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DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN DIESEL EXHAUST PARTICULATE MATTER AND DIESEL FUEL OIL

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SUMMARY

Clean-up procedures were developed for a method for determining the amount of polycyclic aromatic hydrocarbons (PAHs) in diesel exhaust particulate matter and in diesel fuel oils using reversed-phase high-performance liquid chromatography (HPLC). They were based mainly on the elimination of insoluble matter and aliphatic compounds that affect the performance of HPLC, from the dichloromethane extracts of particulate matter or from oils, with the aid of a disposable preparation column containing reversed-phase packings (Sep-Pak C_{18}). Using these procedures, it is possible to detect 1 ng of benzo(*a*)pyrene in 30 mg of particulate matter with more than a 97% recovery or 0.5 ng in 50 μl of oil with 91% recovery. Examples of analyses are given for particulate matter emitted from a diesel test engine and for diesel fuel oils, such as gas oil, residual oil and coal-liquefied oil.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) contained in air-suspended particulate matter attract attention because some of them have mutagenic activity and are thought to promote the generation of cancer in the human lung[1]. In particular, much attention has been focused on diesel particulate emissions, as they are expected to be a significant hazard in the near future with the increase in the number of diesel-powered vehicles owing to their superior fuel economy over gasoline-fuelled vehicles[2]. In addition, there is concern that the emission of particulate matter will accelerate with the use of various alternative fuels, such as refined residual oil, shale oil and coal-liquefied oil to cope with expected future oil shortage[3]. Therefore, it is now necessary to measure the content of PAHs both in diesel exhaust particulate matter and in various oils that are expected to be used as diesel fuels, in order to monitor PAH emissions and control them appropriately.

There have been a number of reports on the determination of the content of PAHs in particulate matter or oils, mostly based on various chromatographic techniques, such as gas chromatography (GC)[4–9] coupled with mass spectrometry (MS)[10,11], thin-layer chromatography (LTC)[12] and high-performance liquid chro-

matography (HPLC)[13–21]. Most PAHs are strong phosphors and each has its own characteristic pattern in both the excitation and emission spectra. Therefore, the fluorescence spectrometer is the most sensitive and most selective detector for PAHs and the combination of this apparatus with HPLC results in the most powerful method for determining PAHs.

There are also a number of HPLC columns for the determination of PAHs, of which the octadecylsilane-bonded, reversed-phase column has been the most commonly used because of its high resolution efficiency for PAHs. The determination of PAHs in particulate matter generally starts with the extraction of the particulate matter using organic solvents, dichloromethane being the most popular because of its high solubility for substances with a wide polarity range[22]. As a result of their high solubility, however, aliphatic compounds, which are harmful to HPLC columns, are also extracted with PAHs. Further, diesel fuel oils naturally contain large amounts of aliphatic compounds. Consequently, prior to using an HPLC column, some clean-up procedures are needed to eliminate aliphatic compounds from these samples; many procedures have been reported, such as liquid–liquid separation[13], column chromatographic separation[14] and TLC[15–18].

The use of a disposable preparation column is one way of separating these harmful compounds from the sample for HPLC analysis. The application of this type of column has been reported for the determination of PAHs in water[23]. In this work, we have developed clean-up procedures for the determination of PAHs in the dichloromethane extract of diesel exhaust particulate matter and in some diesel fuel oils, using this preparation column. The procedures reported here are simple, with high recoveries and sensitivity.

EXPERIMENTAL

The preparation columns used in the clean-up procedure were Sep-Pak C_{18} cartridges (Waters Assoc.), which contain an octadecylsilane-bonded packing with a dead volume of about 0.5 ml. This cartridge is recommended for use with polar eluents, such as water or water–organic solvent mixtures. In this study, acetonitrile and its mixture with water were used as eluents.

The performance of the preparation column was investigated using a thin-layer chromatograph with flame-ionization detection (TLC with FID) (Iatroscan TH-10; Dia-Iatron). Details of this technique have been reported elsewhere[24]. An organic sample is developed with *n*-hexane on the silica gel-coated rod into several main types such as aliphatic hydrocarbons, aromatic hydrocarbons and more polar compounds, and quantified for every type by FID. By analysing each fraction of the effluent from the preparation column, it is possible to establish the elution order of each type and their mutual separation efficiency.

