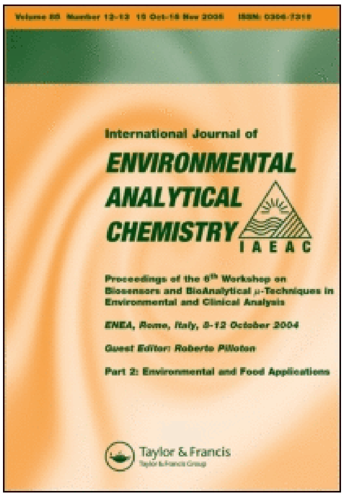

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Identification of Polynuclear Aromatic Hydrocarbons in Diesel Particulate Emissions

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Following collection of diesel particulate samples on high efficiency glass fibre papers, and Soxhlet extraction with cyclohexane, a two-stage clean-up involving DMF/H_2O partition and silica gel thin-layer chromatography is required in order to simplify the extract. Individual compound identification can then be achieved by high resolution gas chromatography using WCOT quartz capillary columns with flame ionisation or computer-assisted electron impact mass spectrometry detection systems. The technique provides a relatively quick and simple enrichment step, whilst the high separating power of the capillary column is able to resolve the many chromatographically similar isomers and substituted PAH members that are present. Investigations indicate that presence of a vast range of PAH species, comprising both substituted and unsubstituted two- to seven-membered ring systems, many of which are known carcinogens and mutagens.

KEY WORDS: PAH, diesel particulate, capillary gas chromatography, mass spectrometry, exhaust emissions.

INTRODUCTION

The incomplete combustion of carbon, hydrogen and other trace elements in a diesel engine results in the production and release to the environment of thousands of different compounds,[1] either as gas phase material or adsorbed on the surface of carbon particles. Due primarily to the improved fuel economy (up to 40% under certain conditions[2]) obtained from diesel engines compared to equally powered petrol engines, the use of diesel powered passenger cars and light trucks is expected to increase

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significantly in the next decade. Concern over possible environmental effects associated with increased diesel particulate emissions to the atmosphere has prompted extensive studies on biological (such as the Ames Microbial Mutagenicity Bioassay Test[3]) and analytical testing of exhaust material.

The definitive identification of PAH in diesel exhaust has caused environmental concern as certain of these compounds, which consist of several fused benzene rings, exhibit marked carcinogenic, mutagenic and tetratogenic effects in laboratory animals.[4] PAH found in diesel exhaust are generally associated with fine particulates which can stay suspended in the atmosphere for long periods of time[1] and are readily taken into the lungs.

The chemical analysis of PAH, and in particular substituted PAH and isomers, in diesel exhaust has recently been made more reliable by improved, highly sensitive analytical techniques. The ability to be able to distinguish between various substituted PAH and their isomers is important as marked changes in carcinogenic and/or mutagenic activity can arise from apparently minor structural differences. For example, chrysene and the 1-, 2-, 4- and 6-methylchrysenes have moderate tumor-promoting activities, whereas the 3- and 5-methylchrysenes are strong tumor initiators.[5] Techniques recently employed for PAH determinations have included TLC,[6,7] HPLC[8–10] and capillary GC, with or without mass spectrometry (ms).[11–13] Most of the methods have employed a series of extensive clean-up procedures, with concomitant sample losses and contamination, to yield a PAH fraction suitable for analysis.

In this paper, we report on the development and application of a quick and simple two-stage clean-up procedure employing solvent partition and TLC which yields a highly enriched PAH fraction suitable for analysis by high-resolution quartz capillary GC. Using this technique, in conjunction with ms detection, over 50 PAH compounds have been successfully identified in the particulate discharge from diesel engines, many of which have not been reported elsewhere.

EXPERIMENTAL

Reagents

All solvents were purchased from BDH Chemicals (Poole, U.K.) and were redistilled in all glass apparatus before use. PAH standard samples were obtained either from the Aldrich Chemical Co. (Gillingham, U.K.) or were received as gifts from other research institutions and were used without further purification.

