to conventional Soxhlet. At the same time, solvent consumption was markedly larger than for the other extraction techniques (see Table 4), which is a serious disadvantage, as mentioned previously. Comparing MAE, SFE and ASE to hot Soxhlet, they also yielded quantitative extraction efficiencies for all PAHs, even for the heaviest ones (≥85%, ≥79% and ≥72%, respectively). Consequently, these techniques must be preferred to the too-long Soxhlet extraction. However, regarding the extraction of nitroPAHs, hot Soxhlet seems to be slightly better (recoveries ≥70%), closely followed by ASE (≥82%, except for 3-nitrofluoranthene), which gave higher values than MAE (52–71%) or SFE (approximately 60%). Moreover, if we focus on the extraction time, ASE seems to be the best extraction technique (see Table 4).

However, we must consider also other possible steps prior to GC–MS analysis. Indeed, SFE has the advantage of requiring only a few solvent collection volume (see Table 4) and in this case, sample concentration by solvent evaporation is not required prior to the chromatographic analysis, which is a serious advantage in terms of sample preparation time but also in terms of volatile compound recovery (naphthalene and biphenyl recoveries are slightly better for SFE extraction than for the other extraction processes). Moreover, with an evaporation step not being necessary, the accuracy of the method and the limits of detection and quantification were slightly better for SFE than the MAE and ASE techniques (see Table 5). However, it must be underlined that if these detection or quantification limits are slightly better for SFE or worse for hot Soxhlet, they are all of the same order of magnitude. The other advantage of SFE is certainly its better selectivity for the more polar organics. Indeed hot Soxhlet, MAE and ASE extractions, which show generally little or no compound class selectivity, led to darker extracts, while extracts from SFE, collected in toluene, were lighter. Although diesel particulates were cleaned before spiking them, only less polar organics were totally removed by methylene chloride. Several blanks were performed, identical to a sample run, and showed no detectable *n*-alkanes, PAHs or nitroPAHs using each extraction technique, but even blank extracts were darker using ASE, MAE or hot Soxhlet while SFE showed clear blank extracts. Co-extraction of matrix interfering compounds, which is a problem when the molecules of interest are in trace concentration, as in real-world samples, is undoubtedly less pronounced when using SFE, which has the greatest potential for selectivity [26]. Finally, although SFE seems to be the most relevant extraction technique in terms of sample preparation prior to GC–MS analysis (with no purification step and no concentration by solvent evaporation), it nevertheless requires the greatest amount of expertise to optimize the extraction conditions (the number of possible influential factors is markedly larger) [14]; MAE and ASE are easier to implement. Finally, MAE is not subject to frit or filter clogging and plugging due to nanometer-size particulates, which is certainly a better guarantee of reproducibility, contrary to SFE or to a lesser extent to ASE, which can sometimes undergo this phenomenon. This embarrassing problem was not taken into account in the accuracy values shown in Table 5, which are all of the same order of magnitude, because there were no clogging incidents when the five replicates (SFE or ASE) were carried out.

As can be seen from the results, the desirable features of minimal organic solvent use, fast extraction time – in the sample preparation prior to analysis but also in the optimization steps – reproducibility, relative ease (and without any consideration of the relative capital cost) does not immediately emphasize one particular extraction technique among SFE, ASE or MAE. All these techniques can challenge Soxhlet or hot Soxhlet in the case of PAH and nitroPAH extractions from very sorptive diesel soot surfaces.

3.4. Extraction of naturally polluted diesel particulate matter

The four extraction techniques previously optimized were performed to extract the diesel particulate matter collected inside a diesel particulate filter placed downstream of the diesel engine and oxidation catalyst. Results for PAHs and nitroPAHs are shown in Table 6, and results for *n*-alkanes are shown in Fig. 6. As expected, the major organics extracted by all the methods were branched and linear alkanes. As shown in Fig. 6, the four extraction techniques produced similar results in regards to linear alkane extractions from the native diesel soot. Differences in results were credited to relatively high relative standard deviations, in a range between

Table 6
Mean concentrations and standard deviations (μg g^{-1}) of PAHs and nitroPAHs extracted from the standard reference material SRM 1650b (m = 0.05 g) and from the diesel soot accumulated inside the diesel particulate filter (m = 0.1 g). Conditions of extraction: see Table 4.