The high-performance liquid chromatograph used for the determination of PAHs consists of a continuous-flow pump (Altex Scientific, 101A), an autosampler (Kyowa Seimitsu, KSST-60J), an ODS column (Beckman Instruments, Ultrasphere-ODS, 250 × 4.6 mm I.D.), a fluorescence spectromonitor (Shimadzu, RF-530) and a chromatogram processor (System Instruments, 7000AS). The mobile phase was acetonitrile–water (70:30, v/v) deoxygenated by bubbling helium through the solvent during the measurement. The flow-rate of the mobile phase was 1.0 ml/min. The

temperature of the column was not regulated; however, it remained within the range 17–18°C.

A fluorescence spectrometer (Shimadzu, RF-540) was used to identify the chromatographic peaks that did not have corresponding standards.

The diesel exhaust particulate matter was emitted from a single-cylinder test engine (ASTM CFR/F5) and was collected on PTFE-coated glass-fibre filter (Pallflex, 142 mm diameter) by passing diluted exhaust gas through the filter. The particulate matter was extracted with dichloromethane in a Soxhlet apparatus for 18 h and concentrated to a few millilitres. This solution was subjected to the clean-up procedures described below.

Four types of oil were examined for the determination of their PAH content. The first was a commercial gas oil commonly used in Japan for diesel automobiles (meeting the requirements of Japanese Industrial Standard JIS K2204), the second was a special gas oil rich in aromatic compounds (Nippon Oil), the third was a petroleum residual oil called C-Grade fuel oil (JIS K2205 1980) and the last was a coal-liquefied oil, wich is distillate produced from Wandoan coal using a 1 ton/day solvent–coal liquefaction plant[25]. A solvent oil for printing ink (Nippon Oil) was used as the solvent to dissolve a known amount of standard PAH, or C-Grade fuel oil, which was too viscous to handle without dilution. A lubricating oil for spindles (Nippon Oil) was used to examine the clean-up performance of the preparation column for the oil analysis. Some characteristics of these oils are given in Table I.

TABLE I

PROPERTIES OF THE OILS EXAMINED

Properties of C-Grade residual oil were not measured.

Oil	Boiling range (°C)	Specific gravity (15/4°C)	Aromatic carbon content ($f_a^\star$) (%)	Elemental composition (%)	
				C	H
Commercial gas oil	184–382	0.8316	13.0	86.7	13.3
Aromatic-rich gas oil	181–331	0.8620	36.0	87.8	12.2
Coal-liquefied oil	205–382	0.9968	64	88.8	8.8
Solvent oil	276–313	0.860	9.8	85.7	13.3
Lubricating oil	220–280	0.8659	10.3	86.4	13.0

  $\star$ Estimated from ^{13}C NMR spectrum[26].

The acetonitrile and water used in the mobile phase in the clean-up procedure and the HPLC analysis were of spectrophotometric grade (Wako) and were used as received. The dichloromethane used as the extraction solvent for the diesel exhaust particulate matter was also of high purity (commonly used for testing agricultural residues) (Wako) and was distilled prior to use. Standard chemicals used were phenanthrene, anthracene, fluoranthene, benzo(a)pyrene [B(a)P], anthraquinone carbazole (Wako), pyrene, benz(a)anthracene [B(a)A], perylene (Tokyo Kasei Kogyo), n-

docecylbenzene,   chrysene,   benzo(*ghi*)perylene   [B(*ghi*)P]   (Aldrich),
benzo(*b*)fluoranthene [B(*b*)F] (R.K. Chemical) and *n*-docosane (Nihon Kuromato
Kogyo). All standards were used as received.

