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Quantification of polycyclic aromatic hydrocarbons (PAHs) in diesel engine combustion by GC/MS

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Summary — After development of a rapid cleanup and GC/MS analysis protocol for quantification of PAHs in fuel and diesel exhaust particles, 50 aromatic compounds have been identified in the particles and the 16 priority pollutant PAHs listed by the US EPA have been quantified. The predominance of phenanthrene, fluoranthene and pyrene has been observed in particles whereas methylated naphthalene and fluorene are predominant in gasoil.

PAH / diesel exhaust / gasoil / growth of PAHs

Résumé — Analyse des HAP (hydrocarbures aromatiques polycycliques) au cours du processus de combustion du gazole par GC/MS. Un protocole de purification et d'analyse par GC/MS pour le dosage d'HAP dans le gazole et dans les émissions de particules par les moteurs diesel a été développé. Cinquante composés aromatiques ont été identifiés dans les particules émises et 16 HAP, polluants prioritaires, ont été dosés. Le phénanthrène, le fluoranthène et le pyrène sont les plus abondants dans les particules, tandis que ce sont le méthylnaphthalène et le fluorène qui prédominent dans le gazole.

HAP / émission diesel / gazole / croissance des HAP

Introduction

Polycyclic aromatic compounds (PACs) and their derivatives are toxic compounds [1, 2] generally formed as the result of incomplete combustion of organic material. They are widely distributed in the environment [3–5]. One of the major identified sources of PACs emissions are diesel engines.

Diesel engines generate fine carbonaceous particles on which PACs are adsorbed with other organic pollutants. PACs in diesel particulate emissions were measured by various methods. HPLC [6–9] is generally preferred because of the reduction of the sample preparation steps and the specificity of UV and fluorometric detection. However, many studies are based on GC/FID and GC/MS measurements [10–12]. Nitrated [13] and oxygenated PACs have also been found in diesel particulate exhaust by GC/MS analyses. LC/GC coupling [14, 15] has permitted a reduction in analyte losses during intermediate sample preparation procedures, and an improvement in both sample preparation recoveries and detection limits, despite the difficulties of coupling the two chromatographic techniques. Diesel exhaust particulate PACs contents have also been compared with air particles and with gasoil fuel PACs contents [15, 16].

Gas chromatographic analysis of PACs requires that the sample be cleaned up thoroughly in order to minimize the risk of chromatographic and detection interferences. Sample preparation protocols include a rather time-consuming extraction step (usually based on either sonication, supercritical fluid extraction [17] or more often Soxhlet extraction) and several pre-purifications in order to isolate PACs from other chemicals which would compromise PAC identification and deteriorate the column performance.

In this study, a rapid cleanup procedure is proposed in order to reduce the sample preparation time, the adsorbant and solvents consumption. An extensive identification of the components of diesel exhaust particles was achieved. In addition to the 16 polynuclear aromatic hydrocarbons (PAHs) considered as priority pollutants by the US EPA [18] (scheme 1), the other PAH isomers were also examined individually. A gasoil fuel sample was also analyzed in order to relate the emissions to the fuel composition. Methylated aromatics are predominant in gasoil whereas they are rarely observed in diesel exhaust where heavier PAHs are found.

Experimental section

Apparatus

GC/MS analyses were performed on a HP 5890 gas chromatograph (Hewlett Packard, Avondale, PA, USA) connected to a HP 5989B mass spectrometer operated in the electron impact mode under standard conditions (ionizing electron energy 70 eV). A 30 m long, 0.25 mm id and 0.25 μm