Stock solutions of the standards were prepared in cyclohexane at mg/ml concentrations and were stored frozen at −15°C in the dark when not in use.

Sample collection and extraction

A small direct injection diesel engine (Petter BA2, variable speed, 1.146 l displacement, operating on Esso gas oil) was used as a source of exhaust. Particulate matter was collected by direct probe sampling of the exhaust with high-efficiency glass fibre filters (6.0 cm diameter, Whatman GF/A) housed in a specially manufactured stainless steel holder; isokinetic sampling was not attempted in this case. A diaphragm pump connected in series to a wet-gas meter was used to draw a known volume of exhaust gas through the filter (100–500 l). The exposed filters were carefully folded into a pre-washed thimble and were Soxhlet extracted in the dark for four hours with 150 ml of cyclohexane. The extract was rotary evaporated (at 25°C) to a small volume and was then made up to 10 ml with cyclohexane.

Solvent partition

The cyclohexane extract (10 ml) was subjected to a dimethylformamide (DMF)/H_2O partition followed by back extraction into cyclohexane[14] (Figure 1). This step removed both non-polar, alkane-type material as well as the more polar compounds present. The final cyclohexane phase was concentrated to a small volume by rotary evaporation and under a stream of dried nitrogen at room temperature.

Thin layer chromatography

Adsorption TLC on silica gel G, using a cyclohexane/toluene (4:1, v/v) mobile phase, was employed to isolate the two- to seven-ring PAH compounds from the non-polar and fluorescent polar organic compounds still remaining after the DMF/H_2O partition. Silica gel G (10 × 20 cm, 250 μm layer) TLC plates were activated at 120°C for 1 h and were pre-eluted with freshly distilled dry diethyl ether before use.

The cyclohexane extract was applied as a 5–6 cm narrow band at the base of the plate, together with a PAH standard mixture. The plate was eluted with cyclohexane/toluene (4:1, v/v) to 15–16 cm above the starting point, dried, and viewed briefly under an ultraviolet lamp. The silica gel area containing the PAH material was removed from the plate and was eluted with 15 ml of methylene chloride. The solvent was evaporated to dryness under a stream of dried nitrogen and the residues were taken up in a known volume of cyclohexane prior to capillary GC.

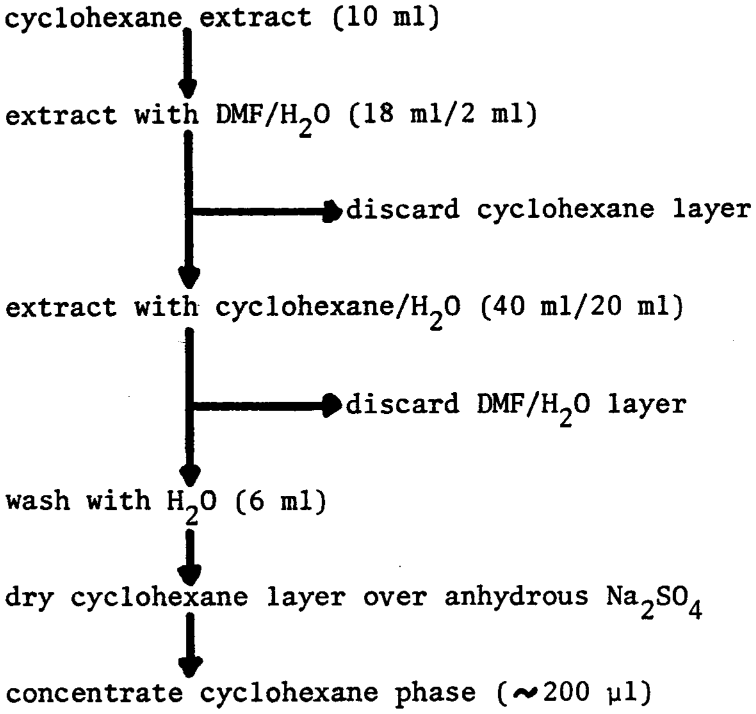

FIGURE 1 DMF/H_2O solvent partition clean-up of sample extract.