RESULTS

Determination of PAH in diesel exhaust particulate matter
      The performance of the preparation column for eliminating aliphatic hydro-
carbons was first investigated.
      Fig. 1 shows the characteristics of four kinds of organic solvents as eluents for
separating *n*-docosane from B(*ghi*)P with the preparation column. About 1 mg each
of *n*-docosane and B(*ghi*)P, which represent aliphatic hydrocarbons and aromatic
hydrocarbons of the extract, respectively, were dissolved in 1 ml of eluent and passed
through the Sep-Pak C_{18}. The column was then eluted with 10 ml of each solvent,
during which the eluent was collected in 1-ml fractions. Each fraction was analysed

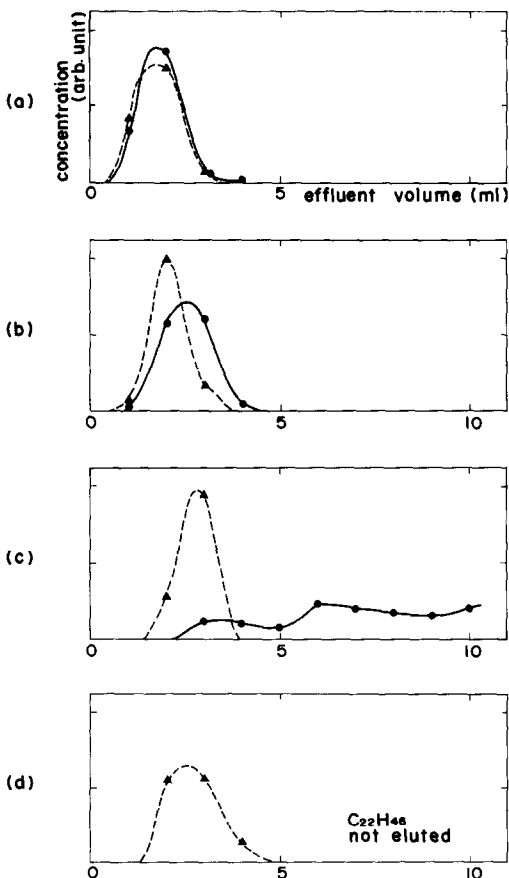Fig. 1. Effect of solvent on the elution of hydrocarbons from the preparation column (Sep-Pack C_{18}).
Solid line, elution of *n*-docosane; broken line, elution of B(*ghi*)P. Eluent: (a) dichloromethane; (b) ethanol;
(c) methanol; (d) acetonitrile. Temperature, 22°C.

using TLC with FID and the concentrations of *n*-docosane and B(*ghi*)P were determined.

When dichloromethane was used as the eluent (Fig. 1a), both *n*-docosane and B(*ghi*)P were eluted immediately and were not separated. As the polarity of the eluent increased, however, the elution of *n*-docosane became slower while that of B(*ghi*)P remained almost the same and, finally, when acetonitrile was used as the eluent, *n*-docosane was not eluted at all. Consequently, by collecting the first 10 ml of the acetonitrile effluent, an aliphatic-free solution for PAH analysis was obtained. Fig. 2 shows the elution of aliphatic and aromatic hydrocarbons of the diesel exhaust extract using acetonitrile. While the elution of aromatic hydrocarbons was almost completed within a few millilitres, the elution of aliphatic hydrocarbons was delayed and greatly decreased.
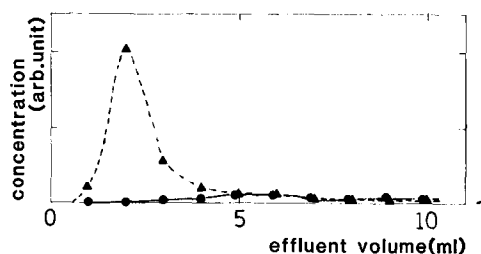

Fig. 2. Elution of hydrocarbons contained in diesel exhaust particulate matter from the preparation column. Column, Sep-Pack C$_{18}$; eluent, acetonitrile. ●, Aliphatic hydrocarbons; ▲, aromatic hydrocarbons.

In order to use the above procedure for removing aliphatic hydrocarbons, it is necessary to change the dichloromethane solution of the extract into an acetonitrile solution. The recovery of the sample during this procedure was examined. Four kinds of PAHs, phenanthrene, chrysene, B(*a*)P and B(*ghi*)P, which have three, four, five and six fused rings, respectively, were dissolved in 1 ml of dichloromethane and dried in a 10-ml vial under a nitrogen stream at 20°C. The dichloromethane was almost evaporated in 6 h. The recovery of each substance was measured using HPLC at 21 and 45 h from the beginning of the evaporation procedure. The results are given in Table II. Whereas chrysene, B(*a*)P and B(*ghi*)P were almost completely recovered (recovery exceeding 100%, resulting from the error of the measurement), 23 and 52% of phenanthrene were lost after 21 and 45 h of treatment, respectively. It was thought that the sublimation of PAHs occurs more readily in a solvent-free situation than in a solvent. Therefore, care was taken not to put the PAHs in a solvent-free situation by adding a few millilitres of acetontrile to the dichloromethane solution of PAHs prior to the evaporation procedure. Under a nitrogen stream at ambient temperature, dichloromethane (b.p. = 40°C) evaporates much faster than acetonitrile (b.p. = 82°C), so that only acetonitrile remains after 45 h of the evaporation procedure. The recovery of each PAH in this instance is given on the third row of Table II and shows that the recovery of phenanthrene increased to more than 90% even after 45 h of treatment.