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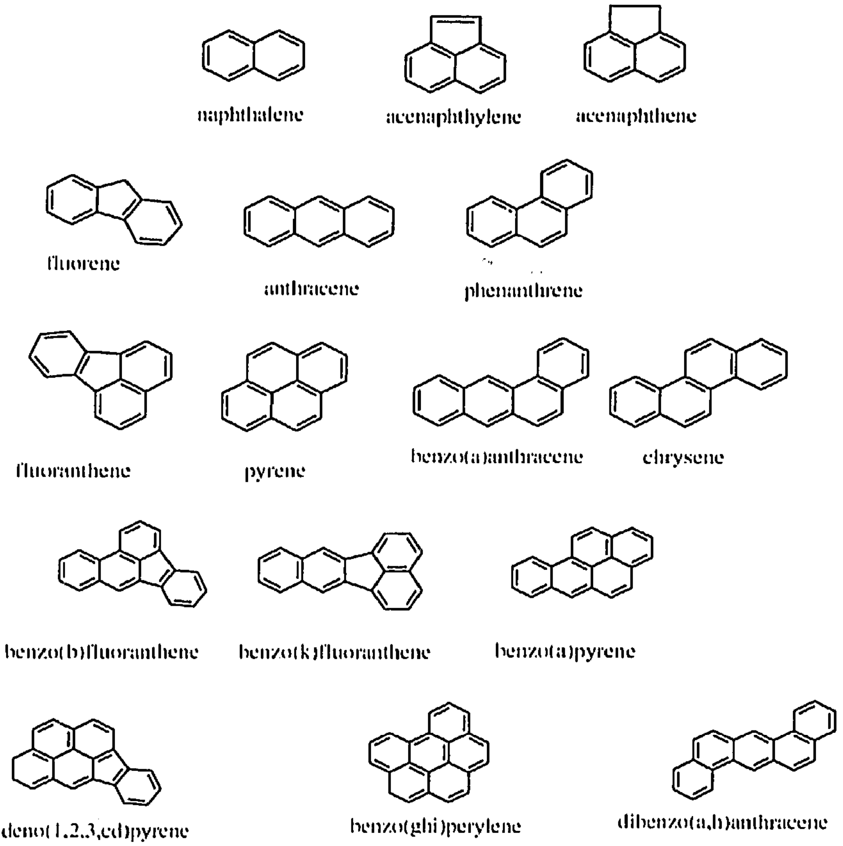

Scheme 1. Sixteen US EPA priority pollutants.

film thickness DB5 column (J&W, Arcueil, France) was used with helium as a carrier gas at a linear velocity of 1 mL/min. The injector temperature was set at 280 °C. The mass spectrometer source temperature and pressure were set at 250 °C and 5 – 6 × 10^{-6} Torr respectively. The mass spectrometer quadrupole was set at 100 °C.

Reagents and materials

Native and deuterated PAHs were purchased from Supelco (Bellefonte, PA, USA) as methylene chloride solutions. A standard solution of 16 US EPA priority pollutants PAHs at 2 mg/mL in dichloromethane was used as a calibrant. HPLC grade dichloromethane was supplied by Burdick & Jackson (Fluka, Buchs, Switzerland). Pentane and methanol were provided by SDS (Vitry-sur-Seine, France). Silica gel 60 with 0.063 to 0.100 mm particle size was purchased from Merck (Darmstadt, Germany). Gravitational columns were homemade from 5 mL disposable Corning pipettes (Prolabo, Paris, France) after cutting the restricted end. Silica gel (1.5 g) was immobilized within the pipette tube between two glasswool plugs.

Samples

Diesel fuel samples were obtained from a car-filling station. Diesel engine particulate exhausts were sampled on filters according to the Standard Sampling Procedure (European Directive (94/12/CE)). Results are expressed in micrograms of PAHs per kilometer, covered on the sampling apparatus.

Chromatographic conditions

The column temperature program was first optimized on the standard mixture in order to achieve the complete separation of all 16 US EPA priority pollutants PAHs in the selected ion monitoring (SIM) mode for preventing peak spreading and for improving the detection limit of high molecular weight compounds. The column temperature was thus monitored from 100 °C (hold 2 min) to 240 °C at 25 °C/min, and then to 320 °C at 5 °C/min throughout this work. In a second step, the chromatographic separation was extended to other PAHs isomers which are not classified among the 16 priority pollutants but which can be present in diesel engine particulate exhausts. A mixture containing five isomers at m/z 228 (chrysene, triphenylene, benzo[*a*]anthracene, tetracene, benzo[c]phenanthrene) and seven isomers at m/z 252 (benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*a*]fluoranthene, benzo[*e*]pyrene, perylene) was chromatographed under the present conditions (fig 1). Compound identification was then based on retention times. Two pairs of isomers coelute: chrysene/triphenylene, and benzo[*b*]fluoranthene/benzo[*j*]fluoranthene. We have demonstrated in previous papers [19, 20] that GC/MS performed under chemical ionization permits their differentiation.

