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The Origin of Polycyclic Aromatic Hydrocarbons in Diesel Exhaust Emissions

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The Origin of Polycyclic Aromatic Hydrocarbons in Diesel Exhaust Emissions

by

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AUTHOR'S DECLARATION

At no time during the registration for the degree of Doctor of Philosophy has the author been registered for any other University award.

Relevant scientific seminars and conferences were regularly attended at which this research was often presented. Several papers were prepared for publication.

Conferences attended:

Emissions, University Institutions Combustion and Engineering Group (UnICEG), Shell Research, Thornton Research Centre, 22/9/93

Alternative Fuels. UnICEG, University of Warwick, 20/12/93

Petroleum Analysis, The Chromatographic Society, Shell Research, Thornton Research Centre 10/11/93

Short Course on Diesel Particulates, University of Leeds, April, 1991 and 1992

Publications:

The sources of Benzo[α]pyrene in diesel exhaust emissions. *The Science of the Total Environment*. In The Press.

Diesel combustion of an alkylated polycyclic aromatic hydrocarbon. *Fuel*, Submitted for publication.

Survival of polycyclic aromatic hydrocarbons during diesel combustion. *Environmental Science and Technology*. Submitted for publication.

Signed.....

Date.....

ABSTRACT

THE ORIGIN OF POLYCYCLIC AROMATIC HYDROCARBONS IN DIESEL EXHAUST EMISSIONS

Paul James Tancell

Emission limits for diesel engine exhaust pollutants are being continually reduced in line with increasingly stringent emissions legislation. Essential to the task of reducing diesel exhaust emissions is an understanding of the origin of the exhaust pollutants. This research has investigated the origin of a group of compounds, polycyclic aromatic hydrocarbons (PAH), in diesel exhaust emissions using ^{14}C-radiotracer techniques developed specifically to investigate the origin of the organic components in diesel emissions. The use of radiotracers in this research has enabled both the extent to which individual PAH survive combustion and the extent to which PAH are pyrosynthesized during combustion to be measured accurately. No other diesel emissions research technique has yielded information which is so unequivocal.

Radio-chromatographic techniques were developed specifically for the identification and quantification of radioactive species present in diesel emissions resulting from the combustion of a single ^{14}C-radiolabelled precursor. Radio-high performance liquid chromatography (radio-HPLC) was the main technique used and was applicable as both a tool for sample fractionation and for analytical measurement. Radio-gas chromatographic techniques (radio-GC) were also developed and applied to the identification of radioactive species in the exhaust emissions.

Diesel exhaust samples were collected from a 2L direct injection Perkins Prima diesel engine using a novel exhaust sampling device, the Total Exhaust Solvent Stripping Apparatus (TESSA) devised previously to sample organic species from automobile exhausts. Diesel combustion experiments were performed on three ^{14}C-radiolabelled PAH, fluorene, pyrene and benzo[α]pyrene (B[α]P), and ^{14}C-n-hexadecane. These were spiked into the diesel fuel and were combusted in the Prima Engine. The extent of survival was 0.04% for B[α]P, 0.17% for pyrene and 0.87% for fluorene. The amount of each PAH in the exhaust emissions derived from pyrosynthetic sources ranged from <20% for B[α]P, to 26.5% for fluorene and 71% for pyrene.

The extent to which individual PAH survive the diesel combustion process was correlated with the molecular orbital distribution of the molecule, and especially the energy levels of the lowest unoccupied molecular orbital (LUMO). It is concluded that the relationship between PAH survival and PAH molecular orbitals (MOs) is owing to the kinetics of combustion reactions and the chemical reactivity of the PAH.

The extent to which individual PAH molecules are formed during combustion varies considerably. From the limited number of experiments performed in the current research it has not been possible to determine the mechanisms responsible for the formation of these PAH during combustion. Mass balance calculations have demonstrated that the degree of pyrosynthesis of the parent PAH molecules

investigated in this research may be accounted for by comparatively low rates of dealkylation of alkyl-substituted derivatives present in diesel fuel.