Capillary gas chromatography

Quartz capillary columns (0.3 mm id), directly wall coated with OV-101, were used to monitor complexity, degree of sample clean-up and final compound separation throughout the procedure. All GC work was carried out on either a modified Pye 104 or Pye 204 chromatograph under temperature programmed conditions (typically: 5 min hold at 40°C, 6°C increase per min to 300°C, hold at 300°C). The injection port temperature was maintained at 275°C. Hydrogen was used as the carrier gas for all separations, except when the machine was being used in conjunction with the ms, in which case it was replaced by helium. Both "Grob-type" splitless and on-column injection techniques were employed.

Solutions containing a series of standard PAH's (fluorene, phenanthrene, anthracene, fluoranthrene, pyrene, chrysene, benz(a)anthracene, benzo(a)pyrene, perylene, benzo(ghi)perylene, dibenzo(a, h)anthracene and coronene) were subjected to the same analytical scheme, including Soxhlet extraction, to monitor any losses or occurrence of contamination (Table I). Good recoveries were obtained for all PAH except for an unexplainably high loss of fluorene and anthracene.

TABLE I
Assessment of overall analytical recoveries for standard PAH

Compound	Abbreviation	Percentage recovery
Fluorene	Fl	42.9 ± 1.2
Phenanthrene	Ph	71.5 ± 2.4
Anthracene	An	30.3 ± 1.0
Fluoranthrene	Flu	88.7 ± 5.1
Pyrene	Py	76.5 ± 4.6
Benz(a)anthracene	BaA	83.7 ± 3.2
Chrysene	Ch	89.4 ± 0.6
Benzo(a)pyrene	BaP	72.5 ± 2.5
Perylene	Pe	66.6 ± 0.1
Dibenz(a, h)anthracene	Dba	90.0 ± 2.5
Benzo(ghi)perylene	Bpe	85.9 ± 1.7
Coronene	Cor	100.0 ± 1.0

Mass spectrometry

The GC was coupled to a double beam high resolution ms (Kratos MS30) by an all-glass jet separator held at 275°C. All spectra were measured at 70 eV with the source temperature being maintained at 200°C. Throughout the chromatographic separation the ms was scanned from m/e 30 to 600 at a rate of 3 sec/decade, all spectra being recorded on a computer data system (Data General Nova 3 using a Kratos DS55 display).

RESULTS AND DISCUSSION

Initial chromatographic development work was performed using a mixture of PAH standards. A typical standard chromatogram shown in Figure 2 illustrates the clear resolution of the isomeric groups, benzo(a)pyrene, benzo(e)pyrene, perylene and chrysene, benz(a)anthracene. The use of hydrogen as the carrier gas resulted in lower elution temperatures and better resolution than nitrogen or helium carriers. This finding is in accordance with other workers.[15] With a maximum temperature of 300°C, under such conditions the elution of coronene, the highest molecular-weight PAH generally found in air and automotive particulates is achieved within 80 min. The OV-101 column also exhibited excellent low bleed and long term stability characteristics.