	SRM 1650b			Diesel soot from DPF			
	NIST certificate	Hot Soxhlet[a]	ASE[a]	Hot Soxhlet[a]	MAE[a]	SFE[a]	ASE[a]
NAPH	5.07 (±0.43)	3.1 (±1.1)	3.3 (±1.0)	3.03 (±0.9)	3.24 (±0.7)	3.71 (±0.6)	2.64 (±1.1)
BIPH	3.57 (±0.37)	4.9 (±2.2)	3.9 (±1.1)	0.71 (±0.30)	0.82 (±0.24)	1.04 (±0.31)	0.80 (±0.31)
ACTY	1.38 (±0.12)	2.7 (±1.3)	1.5 (±0.2)	n.d.	n.d.	n.d.	n.d.
ACE	0.22 (±0.024)	0.5 (±0.4)	0.6 (±0.1)	n.d.	n.d.	n.d.	n.d.
FLUO	1.26 (±0.09)	1.1 (±0.2)	0.9 (±0.3)	0.05 (±0.04)	0.07 (±0.02)	0.09 (±0.03)	0.16 (±0.02)
PHEN	69.5 (±1.9)	59.1 (±5.4)	65.6 (±5.7)	0.62 (±0.13)	0.44 (±0.20)	0.52 (±0.16)	0.60 (±0.15)
ANT	7.67 (±0.47)	9.9 (±1.8)	10.9 (±2.1)	0.27 (±0.10)	0.11 (±0.08)	0.20 (±0.08)	0.28 (±0.09)
FLT	47.3 (±0.8)	43.9 (±5.0)	45.0 (±4.7)	0.07 (±0.04)	0.13 (±0.04)	0.10 (±0.02)	0.08 (±0.03)
PYR	43.4 (±1.6)	40.4 (±4.9)	43.3 (±4.4)	0.11 (±0.04)	0.10 (±0.02)	0.15 (±0.03)	0.16 (±0.03)
B(a)ANT	6.18 (±0.30)	6.8 (±1.9)	7.9 (±1.0)	n.d.	n.d.	n.d.	n.d.
CHRY	13.3 (±1.1)	13.0 (±0.7)	13.8 (±1.1)	n.d.	n.d.	n.d.	n.d.
B(b)FLT	6.77 (±0.84)	8.9 (±2.7)	6.4 (±1.6)	n.d.	n.d.	n.d.	n.d.
B(k)FLT	2.37 (±0.21)	2.8 (±0.2)	2.4 (±0.5)	n.d.	n.d.	n.d.	n.d.
B(e)PYR	6.30 (±0.5)	7.1 (±1.5)	8.1 (±1.9)	n.d.	n.d.	n.d.	n.d.
B(a)PYR	1.17 (±0.09)	2.0 (±0.8)	1.8 (±0.7)	n.d.	n.d.	n.d.	n.d.
PER	0.165 (±0.032)	0.4 (±0.2)	0.5 (±0.2)	n.d.	n.d.	n.d.	n.d.
I(1,2,3,cd)PYR	4.44 (±0.28)	5.6 (±1.2)	6.2 (±1.3)	n.d.	n.d.	n.d.	n.d.
DB(ah)ANT	0.365 (±0.071)	2.7 (±1.2)	3.3 (±1.4)	n.d.	n.d.	n.d.	n.d.
B(ghi)PER	5.91 (±0.18)	5.4 (±0.9)	5.8 (±0.8)	n.d.	n.d.	n.d.	n.d.
1N-NAPH	0.0857 (±0.0013)	0.10 (±0.05)	0.10 (±0.04)	1.91 (±0.5)	1.63 (±0.5)	1.24 (±0.6)	1.24 (±0.6)
2N-FLUO	0.0455 (±0.0014)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
9N-ANT	5.89 (±0.31)	7.5 (±1.8)	7.9 (±1.4)	0.30 (±0.2)	0.14 (±0.09)	0.33 (±0.11)	0.14 (±0.08)
3N-FLT	0.0651 (±0.0034)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1N-PYR	18.2 (±0.2)	16.3 (±2.9)	16.0 (±1.4)	1.13 (±0.2)	1.50 (±0.3)	1.42 (±0.3)	1.15 (±0.2)
$\sum$PAHs	226.3	220.3	231.2	4.86	4.91	5.81	4.72
$\sum$nitroPAHs	24.3	23.9	24.0	3.34	3.27	2.99	2.53

[a] n = 3 duplicates.

6 and 17% (for values comprising all the extraction methods). Profiles of diesel soot presented all the typical unimodal distributions for n-alkanes, from C_{16} to C_{34}, with a maximum at C_{24}–C_{25}, with similar proportions of odd and even n-alkanes. However, linear alkanes extracted from the diesel particulate filter soot were not as concentrated as those extracted from diesel soot reference materials. Our results show a total concentration of n-alkanes ranging from 215 μg g^{-1} (ASE extraction) to 305 μg g^{-1} (hot Soxhlet extraction), while concentrations are significantly higher for SRM diesel particulates (508 μg g^{-1} for SRM 1650a [2] and 529 μg g^{-1} for SRM 1650b, with the latter mean value being obtained from four extractions by hot Soxhlet and MAE). This lower level of n-alkanes extracted from DPF particulates is linked to the lower soluble organic fraction, which appeared to be effectively half of that of SRM 1650b.