Combining the above procedures, a series of simple clean-up procedures for the determination of PAHs in diesel exhaust particulate matter were developed as

TABLE II

LOSS OF PAHs DURING EVAPORATION OF THE SOLVENT IN A NITROGEN STREAM AT AMBIENT TEMPERATURE

Procedure	Phenanthrene (%)	Chrysene (%)	B(a)P (%)	B(ghi)P (%)
21 h*	77	102**	100	105
45 h	48	102	98	104
45 h (in CH$_3$CN)	94	101	97	101
45 h (in CH$_3$CN) + preparative column	98	101	97	101

   * Time of the evaporation procedure under a nitrogen stream at ambient temperature.
  ** Recoveries that exceed 100% resulted from the error of the measurement.

shown in the flow chart in Fig. 3. Recoveries of PAHs from the dichloromethane extract through to the HPLC analysis were confirmed to be more than 97%, as indicated on the bottom row of Table II.

    Fig. 4 is an HPLC trace for a mixture of standards. Under the described conditions, the resolution efficiency of the column was about 13,000 plates for anthracene and the detection limit was about 5 pg (signal-to-noise ratio, S/N = 2) for B(a)P. The detection limit was maximal (2.3 pg, S/N = 2) when the mobile phase was 100% acetonitrile with a flow-rate of 0.5 ml/min. This can be expressed in other terms as 1 ng in 30 mg of particulate matter, or 0.15 ppb in dichloromethane.

    Fig. 5 shows the HPLC traces for the extracts of diesel exhaust particulate matter using the clean-up procedures developed here. Fig. 5a is for the extract of
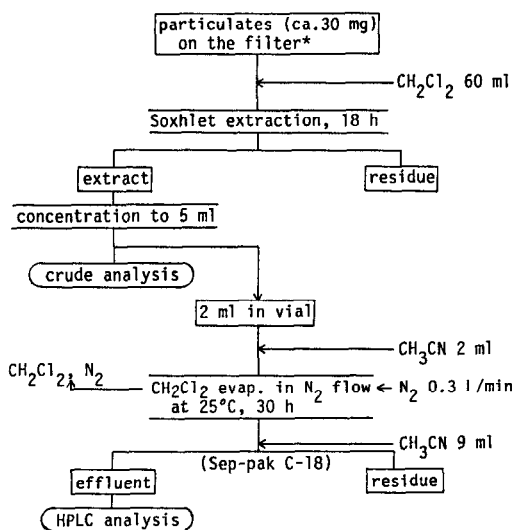
    * Pallflex Prod. Corp. TX40HI20-WW, 142 mmɸ