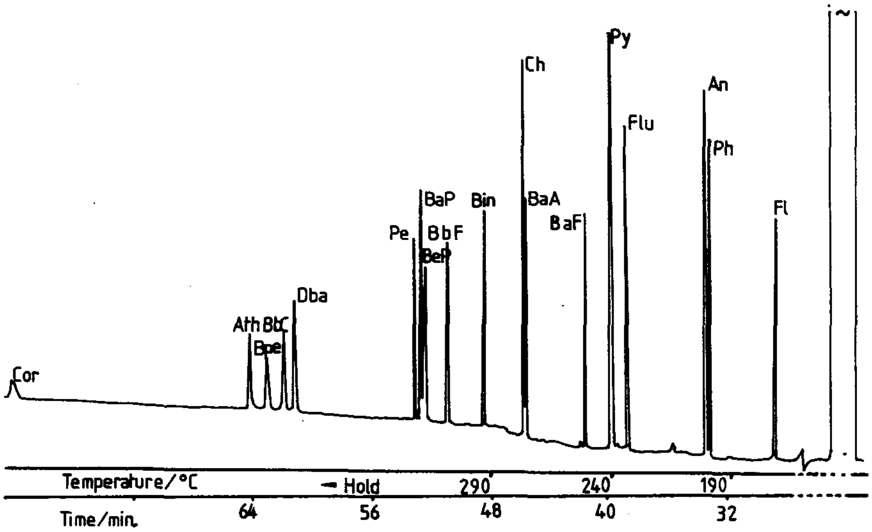

FIGURE 2 Gas chromatogram of a standard PAH mixture obtained using a 50 m OV-101 column temperature programmed from 40°C to 300°C at 6°C/min following a 5 minute hold at 40°C. (Peak identification as Table I with the following additions: Benz(a)fluorene, BaF; Binaphthyl, Bin; Benzo(b)fluoranthene, BbF; Benzo(e)pyrene, BeP; Benzo(b)chrysene, BbC; Anthanthrene, Ath).

The clean-up of the cyclohexane extract achieved by TLC and the DMF/H_2O partition is shown in Figure 3. Both TLC and solvent partitioning were effective in removing much of the unresolved alkane material (derived from the fuel and lubricating oil) from the extract. However, neither method produced a chromatogram in which individual PAH compounds could be identified. A short column (12 cm × 1 cm id) of basic alumina (Brockman Grade 1, BDH Chemicals) was tried as an alternative clean-up procedure. Results were similar to those obtained by TLC, but the technique was abandoned because of low recoveries and poor reproducibility.

The combination of a DMF/H_2O partition followed by silica gel TLC resulted in a chromatogram (Figure 4) in which several PAH compounds could be identified based on their retention times compared to standards (Figure 2). This enriched extract was used in the ms study to characterise further compounds for which standard were not available.

The total ion chromatogram (TIC) of the PAH fraction is shown in Figure 5. A search of the TIC was made to determine the identity of the peaks produced and spectra were compared with those from ms libraries.[16]

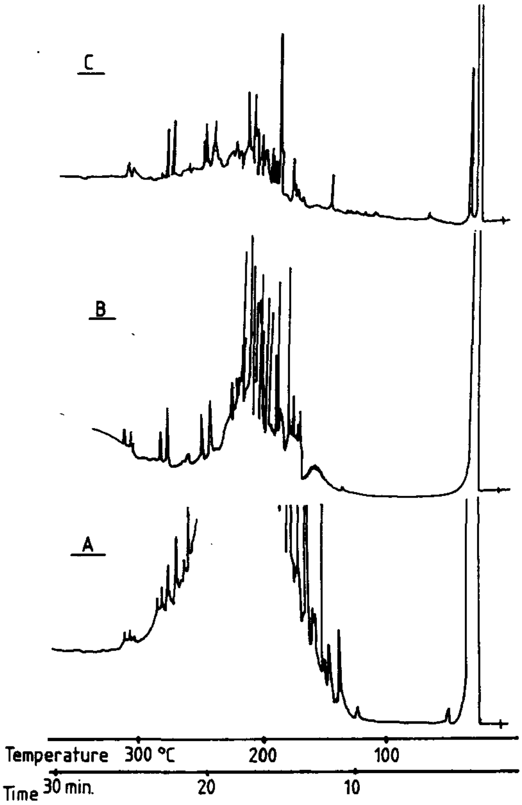

FIGURE 3 Gas chromatograms of a diesel exhaust extract following various stages of sample clean-up: (A) Cyclohexane extractable material; (B) Extract after silica gel TLC; (C) Extract after DMF/H_2O partition. All chromatograms were obtained using a 20 m OV-101 column temperature programmed from 40°C to 300°C at 12°C/min.