The importance of dealkylation reactions during diesel combustion, was investigated by combusting a low aromatic fuel spiked with a non-radiolabelled alkyl-PAH, 2- and 3-ethylphenanthrene (2- and 3-EtPa), which were synthesized for this purpose. The 2 and 3-EtPa isomers were recovered in yields of 0.35% and 0.3% respectively. No dealkylation of the EtPa was detected. A statistically significant increase in the emissions of 3-methylphenanthrene (3-MePa) was detected and was equivalent to a conversion rate of 0.0004% of the EtPa spike. It is proposed that the ease with which individual alkyl-PAH isomers are dealkylated varies for specific isomers, and is dependent on the position of the alkyl-substituent on the aromatic nucleus. The major product from the combustion of the EtPa was vinylphenanthrene (ViPa) which produced in a yield equivalent to a conversion of 0.01% of the EtPa spike.

Radiotracer experiments with ^{14}C-*n*-hexadecane were performed to investigate the origin of the aliphatic component of diesel emissions. The extent of hexadecane survival was 0.35%. Approximately two thirds of the hexadecane in the emissions was derived from pyrosynthetic sources. The most probable source of the pyrosynthesized hexadecane in the emissions was `thermal cracking of higher molecular weight aliphatic species in diesel fuel during the combustion process. This process may account for a significant proportion of lower molecular weight *n*-alkanes emitted in diesel emissions.

Contents

List of Figures

List of Tables

List of Abbreviations

Polycyclic Aromatic Hydrocarbons (PAH)

Np	Naphthalene
MeNp	Methylnaphthalene
diMeNp	Dimethylnaphthalene
triMeNp	Trimethylnaphthalene
Fl	Fluorene
DBT	Dibenzothiophene
Pa	Phenanthrene
Fa	Fluoranthene
Py	Pyrene
Ch	Chrysene
B[α]P	Benzo[α]pyrene
ViPa	Vinylphenanthrene
EtPa	Ethylphenanthrene
MeEtNp	Methylethylnaphthalenes

General abbreviations

ACN	Acetonitrile
a_{or} and a_{os}	Coefficients of the non-bonding MOs adjacent to the point of substitution
Air/Fuel ratio	∅
α	Coulomb integral
β	Resonance integral
Bq	Bequerel
b. pt.	boiling point
CARB	Californian Air Resources Board
CEN	European Committee for Standardisation
cps	counts per second
d_{10}-Pa	deuterated phenanthrene
DCM	Dichloromethane
DI	Direct injection
EEC	European Economic Community
EGR	Exhaust gas recirculation
EPA	Environmental Protection Agency
EUDC	European Urban Driving Cycle
FID	Flame ionisation Detection
FTP	Federal Test Procedure
GC	Gas chromatography
GC/MS	Gas Chromatography/ Mass Spectrometry
HCs	Hydrocarbons
HGVs	Heavy goods vehicles
HOMO	Highest occupied molecular orbital
HPLC	High performance liquid chromatography
IDI	Indirect injection
I.R.	Infra-red
I.S.	Internal Standard

IARC	International Agency for Research on Cancer
K	Kelvin
KW	kilowatt
LDVs	Light duty vehicles
LOMO	Lowest unoccupied molecular orbital
MeOH	Methanol
MO	Molecular Orbital
mV	millivolts
MVEG	Motor Vehicle Emissions Group
n-C_{16}	Hexadecane
Nm	Newton meters
NO_x	Nitrogen oxides
PAC	Polycyclic aromatic compounds
PMO-MO	Perturbation Molecular Orbital
PM	Particulate matter
PM_{10}	Particulate matter less than 10 micrometers in diameter
ppm	Parts per million
QUARG	Quality of Urban Air Review Group
R	Gas Constant
REPE	Resonance energy per pi-electron
rpm	Revolutions per minute
SCF-MO	Self-Consistent Field-Molecular Orbital
SMMT	Society of Motor Manufacturers and Traders
SOF	Solvent Organic Fraction
SOMO	Singly occupied molecular orbital
T	Temperature
TESSA	Total Exhaust Solvent Scrubbing Apparatus
TGA	Thermogravimetric analysis
µCi	micro-Curies
UHC	Unburned hydrocarbons
UNECE	United Nations Economic Commission for Europe
UV	Ultra violet
$\Delta\pi_E$	change in π-electron energy
VOC	Volatile organic compounds