Fig. 3. Clean-up procedures for diesel exhaust particulate matter for PAH analysis.
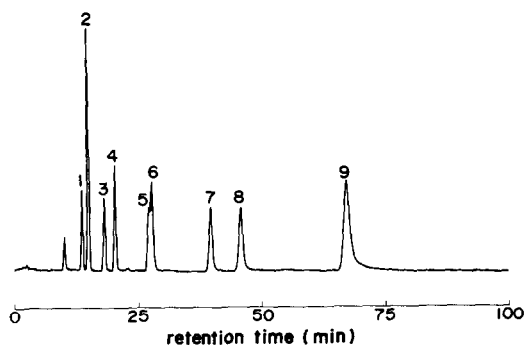
Fig. 4. HPLC trace of standard mixtures of PAHs. Column, Beckman Ultrasphere-ODS (250 × 4.6 mm I.D.); mobile phase, acetonitrile–water (70:30, v/v); flow-rate, 1.0 ml/min; sample size, 40 μl; fluorescence spectromonitor, excitation wavelength = 250 nm, emission wavelength = 420 nm. Peaks: 1 = phenanthrene (4.32 ng); 2 = anthracene (0.46 ng); 3 = fluoranthene (4.28 ng); 4 = pyrene (1.68 ng); 5 = chrysene (1.94 ng); 6 = B(*a*)A (0.82 ng); 7 = B(*b*)F (1.04 ng); 8 = B(*a*)P (0.44 ng); 9 = B(*ghi*)P (4.28 ng).
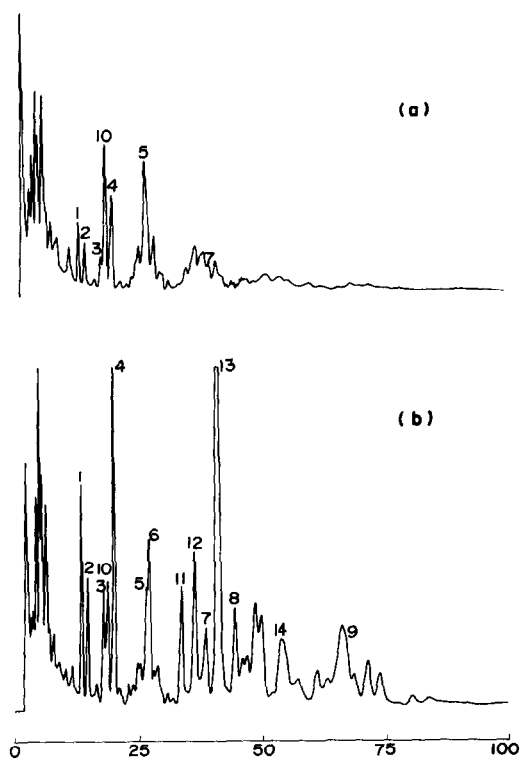

Fig. 5. HPLC trace of extracts of diesel exhaust particulate matter. (a) Emission of commercial gas oil; (b) emission of a mixed fuel of 1-methylnaphthalene (76 vol.-%), *n*-hexadecane (19 vol.-%) and a cetane-number improver (principally hexyl nitrate, 5 vol.-%) HPLC conditions as in Fig. 4. Peaks: 1–9, as in Fig. 4; 10 = substituted phenanthrene; 11 = 1,1-binaphthyl; 12 = 2,2-binaphthyl; 13 = benzo(*k*)fluoranthene [B(*k*)F]; 14 = substituted B(*k*)F.

diesel exhaust particulate matter when commercial gas oil was burnt. The main peaks were confined to an elution time of less than 30 min and correspond to substances with less than four fused rings. Characteristic peaks of alkylated phenanthrene, pyrene and B(a)A were identified from a comparison of their retention times with those of the standards. Fig. 5b is for the extract of exhaust particulate matter when a mixture of 1-methylnaphthalene, n-hexadecane (Special Grade, Tokyo Kasei) and a cetane-number improver that consists mainly of hexyl nitrate (DII-2, Ethyl Corp.) (76:19:5 by volume) was used as the diesel fuel. The scale is the same as that in Fig. 5a. Comparing Fig. 5b with Fig. 5a, it can be seen that the fluorescent species were increased; the increase in the latter half of the chromatogram is particularly prominent. Forty to fifty peaks were observed in this chromatogram and some of them were identified from comparison with the standards or by taking the fluorescence spectra of the corresponding parts of the effluent from HPLC. One example of the fluorescence spectra is shown in Fig. 6, in which benzo(k)fluoranthene was identified by comparison with the standard spectrum[27]. Binaphthyls, which are outstanding in the chromatogram, are obviously the dimerization products of 1-methylnaphthalene, and other species near these peaks are also thought to be products of similar dimerization reactions.
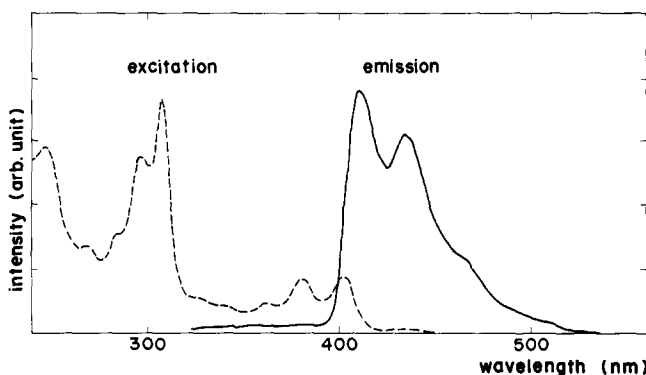