Internal standards

Electron impact spectra of PAHs all exhibit the molecular ion $M^{+\cdot}$ as the base peak. Hardly any fragments were observed. The second most abundant peak $[M + 1]^+$ of the

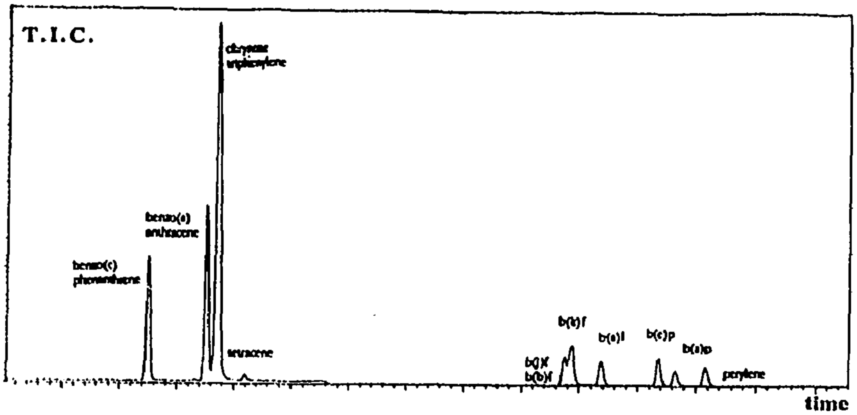

Fig 1. Chromatogram of PAHs with molecular masses at 228 and 252 u. b(b)f: benzo[*b*]fluoranthene; b(j)f: benzo[*j*]fluoranthene; b(k)f: benzo[*k*]fluoranthene; b(a)f: benzo[*a*]fluoranthene; b(e)p: benzo[*e*]pyrene; b(a)p: benzo[*a*]pyrene. TIC: total ion current.

mass spectrum results from the isotopic contribution. The ^{13}C contribution at mass M + 1 was used to confirm the identification of the molecule by checking the isotopic abundance.

Fully deuterated PAHs were chosen as quantification internal standards. Relative response factors (RRF) were established for each PAH relatively to four deuterated internal standards: acenaphthene-d_{10}, anthracene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} [21].

Sample preparation

The sample preparation includes an extraction step followed by different fractionations in order to isolate the PAH fraction from other organics. The soluble organic fraction (SOF) was separated into different chemical classes which were characterized by GC/MS in the full scan mode.

- *Soxhlet extraction*

About 5 mg of diesel exhaust particles collected on Teflon-coated glass fiber filters following the normalized sampling procedure was extracted, via a Soxhlet apparatus, with 350 mL dichloromethane for 24 h. Prior to extraction, 30 μL of each internal standard solution at 10 ng/μL in dichloromethane were deposited on the filters. Surrogates were left soaking with the particles for 2 h before extraction began. After extraction of the SOF, the solvent was concentrated to 1–3 mL in a rotary evaporator and taken to near dryness under a nitrogen flow; 200 μL of pentane was then added.

- *Silica-gel cleanup of diesel exhausts*

The SOF was first injected without treatment into the chromatograph in order to evaluate the complexity of the matrix (fig 2). The extract was then purified by obtaining a separation into different chemical classes on a thin gravitational column, with different eluents. Each collected fraction was evaporated under nitrogen down to 30 μL, and analyzed by GC/MS as explained before (fig 3).

The glass column was packed with 1.5 g silica gel and a top layer of anhydrous sodium sulfate and was washed with 6 mL of pentane before use. A fluorescent lamp was used to monitor the migration of aromatics along the column. When the protocol is complete and volumes are well established for a precise amount of Diesel particles, the fluorescence lamp is discarded so that photosensitive compounds will not be degraded.

- *Silica-gel cleanup of gasoil*

In order to verify the validity of the method developed in this work, we applied it to a sample of gasoil. The raw gasoil diluted in dichloromethane was first injected into the chromatograph (fig 4). The cleanup procedure was then applied on a 5 μL sample of gasoil. Chromatograms of the two collected fractions (pentane

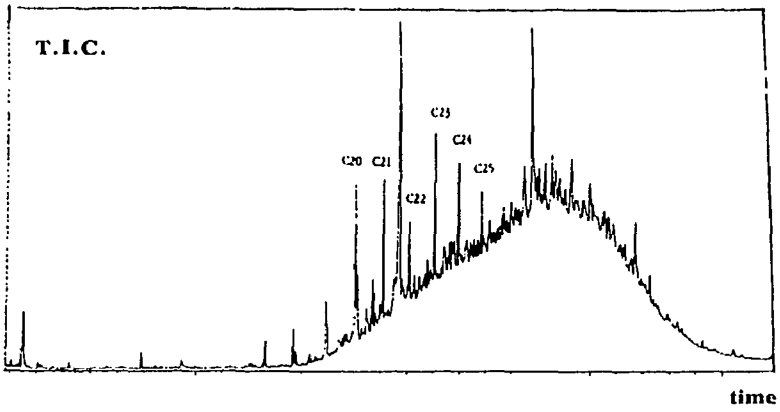

Fig 2. Chromatogram of diesel particulate raw extract.