Chapter 1

INTRODUCTION

1.1 The growth in the diesel car market

In recent years the UK has experienced a significant increase in the number of new diesel cars sold. The number of new diesel passenger car registrations doubled between 1987 and 1992 and accounted for 12.6% of all new car registrations in 1992 compared with just 5.6% in 1987 (SMME, 1993). Substantial increases in diesel car sales have also been observed in other Western European countries and especially France and Germany (Fig. 1).

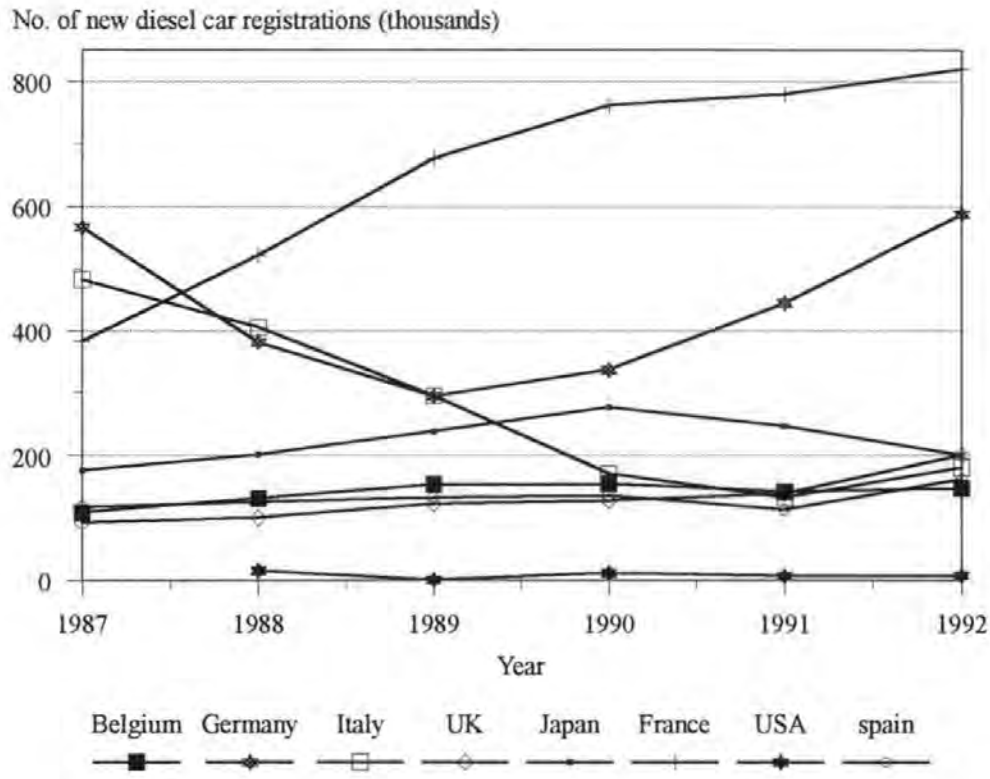


Figure 1. New diesel car registrations in selected European countries, the USA and Japan.