Fig. 6. Fluorescence spectra of peak No. 13 in Fig. 5 [B(k)F]. Excitation spectrum: emission wavelength = 460 nm, excitation slit = 2 nm, emission slit = 5 nm. Emission spectrum: excitation wavelength = 306 nm, excitation slit = 5 nm, emission slit = 2 nm.

Determination of PAH in diesel fuel oil

As the clean-up procedure necessary before determining the content of PAHs in diesel exhaust particulate matter was succesful, a similar procedure was also attempted for the analysis of diesel fuel oil.

First, 100% acetonitrile was used as the eluent for the separation procedure with the same type of preparation column used in the method for the extracts of particulate matter, namely, 50 μl of the lubricating oil were allowed to permeate directly around the uppermost part of the column and then eluted with 10 ml of acetonitrile. Fractions of 1 ml of the effluent were analysed using TLC with FID and the elution order of each type of organic compound was determined. Fig. 7a shows the results. Unlike the extracts of particulate matter, the separation between aliphatic hydrocarbons and more polar compounds was not complete. Therefore, the eluents
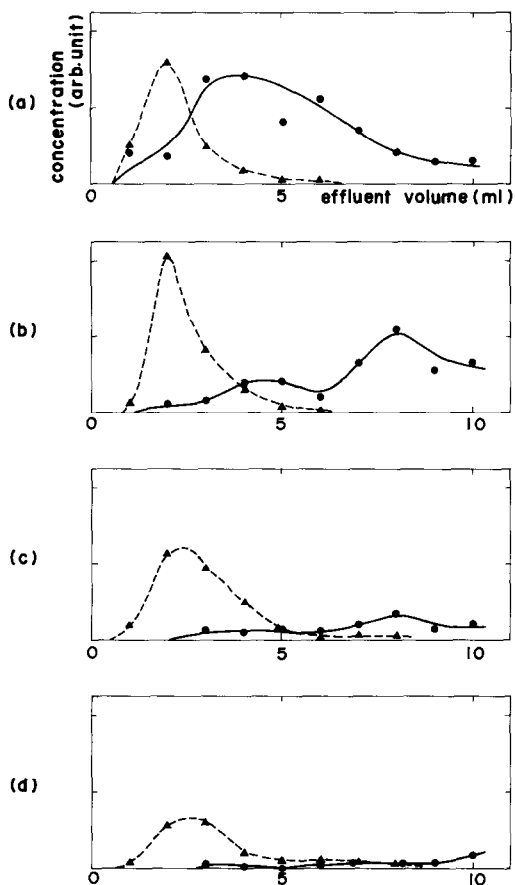
Fig. 7. Effect of water concentration in acetonitrile–water eluent on the elution of lubricating oil. ●, Elution of aliphatic hydrocarbons; ▲, elution of aromatic hydrocarbons. Eluent: (a) acetonitrile; (b) acetonitrile water (95:5); (c) acetonitrile–water (90:10); (d) acetonitrile–water (85:15).

were changed to more polar solvents, *viz.*, mixtures of acetonitrile and water. Fig. 7b, c and d show the elution rate of each type of organic compound in the lubricating oil when the water content of the eluent was 5, 10 and 15%, respectively. As the water content increased, the elution of aliphatics decreased and elution within the initial 10 ml became negligible when the water content was 15%. The elution of B(*a*)P and B(*ghi*)P were measured under the last condition to examine their recovery. The results for the concentrations of B(*a*)P and B(*ghi*)P in 1-ml fractions of the effluent are shown in Fig. 8. The peaks were at an elution volume of about 3 ml and the elutions were almost complete within 10 ml for both species, so that the recovery of PAHs was sufficient. Recoveries of B(*a*)P dissolved in the solvent oil are shown in Table II for several concentrations. The recovery was about 91% and did not vary with the concentration of B(*a*)P.