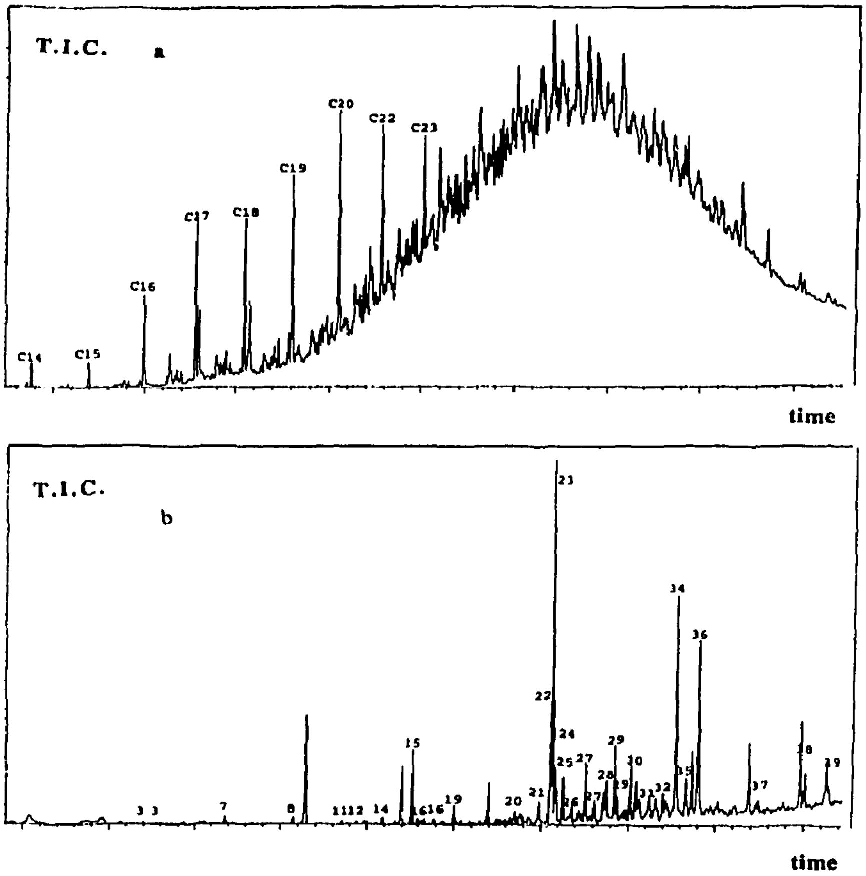

Fig 3. Chromatograms of fraction 1 (a) and fraction 3 (b) of cleaned-up diesel extract.

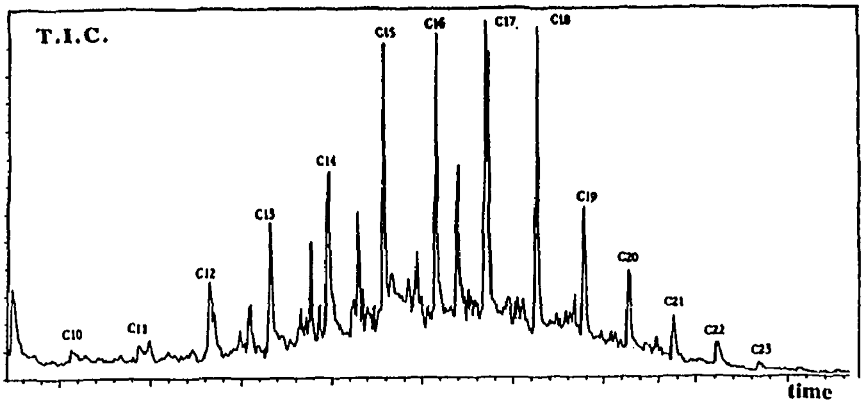

Fig 4. Chromatogram of raw gasoil.

and dichloromethane/methanol 1:1) are presented in figure 5.