Source: SMMT, 1993

Several factors have contributed to the growth in diesel car sales. With increasing taxation on fuels, the superior fuel economy of diesel powered vehicles, compared to their petrol equivalents, has become an important factor for many consumers in their choice of vehicle. A substantial adjustment in the consumers general perception of the diesel engine. Sales of diesel powered passenger cars were previously disadvantaged by noisy driving conditions, lack of power and the emission

of significant quantities of black smoke, all of which enforced the general impression of the diesel as suitable only for commercial use. Major advances in diesel engine design, resulting in increased power output and an improved engine performance, have largely overcome these problems. Advances in engine design have also improved the diesel combustion process with modern engines having very low emissions of particulate material. The relative fuel economy of diesels introduced significant financial incentives to the consumer to purchase diesel cars. In recent years however, tax incentives on unleaded petrol, introduced by the government to reduce the emission of leaded compounds into the environment, have reduced somewhat the attractiveness of diesels.

1.2 Environmental impact of diesel exhaust emissions

The increasing use of the diesel engine in automotive transportation has raised concerns regarding the potential environmental impact of an increase in the atmospheric burden of diesel exhaust pollutants. The effects are likely to be felt most strongly in urban areas, where exhaust pollutant levels already represent a hazard to public health (Quality of Urban Air Review Group, QUARG, January 1993). Of primary concern, are emissions of nitrogen oxides (NO_x) and particulate matter (PM). Particulate emissions are 30 to 100 times greater from light-duty diesels than from comparable catalyst-equipped petrol engines (Andrews, 1993). Nationally, emissions of NO_x and particulates from road transport sources are predicted to fall. In urban areas, however, pollutant concentrations may remain static for some time or even increase in the near future, owing to greater diesel usage (QUARG, December 1993).

Diesel exhaust particulates are also a significant factor in the soiling of buildings in urban areas. Adsorbed organic compounds on the surface of the particulate make them prone to deposition on stone surfaces. The cost of the stone cleaning operation in the UK in has been estimated at 74 million pounds annually (Newby *et al.*, 1991).

Whilst diesel emissions of NO_x and particulates are a cause for concern, an increased market share of diesel vehicles may offer benefits with respect to emissions of CO and HCs, both of which are undesirable in terms of human health. HCs play an important role in the formation of photochemical smogs, which are a regular

phenomenon in larger European cities. Diesel emissions of HCs and CO are low owing to the high efficiency of the diesel combustion process and are comparable with emissions from catalyst equipped petrol driven vehicles. The low volatility of diesel fuel also results in low evaporative emissions of HCs in comparison with emissions from petrol vehicles. Diesels may also offer benefits in terms of cold-start emissions, which, it has been estimated, contribute a third of the total volatile organic carbon (VOC) emissions and CO emissions from passenger cars (Holman *et al.*, 1993). Cold start emissions of CO and HCs from diesels are considerably lower than those of catalyst-equipped petrol vehicles. An increase in diesel usage may offer positive environmental benefits by reducing cold start emissions of HCs and CO.

The greater fuel economy of diesels leads to emissions of CO_2, the primary greenhouse gas, that are on average 10% lower than their petrol counterparts (Wade *et al.*, 1993). An increased market share of diesel powered passenger cars has been predicted to have only a small impact on the overall global warming potential from automotive transportation (Wade *et al.*, 1993).

1.3 Current and predicted levels of diesel emissions

A detailed analysis of the contribution of diesel emissions to current and predicted levels of air pollutants in the UK for 1991 has recently been presented (QUARG, December 1993). The data in this section and in Table 1.1 summarises the 1991 information found in that report.

The diesel contribution of carbon monoxide (CO), sulphur dioxide (SO_2) and volatile organic compounds (VOC) to the total is comparatively minor, and reflects both the composition of diesel fuel and the efficiency of the diesel combustion process. With respect to black smoke (which is essentially the carbon fraction of particulate matter) and NO_x it is clear that diesel powered vehicles have become significant polluters, contributing 38.6% and 20.6% of the national total respectively. In urban environments, the diesel contribution to these pollutants is even more pronounced. For example, diesels as a whole were responsible for 86.6% of black smoke and 31.6% of NO_x emissions in London. At present, in both urban and rural areas, heavy goods vehicles (HGVs) are the principle polluters accounting for between 70% and 80% of total diesel emissions, whilst passenger cars and light duty

vehicles (LDVs) each contribute on average about 7% to 8% of pollutants (Table 1.1.).