Based on the above results, the clean-up procedures for diesel fuel oils were performed as follows:
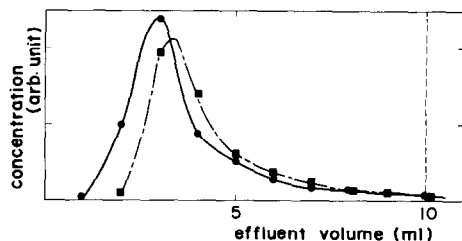
Fig. 8. Elution of B(*a*)P and B(*ghi*)P from the preparation column with acetonitrile–water (85:15). ●, B(*a*)P; ■, B(*ghi*)P.

TABLE III

RECOVERY OF B(*a*)P DISSOLVED IN THE SOLVENT OIL BY THE CLEAN-UP PROCEDURES

B(a)P concentration in solvent oil (mg/l)	Recovery (%)
0.22	88.2
0.44	93.6
1.10	89.2
2.20	90.0
4.40	92.3
	Mean: 90.7 ± 2.2

   (1) Wash the preparation column (Sep-Pak C_{18}) with 5 ml of acetonitrile–water (85:15, v/v).

   (2) Permeate 50 μl of test oil directly on the uppermost part of the Sep-Pak C_{18} with a microsyringe.

   (3) Elute the oil with acetonitrile–water (85:15) and collect the initial 10 ml effluent into a 10-ml measuring flask.

   (4) Inject 5–40 μl of the effluent into the HPLC system and measure the concentration of PAHs under the same conditions as for the analysis of extracts of particulate matter.

   The detection limit of B(*a*)P using these procedures was estimated to be 10 ppb in the oil.

   These procedures were applied to analyses of commercial oil, aromatic-rich gas oil, C-Grade fuel oil and coal-liquefied oil, and the results are shown in Fig. 9a, b, c and d, respectively (all on the same scale). Based on these results, some PAH concentrations were determined, and are presented in Table IV.

   It is also clear that the clean-up procedures with the preparation column were successful in the determination of PAHs in diesel fuel oils. There remains the fine adjustment of the water concentration in the eluent for the preparation column, to maximize the recovery of PAHs while at the same time keeping the elution of aliphatic compounds below a level that is harmful to the HPLC column.
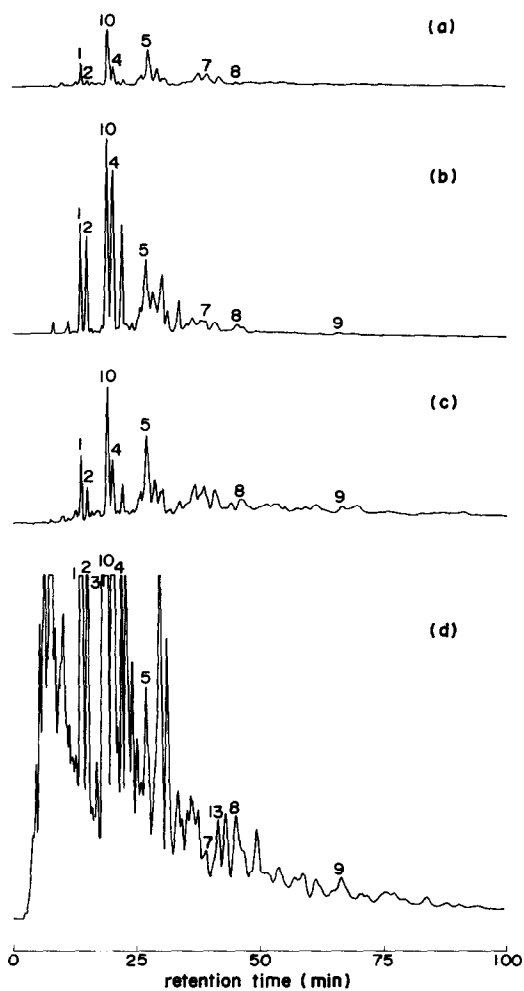
Fig. 9. HPLC traces of oils (all on the same scale). Conditions as in Fig. 4. (a) Commercial gas oil; (b) aromatic-rich gas oil; (c) C-Grade fuel oil; (d) coal-liquefied oil. Peak numbers as in Fig. 4.