Results

Qualitative results of diesel exhausts

The chromatogram of the raw extract shows the presence of alkanes as major components (fig 2). Alkanes were easily eluted from the silica cleanup column with 6 mL of pentane. Pentane fraction 1 (fig 3a) contained a wide variety of saturated hydrocarbons: linear alkanes with 14 to 22 carbon atoms were identified and correspond to the major peaks in the chromatogram. Other peaks often coeluted and were difficult to attribute. Small peaks between linear alkanes were thought to be isomer-branched alkanes. With dichloromethane, the solvent strength increases and aromatics begin to migrate. Fraction 2 (the first 2 mL dichloromethane

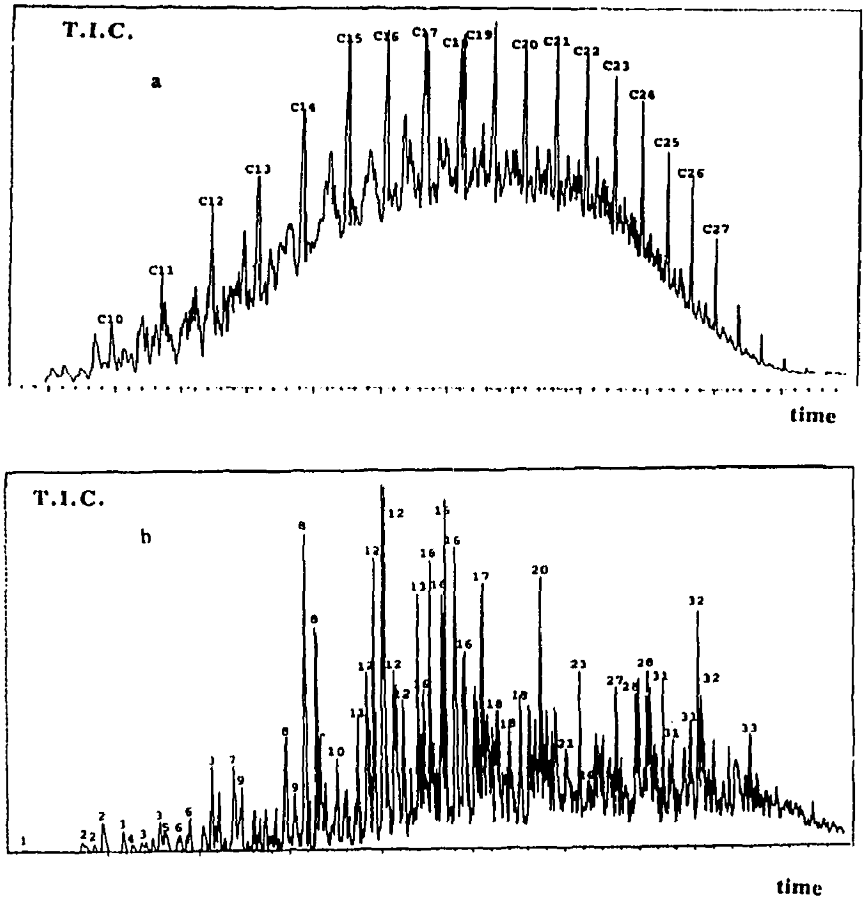

Fig 5. Chromatograms of fraction 1 (a) and fraction 2 (b) of cleaned-up gasoil.

fraction) was collected until the aromatic compounds reached the bottom of the column. This fraction mostly contained aliphatic hydrocarbons. Linear alkanes from 14 to 22 carbon atoms were again the only easily identified components. Fraction 3 contained slightly more polar compounds: PAHs formed a large part of the fraction and alkylated and sulfur-containing aromatic compounds corresponded to the major peaks of the chromatogram (fig 3b). All the components identified in this fraction are listed in table I.

For quantitation, internal standards (phenanthrene-d_{10} and chrysene-d_{12}) were added to fraction 3 which was then analyzed by GC/MS in the SIM mode. High molecular weight PAHs, which were hardly distinguishable in the full scan mode, were now attributed unambiguously. More polar aromatics were recovered in fraction 4 in a following 2 mL dichloromethane elution. Few compounds could be identified due to the low signal-to-noise ratio. Most of identified compounds were ketones (fluorenone, anthracenone, anthracenedione and cyclopenta[*def*]phenanthrenone), some aldehydes were also identified (naphthalenecarboxaldehyde and biphenylcarboxaldehyde), and one acid (phenanthrenecarboxylic acid). In the last fraction 5, aromatics like benzothiazole, alkylated phenols, (hydroxymethyl)-benzaldehyde and hydroxybenzaldehyde, trimethylphenylethanone and aliphatic acids (nonanoic acid) were found. A few nitrated derivatives were identified (nitromethylphenol and nitrodimethylphenol). An additional cleanup to isolate nitrated compounds at trace levels should be developed.