A complete list of compounds characterised in the sample is given in Table II.

Ionisation of PAH produces very little fragmentation and usually gives an intense molecular ion. This can be advantageous in determining the molecular mass of a molecule, but the lack of fragmentation makes the differentiation of isomers difficult. An efficient chromatographic separation is therefore essential. Spectra of methyl-substituted members always showed the loss of a methyl group from the parent ion. The exact position of substitution of the alkyl group could not however be directly determined by ms and other techniques, such as nuclear magnetic resonance spectroscopy would have to be used to elucidate their structures more precisely.[17,18]

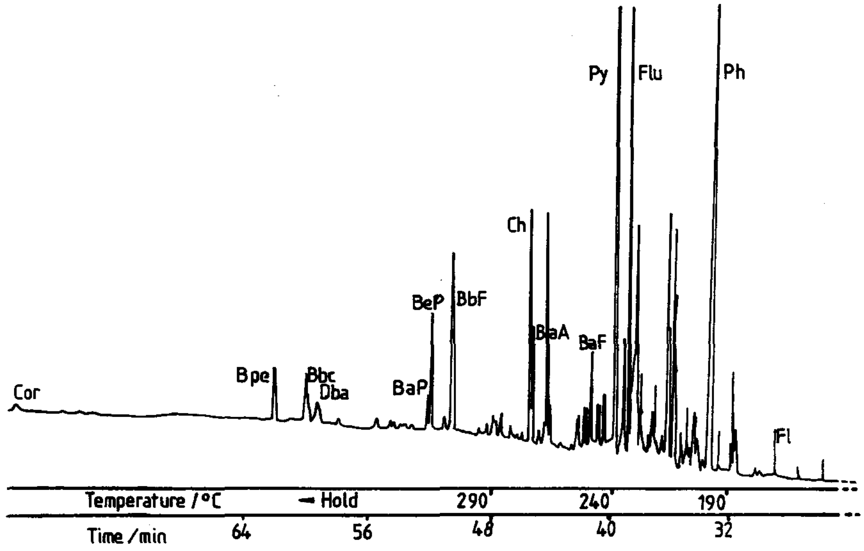

FIGURE 4 Chromatogram of a diesel exhaust extract after both DMF/H_2O partition and TLC. (Separation performed on a 50 m OV-101 column temperature programmed from 40°C to 300°C at 6°C/min after being held at 40°C for 5 minutes. H_2 carrier gas).

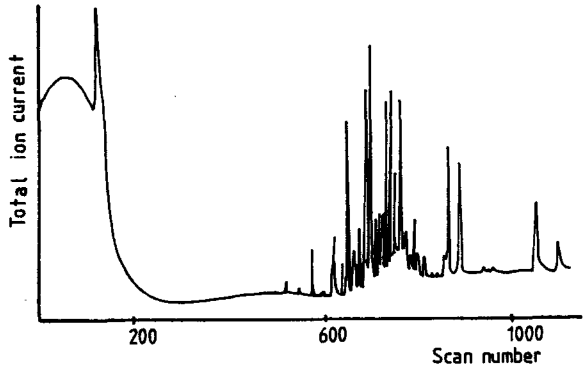

FIGURE 5 Reconstructed total ion current trace from gas chromatographic separation of enriched diesel exhaust particulate PAH detected by mass spectroscopy (chromatographic conditions as Figure 4 except for the use of helium carrier gas).