Table 1.1. Contribution of Diesels to UK National Air Pollutant Emissions, 1991[a].

Pollutant	Diesel contribution % (all vehicles)	Diesel Contribution %			
		HGV	Cars	LGV	Buses & coaches
CO_2	5.9	71.6	7.4	7.4	13.7
Black Smoke	38.6	71.7	7.3	6.8	14.1
CO	2.3	68.3	8.5	8.5	14.6
SO_2	1.2	71.7	7.1	7.0	14.2
VOC	6.5	70.5	8.4	8.4	12.7
NO_x	20.6	81.2	1.7	1.6	15.5

[a]Adapted from Second Report of the Quality of Urban Air Review Group, December 1993.

Future trends in diesel emissions will be affected by a number of factors including new legislative limits for exhaust pollutants, the number of new diesel car sales and the implementation of exhaust gas "after treatment". The 1993 QUARG report assessed these and additional related factors and used this information to predict future emissions of NO_x, particulates and SO_2. Diesel contribution of other pollutants such as VOC and CO are minor compared to the total UK emissions and were not considered in the report.

NO_x emissions arising from road transport have doubled since 1970. An increase in the number of petrol vehicles is largely responsible for the majority of this increase. The diesel contribution to NO_x decreased in this time from about 60% in 1970 to 40% at the present. The forecast for NO_x emissions predicts a decline to 1970 levels by the year 2005 as a consequence of new emission limits, before rising again owing to increased mileage. The diesel contribution to NO_x is predicted to become increasingly significant during this time. Since 1970, total black smoke emissions have almost halved. However, the relative contribution from road transport has increased significantly during this period, and is mainly a consequence of diesel emissions of black smoke. The situation is predicted to remain relatively

stable into the future, although a slight increase is expected up until 1996 when the implementation of more stringent particulate controls are expected to reduce emissions. After this period emissions have been predicted to remain relatively constant. The diesel contribution to road transport SO_2 is predicted to drop sharply in 1996 with the introduction of a sulphur limit for fuels of 0.05% (see Section 1.8.3). Emissions of SO_2 are then predicted to increase owing to increased mileage.

1.4 European vehicle emission legislation

Vehicle emissions legislation was first introduced in the early 1960s in Los Angeles as a response to the problem of photochemical smogs. Events in the US prompted the United Nations Economic Commission for Europe (UNECE) in the late 1960s to establish emission limits for European Countries. UNECE had no powers of enforcement and implementation of the regulations in member states was voluntary. However, following the incorporation of UNECE regulations into European Economic Community (EEC) law, in a series of directives, implementation of the regulations became mandatory for all states signatory to the European Community (EC) treaty.

1.4.1 Test procedures

The current EEC method for testing emissions divides vehicles into two categories, light duty vehicles (LDVs) including cars and vans less than 3.5 tonnes in weight and heavy goods vehicles (HGVs) greater than 3.5 tonnes in weight. Only LDV legislation is considered in this review. Emissions from LDVs are measured on a chassis dynamometer, according to the test procedure ECE 15 + Extra Urban Driving cycle (EUDC). The ECE 15 test is that originally devised by the UNECE and is designed to simulate driving conditions that are encountered in an urban driving environment. The EUDC was introduced in 1991 and has been designed to include a period of simulated faster driving.