Choice of internal standards and recovery yields

In the analytical procedure, deuterated chrysene and phenanthrene were chosen as quantitative internal standards for the PAH determination and were introduced directly on the sampling filters before extraction. Deuterated anthracene and acenaphthene were used to evaluate internal standards recoveries and were introduced just before chromatographic analysis after the sample preparation. The internal standard of a given PAH was chosen according to the value of the recovery yields of the PAH under study. Recovery yields of small PAHs are close to that of phenanthrene-d_{10}, which indicates an identical behavior of the deuterated molecule and the small PAHs during the extraction and cleanup procedures. Phenanthrene-d_{10} was then used to quantitate small PAHs (with molecular weights between 128 and 228 amu) whereas chrysene-d_{12}, which has a recovery yield comparable to the high molecular weight PAHs, was used to quantify such PAHs (molecular weights above 228 amu). The protocol was applied to six diesel emission filters. Analyses were repeated at least twice in order to check the repeatability of the method. Recoveries calculated for

Table I. List of the components identified on chromatograms figure 5b (fraction 3).

1	Dimethylbenzene	28	Methylphenanthrene
2	Trimethylbenzene	29	Cyclopenta[*def*]phenanthrene
3	Tetramethylbenzene	30	Phenylnaphthalene
4	Dihydronaphthalene	31	Dimethyldibenzothiophene
5	Methyldihydronaphthalene	32	Dimethylphenanthrene
6	Pentamethylbenzene	33	Trimethylphenanthrene
7	Naphthalene	34	Fluoranthene
8	Methylnaphthalene	35	Aceanthrylene or Acephenanthrylene
9	Dimethyldihydronaphthalene	36	Pyrene
10	Dimethyltetrahydronaphthalene	37	Methylpyrene
11	Biphenyl	38	Benzo[*ghi*]fluoranthene
12	Dimethylnaphthalene	39	Chrysene triphenylene
13	Methylbiphenyl	40	Benzo[*a*]anthracene
14	Acenaphthene	41	Benzofluoranthene (b and j)
15	Alkylphenol	42	Benzo[*k*]fluoranthene
16	Trimethylnaphthalene	43	Benzo[*e*]pyrene
17	Dimethylbiphenyl	44	Perylene
18	Tetramethylnaphthalene	45	Benzo[*a*]pyrene
19	Fluorene	46	Indenoperylene
20	Methylfluorene	47	Benzo[*g*,*h*,*i*]perylene
21	Dibenzothiophene	48	Dibenzanthracene
22	Phenanthrene-d_{10}		
23	Phenanthrene		
24	Anthracene-d_{10}		
25	Anthracene		
26	Dimethylfluorene		
27	Methyldibenzothiophene		

Table II. Quantification of PAHs relatively to phenanthrene-d_{10} and chrysene-d_{12} using various filters (μg/km)[a].

PAH	*Filter*						*A* ± *SD*	*LOD*
	1	2	3	4	5	6		
Phenanthrene-d_{10}								
Naphthalene	0.20	0.22	0.28	na	0.17	0.22	0.22 ± 0.04	0.01
Fluorene	0.22	0.22	0.25	0.25	0.22	0.25	0.28 ± 0.03	0.007
Phenanthrene	5.8	5.94	6.7	6.2	5.7	5.8	6.02 ± 0.37	0.007
Anthracene	0.6	0.78	0.81	0.64	0.59	0.56	0.66 ± 0.11	0.007
Fluoranthene	3.6	3.44	3.7	3.7	3.5	3.6	3.60 ± 0.10	0.007
Pyrene	6.9	4.676	5.1	7.6	3.7	3.8	5.30 ± 1.6	0.007
Chrysene	0.64	0.50	0.48	0.28	0.28	0.25	0.41 ± 0.16	0.01
Benzo[*a*]anthracene	na	0.67	0.62	0.53	0.62	0.59	0.61 ± 0.05	0.01
Benzofluoranthenes	0.36	0.59	0.50	0.42	0.45	0.42	0.46 ± 0.08	0.03
Benzo[*a*]pyrene	0.67	0.76	0.62	0.50	na	na	0.64 ± 0.11	0.03
Indenopyrene	na	0.81	0.59	0.30	0.20	0.14	0.41 ± 0.28	0.06
Benzoperylene	na	0.20	0.25	0.25	0.22	0.22	0.23 ± 0.02	0.06
Dibenzanthracene	nd	nd	0.14	0.17	0.11	0.06	0.12 ± 0.05	0.06
Chrysene-d_{12}								
Naphthalene	0.25	0.22	0.34	na	0.20	0.25	0.25 ± 0.05	0.01
Fluorene	0.31	0.22	0.34	0.34	0.25	0.28	0.29 ± 0.05	0.007
Phenanthrene	7.3	5.8	8.15	7.7	6.3	6.4	6.9 ± 0.9	0.007
Anthracene	0.73	0.76	0.98	0.81	0.62	0.64	0.76 ± 0.13	0.007
Fluoranthene	4.4	3.3	4.5	4.6	3.8	4.0	4.1 ± 0.5	0.007
Pyrene	8.3	4.3	6.0	na	3.8	4.0	5.3 ± 1.9	0.007
Chrysene	0.84	0.48	0.59	0.36	0.31	0.28	0.48 ± 0.21	0.01
Benzo[*a*]anthracene	na	0.67	0.76	0.67	0.67	0.64	0.68 ± 0.05	0.01
Benzofluoranthenes	0.48	0.56	0.59	0.50	0.45	0.42	0.50 ± 0.06	0.03
Benzo[*a*]pyrene	0.81	0.70	0.73	0.62	na	na	0.72 ± 0.08	0.03
Indenopyrene	0.90	0.84	0.76	0.42	0.22	0.17	0.56 ± 0.31	0.06
Benzoperylene	0.81	0.20	0.31	0.34	0.25	0.25	0.36 ± 0.23	0.06
Dibenzanthracene	n.d.	n.d.	0.20	0.20	0.11	0.06	0.14 ± 0.07	0.06