TABLE II

List of PAH tentatively identified by GC-MS in diesel exhaust particulates

Scan no.	Compound	Molecular mass
522	Acenaphthylene	152
550	Dibenzofuran	168
576	Fluorene	166
583	Methylfluorene	180
589	Methyldibenzofuran	182
591	Unknown	
595	Methyldibenzofuran	182
599	Methyldibenzofuran	182
618	Methylfluorene	180
619	Methylfluorene	180
621	Methylfluorene	180
625	Methylfluorene	180
638	Dibenzothiophene	184
648	Phenanthrene	178
653	Anthracene	178
660	Benzo(h)quinoline	179
665	Acridine	179
670	Dimethylfluorene	194
674	Methyldibenzothiophene	198
676	Dimethylfluorene	190
680	Methydibenzothiophene	198
685	Unknown	
688	Methylphenanthrene/anthracene	192
690	Methylphenanthrene/anthracene	192
696	Methylphenanthrene/anthracene	192
698	4H-cyclopenta(def)phenanthrene, methylphenanthrene	190, 192
708	Ethyldibenzothiophene[a]	212
709	4H-cyclopenta(def)phenanthrene	190
715	Ethyldibenzothiophene[a]	212
717	Unknown	
720	Ethyldibenzothiophene[a]	212
724	Ethylphenanthrene/anthracene[a]	206
728	Ethylphenanthrene/anthracene[a]	206
733	Ethylphenanthrene/anthracene[a]	206
736	Ethylphenanthrene/anthracene[a]	206
744	Fluoranthene	202
752	Benzacenaphthylene	202
756	Benz(def)dibenzothiophene	208
762	Pyrene	202
769	Ethylmethylphenanthrene/anthracene[b]	220
773	Ethylmethylphenanthrene/anthracene[b]	220
776	Ethylmethylphenanthrene/anthracene[b]	220
784	Methylfluoranthene	216
789	Ethylmethylphenanthrene/anthracene[b]	220

TABLE II (continued)

Scan no.	Compound	Molecular mass
793	Benzo(a)fluorene	216
799	Methylpyrene and benzo(a)fluorene	216
801	Ethylmethylphenanthrene/anthracene[b]	220
803	Methylpyrene/fluoranthene	216
812	Methylpyrene/fluoranthene	216
815	Methylpyrene/fluoranthene	216
824	Naphthobenzothiophene	234
836	Ethylpyrene/fluoranthene	230
857	Naphthobenzothiophene	234
863	Benzo(ghi)fluoranthene	226
874	Naphthobenzothiophene	234
884	Benz(a)anthracene	228
888	Chrysene	228
900	Methylnaphthobenzothiophene	248
941	Methylchrysene/benz(a)anthracene	242
961	Binaphthyl and methylchrysene/benz(a)anthracene	254, 242
1052	Benzofluoranthene	252
1068	Benzofluoranthene	252
1100	Benzo(e)pyrene	252
1104	Benzo(a)pyrene	252
	Dibenz(a, h)anthracene[c]	278
	Benzo(b)chrysene[c]	278
	Benzo(ghi)perylene[c]	276
	Coronene[c]	300

[a] Could also be dimethyl-.
[b] Could also be trimethyl- or propyl-.
[c] Identified by retention time only.

S, N and O hetero-atom PAH were also found to be present in the sample with the sulphur heterocycles being the most abundant. Compounds other than PAH or polar derivatives of PAH (e.g. carboxylic acids, quinones, etc) were not detected in the sample, thus indicating the efficiency of the fractionation procedure. It is suspected that fluorescent bands found near the base of the TLC plate contain the polar PAH constituents of the diesel extract and investigations of these bands is currently being undertaken, as in many cases these derivatives have a stronger carcinogenic activity than their unsubstituted parent molecules. Engine and fuel effects on the overall PAH emission are also being considered.

CONCLUSIONS

In order to exploit fully the potential of recent developments in high performance GC techniques, it has become necessary to redesign sample extraction and clean-up procedures for complex problems such as the identification of PAH in vehicular emissions. Of particular importance in such analyses is the ability to differentiate between compounds of similar chromatographic behaviour but with widely differing toxicological properties. Even with the exceptional resolution achievable by modern capillary-column chromatographic techniques, sample clean-up techniques are still required but can be confined to two simple complementary stages, thereby minimising losses of material of interest and reducing the analysis time. The reported procedure has proved to be simple and reliable in routine use and has provided an invaluable tool in the identification of many potentially toxic components of diesel exhaust emissions.

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