TABLE IV

CONCENTRATIONS OF SOME PAHs IN THE OILS EXAMINED (mg/l)

Compound	Commercial gas oil	Aromatic-rich gas oil	C-Grade fuel oil	Coal-liquefied oil
Phenanthrene	202	974	447	$33.2 \cdot 10^3$
Anthracene	1.9	30.1	8.4	291
Fluoranthene	$-^*$	−	−	$6.5 \cdot 10^3$
Pyrene	50.2	422	122	$5.4 \cdot 10^3$
B(b)F	13.8	−	17.2	70.8
B(a)P	1.9	6.7	5.6	64.5
B(ghi)P	−	16.7	−	87.8

* Not distinguished in the chromatogram.

DISCUSSION

In the analysis of the extract of diesel exhaust particulate matter, it is not necessary to carry out an extra filtration procedure to eliminte any particulate matter or fraction of the filter suspended in the extract solution, because these insoluble matters are filtered by the preparation column during the separation of aliphatic hydrocarbons.

Using 100% acetonitrile as the eluent, the separation of aliphatic hydrocarbons was not adequate for the clean-up procedure of diesel fuel oil. It is thought that the oils contain lower molecular weight aliphatics than the extracts of particulate matter. These smaller aliphatics may partly pass through the preparation column but still damage the performance of the HPLC column. We did not investigate which oils the clean-up procedures reported here can be extended to, but as far as diesel fuels (b.p. = 200–360°C) are concerned, degradation of the column was not observed.

The simplest form of the HPLC analysis of the extracts of particulate matter may be attained by the use of a guard column and direct injection of the extract solution. In this instance, however, the extract solvent is restricted to that which has a polarity similar to that of the HPLC mobile phase, because when a much stronger eluent than the mobile phase is injected with the sample, the chromatogram peaks are broadened and the high resolution efficiency of the HPLC column is spoiled. The combination of the dichloromethane sample solution and the acetonitrile–water mobile phase is a typical instance. After all, if one wants to use dichloromethane as the extraction solvent, some procedure for changing the solvent into a weaker solvent, such as acetonitrile, would be necessary and the labour would be almost equal to that reported here.

Although this report deals principally with the development of an analytical procedure for PAHs, some conclusions can be drawn from the results in Figs. 5 and 9 about the emission of PAHs from diesel engines. (i) The amount and quality of PAH emission vary considerably with change of the fuels. Obviously, the PAHs are produced by chemical reactions during combustion, not always the unburnt residue of the fuel. (ii) The contents of PAHs and fluorescent species vary substantially from oil to oil. In particular, the coal-liquefied oil analysed here contained almost 100 times more PAHs than the commercial gas oil.

These conclusions lead to the prediction that the increase in the utilization of alternative fuels that contain large concentrations of aromatic compounds will cause extensive PAH emission and will be a serious environmental problem. In this connection, experiments to find relationships amont fuels, combustion and emission are now being conducted using another test diesel engine and fuels composed of mixtures of pure hydrocarbons and some characteristic diesel fuels.

CONCLUSION

Clean-up procedures have been developed for the determination of PAHs in the dichloromethane extracts of diesel exhaust particulate matter and diesel fuel oils, using a reversed-phase preparation column (Sep-Pak C_{18}), and the following results were obtained.

(1) PAHs extracted into dichloromethane together with aliphatic hydrocar-

bons were successfully determined by reversed-phase HPLC by conducting a series of clean-up procedures, during which the solvent was changed from dichloromethane to acetonitrile and insoluble matter and aliphatic hydrocarbons were eliminated by using a preparation column, in order not to affect the performance of the HPLC column. The recoveries of PAHs were more than 97% and the detection limit of benzo(a)pyrene was 0.15 ppb in dichloromethane or 1 ng in 30 mg of particulate matter.

(2) PAHs in diesel fuel oils were also determined using a procedure similar to (1) except that acetonitrile–water (85:15, v/v) was used instead of 100% acetonitrile as the eluent for the preparation column. The recovery of benzo(a)pyrene was about 91% and its detection limit was 10 ppb in oil or 0.5 ng in 50 μl of oil.

These analytical procedures can be applied in studies to establish relationships among fuels, combustion, emission and this subject are now in progress.

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