na: not analyzed (due to interference); nd: non detected (below detection limit); A: average; SD: standard deviation; LOD: limit of detection; [a]: μg of PAHs by virtual kms on the sampling apparatus.

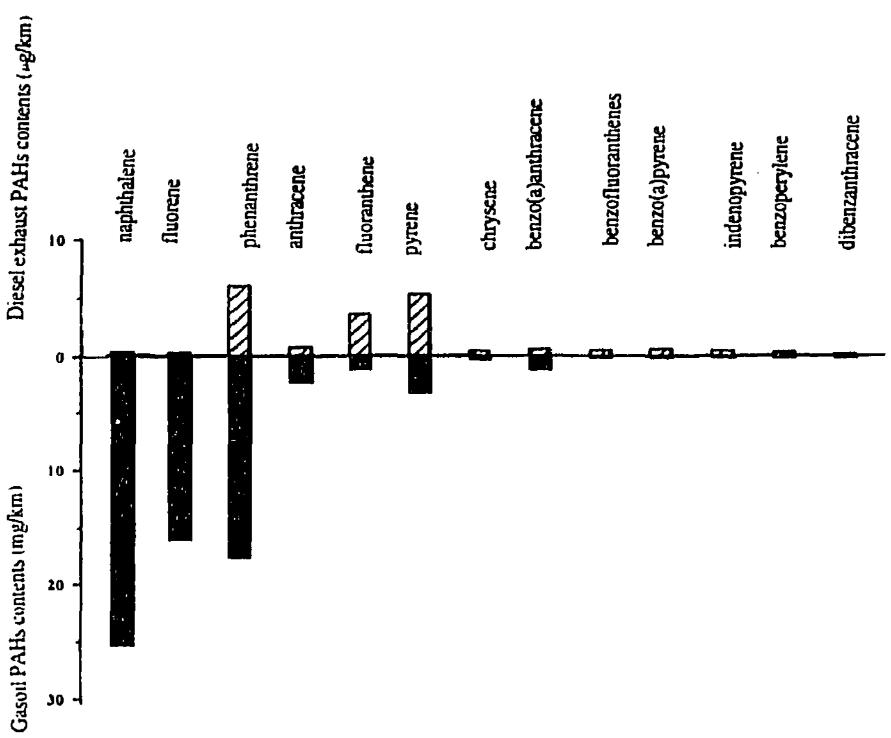

Fig 6. PAH distribution pattern of original diesel fuel (mg/km), and diesel particulate content (µg/km).

the quantitative internal standards (phenanthrene-d_{10} and chrysene-d_{12}) relatively to the recovery internal standards (acenaphthene-d_{10} and anthracene-d_{10}) all lie between 70–80%.

Quantification and repeatability

The PAHs content of the diesel emission filters is summarized in table II. The average value (A) and the standard deviation (SD) are reported together with the whole procedure limit of detection (LOD). The standard deviation is about 10–20% for most PAHs except for pyrene, chrysene, indenopyrene and dibenzanthracene for which it increases (30 to 67%). Results obtained using the two different internal standards are close principally for highest PAHs and allow confirmation of the quantitative results. Quantification of PAHs in the gasoil fuel (table III) leads to the same conclusion.