1.4.2 Light duty vehicle emission standards - Historical development

A brief summary of the development of emissions standards in Europe is presented in this section. For a more detailed review on this subject refer to Dunne,

(1993). Emissions legislation in Europe was first introduced in 1970 through the UNECE in ECE regulation No. 15 (UNECE, 1970, quoted QUARG, 1993). This regulation covered only gaseous carbon monoxide (CO) and hydrocarbon (HC) emissions from the ECE 15 drive cycle and applied only to vehicles of less than 3.5 tonnes. ECE Regulation No. 15 was incorporated into EC Directive 70/220/EEC (European Community, 1970).

After 1970, emission limits were progressively tightened in line with increasing environmental concerns over the impact of vehicle exhaust emissions. Four new regulations were introduced by UNECE and were incorporated directly into the corresponding EC directives up to 1983:

ECE Reg No. 15.01 -Directive/74/290/EEC
ECE Reg No. 15.02 -Directive/77/102/EEC
ECE Reg No. 15.03 -Directive/78/665/EEC
ECE Reg No. 15.04 -Directive/83/351/EEC (introduced limits for NO_x)

In 1985, at the meeting of the Council of Ministers in Luxembourg, a change in the legislation was agreed to bring European standards into line with equivalent US legislation. Emission limits thus became dependent on engine capacity with three categories being defined: > 2L ; 1.4 to 2L ; and <1.4L. The new limits were included in the EC directive 88/76/EEC. Subsequent EC directives, 88/436/EEC and 89/458/EEC retained these categories whilst tightening the emission limits. Directive 88/436/EEC introduced limits for the emission of diesel particulate matter (PM).

1.4.3 Light duty vehicles - Current and predicted emission levels

In 1991 all preceding legislation was superseded by the Directive 91/441/EEC, (also known as the consolidated emissions directive) The emissions limits for passenger cars are summarised in Table 1.2.

Table 1.2. Directive 91/441/EEC limits for passenger cars designed for up to 6 occupants

	CO (g/Km)	HC + NO_x (g/Km)	Particulates (g/Km)
New Models			
type approval: 1.7.92	2.72	0.97	0.14
production conformity: 31.12.92	3.16	1.13*	0.18*
Test Procedure: ECE R15 + the Extra Urban Driving Cycle			

*For DI diesels, production conformity limits for HC + NO_x and particulates are multiplied by a factor of 1.4 until end December 1994.

The Commission recently introduced Directive 93/59/EEC for vans which establishes emission limits for vans and light duty commercial vehicles below 3.5 tonnes of similar severity to those for passenger cars. Limit values are specified in Table 1.3. The proposed introduction dates were 1 October 1993 for new vehicles and 1 October 1994 for conformity of production. The directive removed a loophole in Directive 91/441/EEC that allowed car-derived vans to comply with less-stringent emission limits than the catalyst equipped car itself.

Table 1.3. Proposed emissions limits for light duty vehicles: Directive for Vans

		LIMIT VALUES		
Vehicle Category	Ref. mass (Kg)	HC + NO_x [g/Km]	CO [g/Km]	Particulates [g/Km]
N1:	1250	0.97 (1.13)	2.72 (3.16)	0.14 (0.18)
	1250-1700	1.40 (1.60)	5.17 (6.00)	0.19 (0.22)
	1700-	1.70 (2.00)	6.90 (8.00)	0.25 (0.29)
Test Procedure: ECE R15 + the Extra Urban Driving Cycle (EUDC)				

1.4.4 Passenger car emission limits 1995/6

Directive 91/441/EEC states that further reductions in emission levels for passenger cars are to be introduced by 1 January 1996. In a Proposed Council Directive, COM (92) 572 Final SYN 448 (23 December 1992), the Motor Vehicles Emission Group (MVEG) for the EC have proposed new emission limits (Table 1.4).

Objections to the new emissions standards have been raised by some, since it is felt that by differentiating between vehicle types, the new emission limits could undermine the trend toward simpler, more uniform standards.