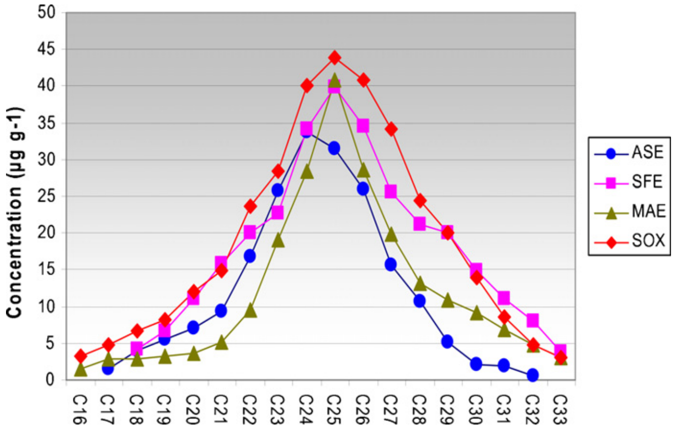

Fig. 6. Extraction of n-alkanes, by hot Soxhlet, MAE, ASE and SFE, from the naturally polluted diesel soot (m = 0.1 g) collected inside the diesel particulate filter. Conditions of extraction: see Table 4.

On further analysis, the results from the extraction of PAHs from DPF soot were more astonishing than first thought. Levels of PAHs were particularly low, and no particular type of heavy particulate PAHs was detected from the extracts, whichever extraction method was used (Table 6). It must be underlined that using the single-ion monitoring mode for MS detection and quantitation of DPF soot, no interfering peaks coeluted with our target PAHs. Indeed, matrix interferents were particularly poor (which was certainly linked to the poorly soluble organic fraction of DPF soot). Although DPF soot extracts were slightly cleaner after SFE extractions and slightly dirtier after hot Soxhlet extractions, further cleanup was thus not required for hot Soxhlet, ASE or MAE extractions. The optimized conditions of extraction, as developed in this work, were thus applied to SRM 1650b particulates, and results were in good agreement with certified values (Table 6). With the same extraction conditions, extracts from SRM 1650b appeared 44 times more PAHs concentrated than the DPF soot. Apolar matrix interferents were markedly more important, particularly for hot Soxhlet extracts, when SRM 1650b was extracted: this led certainly to obtain worse results in terms of repeatability. We recall that the drastic extraction conditions were specifically developed to make sure that even 4–6 ring PAHs could be quantitatively extracted from a particularly retentive carbonaceous surface. Consequently, the very low levels of PAHs, extracted from the native diesel soot accumulated inside the DPF, could not be attributed to the inefficiency of the analytical procedure, but rather to the collection conditions. As mentioned earlier, the temperature reached inside the DPF during the collecting process was higher than 300 °C, while SRM diesel particulates are collected after air dilution to approximately 50 °C. At these temperatures, it appears that hydrocarbons can more efficiently condense on soot particulates at 50 °C than on particulates trapped inside the hot DPF (consequently, soluble organic fraction is poorer on soot collected inside the particulate filter). The diesel particulate filter associated with the oxidation catalyst is also responsible for the important PAH abatement. This confirmed that was already observed in a previous study [27], which demonstrated a large reduction in aromatics and a smaller reduction of alkanes when using a DPF.

Concerning the relatively high proportion of nitroPAHs compared to PAHs, it must be emphasized that the oxidation catalyst used to oxidize CO and hydrocarbon emissions was also able to convert NO to NO_2. Moreover, the NO_2 also contributes to the oxidation and the decrease of the trapped carbonaceous particulates, producing CO and CO_2 [28]. If this reaction is not complete, then one could see that a great part of the PAHs could react with NO_2 during the combustion process to form nitroPAHs [29]. Consequently, the catalyst DPF tends to increase the ratio of nitroPAHs to PAHs on soot particulates.

4. Conclusions

Four extraction techniques, namely hot Soxhlet, MAE, SFE and ASE, were optimized to extract heavy *n*-alkanes, PAHs and nitroPAHs from very sorptive diesel particulates, which were collected inside a diesel particulate filter and are among the most refractory of all the environmental matrices to conventional extractions. Using non-classical extraction solvent mixtures, composed of pyridine and a basic or acidic co-solvent (to better desorb PAHs and nitroPAHs, respectively), all four techniques afforded quantitative PAH extractions (>80%) and fair nitroPAH recoveries (>60%). Although the hot Soxhlet extraction, which was an improvement over the classical Soxhlet extraction, produced better recoveries of nitroPAHs, factors other than the "quantitative recovery need" were taken into account to determine the best choice of extraction technique. SFE seemed to be the best extraction technique with regard to solvent and time consumption (including sample preparation prior to analysis) and also in terms of selectivity, which is a real advantage for the analysis of naturally polluted diesel particulates. MAE and ASE held the advantage of being the "easy options" (including the method development) and of the ability to simultaneously extract multiple samples in an automated system. Finally, the four extraction techniques were used to extract a naturally polluted diesel soot and produced similar results. The soot, collected inside a catalytic diesel particulate filter, showed a low level of soluble organic fraction and *n*-alkanes compared to diesel soot reference materials. PAHs and nitroPAHs were 44 times and 8 times, respectively, less concentrated than values reported for SRM 1650b. One can conclude that the catalytic DPF is particularly efficient at reducing the total PAH amount on diesel particulates, but the ratio of nitroPAHs to PAHs was observed to be significantly enhanced. High temperature conditions inside the DPF can also be a reason for the poor condensation of hydrocarbons on the carbonaceous surface, and the next step of this study will be to determine if a large portion of the non-adsorbed PAHs are found in the exhaust gas downstream of the DPF barrier.

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