An accurate interpretation should include a discussion about the sampling cycle, the nature of the engine surveyed, and various parameters influencing the PAH formation. The composition of particles from internal combustion engines varies with [22] engine parameters such as engine type and design, size, accumulated operation cycle and time, emission control system, engine operating conditions, including length of cold start period, air/fuel ratio, engine load, lubricant type, fuel composition, maintenance schedule for engine adjustment and lubricant replacement.

Discussion

The contribution of fuels and lubricant to particulate and aerosol formation is a combination of various sources and processes: unburned fuel components, partially oxidized products from the combustion of fuel, pyrolysis products of fuel constituents and combustion of lubricant components.

Table III. Results of gasoil quantitation relatively to phenanthrene-d_{10} (mg/km).

	Gasoil	*LOD*
Naphthalene	25.2 ± 1.7	0.01
Fluorene	16.0 ± 0.4	0.007
Phenanthrene	17.5 ± 0.6	0.007
Anthracene	2.3 ± 0.15	0.007
Fluoranthene	1.2 ± 0.1	0.007
Pyrene	3.2 ± 0.1	0.007
Chrysene triphenylene	0.3 ± 0.07	0.01
Benzo[*a*]anthracene	1.2 ± 0.2	0.01
Benzofluoranthenes	0.1 – 0.2	0.03
Benzo[*a*]pyrene	0.1 – 0.2	0.03
Indenopyrene	0.1 – 0.2	0.06
Benzoperylene	0.1 – 0.2	0.06
Dibenzanthracene	0.1 – 0.2	0.06

The comparison of the repartition pattern of the various PAHs found in this study between the original diesel fuel on the mg/km scale, and the diesel engine exhausts on the µg/km scale (fig 6) permits the following observations: (i) the lowest PAHs (naphthalene, fluorene) are nearly totally consumed during the combustion process; (ii) higher molecular weight PAHs are either formed or more persistent during combustion (fluoranthene, pyrene, phenanthrene); and (iii) phenanthrene is predominant in the gasoil and exhaust PAHs patterns.

It is often proposed that the PAHs found in diesel exhausts survive the combustion process because of the inertness to complete oxidation of these species. There is evidence that some PAHs in the diesel emissions could be formed during combustion. The exact mechanism of PACs formation during combustion is not understood in detail. Three different reaction mechanisms are currently considered as possible during the combustion process: Diels–Alder cyclisation; radical reactions [23]; and ionic reactions. Multivariate statistical analysis of gasoil and emissions [24] and a radiotracer technique [25] have demonstrated that about only 1% of the original fuel survives the combustion.

It has also been shown that acetylene is formed during combustion. Ciajolo et al [26] have demonstrated that small aromatics including naphthalene and methylnaphthalene are some of the precursors of the alkyne formation. This could explain the consumption of naphthalene observed here. Phenanthrene could be consumed too and also be formed from a smaller molecule.

The direct analysis of the diesel fuel (fig 5b) shows that dimethylnaphthalene (peak 12) appears under different isomeric forms in a much higher quantity that naphthalene itself (peak 7). The same remark can be made for methylfluorene (peak 20) while fluorene is in lower quantity (peak 19).

The methylated species are practically not found in the diesel exhaust (fig 3b) in contrast with Rogge's observations [27] in which emissions of alkyl-substituted PAHs were particularly high when compared to the emission rates for most individual unsubstituted PAHs. Due to existing differences between the type of vehicle, the sampling techniques and the applied analytical procedures, reported PAHs values from diesel exhausts are often quite different. Methylated species can be consumed either through combustion or by being involved in the formation of higher PAHs.

Conclusion

The analytical protocol involving GC/MS described here has proven its efficiency for quantitation of PAHs in gasoil and diesel exhausts. However, two pairs of isomers remain unresolved (chrysene/triphenylene, benzo[*b*]fluoranthene/benzo[*j*]fluoranthene). They can only be resolved by using a more separative column or chemical ionization mass spectrometry [19, 20]. Comparison of PAHs content in gasoil and in diesel exhausts reveals that lowest PAHs are well consumed, whereas the highest PAHs are either formed or more resistant against combustion. Although the combustion process involves the coupling of chemical and physical effects, leading to complex mechanisms and various reactions, some reactional processes should be modelled in order to understand how the three more abundant PAHs in the diesel exhausts (phenanthrene, fluoranthene, pyrene) can be synthesized from three PACs which are particularly abundant in the studied fuel (1,2-dimethylnaphthalene, methylfluorene and phenanthrene) and missing in the exhausts.

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