Table 1.4. 1995/96 emission limits for passenger cars (category M*)

	CO (g/Km)	HC + NO_x (g/Km)	Particulates (g/Km)
Gasoline vehicles	2.2	0.5	-----
Diesels:			
IDI	1.0	0.7	0.08
DI**	1.0	0.9	0.10
Type approval: 1.1.1995			
Conformity of Production 1.1.1996			

* Except-vehicles designed to carry more than 6 persons or whose maximum mass exceeds 2500Kg.
** limits for HC + NO_x and particulates are valid until 30 September 1999

1.5 The diesel combustion process

Diesel combustion operates under the mechanism of compression ignition (CI) in contrast to the petrol engine which is spark-ignition (SI) operated. The majority of both types of engine in use at present, operate under a four stroke combustion regime. In the four stroke diesel the four stages of the operational cycle are:

1) Inlet stroke:- air is inducted into the cylinder

2) Compression stroke:- the inducted air is compressed to 35-50 atm and is heated to 900-1000K

3) Expansion stroke:- shortly before the end of the compression stroke, fuel is injected into the cylinder where it mixes with the hot air and ignites, the increase in pressure forces the piston down

4) Exhaust stroke:- the exhaust gases are forced out of the cylinder by the rising piston

Diesel engines may be classified according to the fuel injection system used. In the indirect injection diesel engine (IDI), fuel is injected into a pre-chamber where fuel/air mixing occurs and initial combustion takes place (Fig 1.2a). The partially

oxidised fuel mixture swirls into the main chamber where the combustion process is completed. In direct injection diesels (DI), fuel is injected as a fine spray directly into the combustion chamber into a bowl in the crown of the piston (Fig 1.2b.). The compression ratios in these two types of engine, 10:1 for petrol engines compared to 18:1 for IDI diesels or 22:1 for DI diesels reflect the differences in the mechanism of combustion. Higher compression ratios are required in diesel combustion to generate the higher temperatures necessary to ignite the diesel fuel.

The second major difference between petrol and diesel engine operation, is that diesel engines are able to operate with much wider fuel/air ratios, (*e.g* 120:1 at idling to 20:1 at full load). This is the principal reason for the versatility of the diesel engine particularly with regard to load carrying capacity. Petrol engines are restricted to operating within a much narrower range of fuel/air mixtures, nominally 10:1 to 20:1, but operating ideally, as close to stoichiometric conditions as possible (14.7:1).

During the diesel combustion cycle two different combustion regimes can be identified. A fraction of the fuel injected during the ignition delay period will evaporate to form a homogenous mixture and will burn under pre-mixed conditions. The remaining fuel injected will burn off the injector tip under diffusion controlled combustion (Barbella *et al.*, 1989). Since the majority of diesel fuel is injected after ignition, the process of diesel fuel combustion is essentially diffusion controlled (Lida *et al.*, 1988). The different physical and chemical processes occurring in these two stages are reflected in the emission characteristics. The premixed stage is characterised by cleaner and more complete combustion due to the well mixed nature of the fuel and oxidant. Fuel oxidation in the diffusion stage is generally less efficient owing to the reduced mixing of fuel and air. Particulates are formed predominantly during the diffusion burning period as the flame propagates towards the core of the fuel spray. Here, local air-fuel ratios will be richer than at the fuel periphery where combustion started, leading to incomplete combustion of the fuel and hence formation of soot (Fig. 1.3). At the core of the flame, the air/fuel ratio, $\varnothing$, is greater than the rich flammability limits for combustion, $\varnothing_R$, and the fuel will not burn (Williams *et al.*, 1986). Similarly, at the very edges of the flame front, $\varnothing$ may be below the lean limit of combustion, $\varnothing_L$, and the mixture will be too lean for

combustion to take place (Williams *et al.*, 1986). In the latter case significant pyrolysis of the fuel vapour may occur. The combustion of many different fuel types have been studied under diffusion and premixed conditions to determine the mechanisms of soot formation (Haynes and Wagner, 1981).

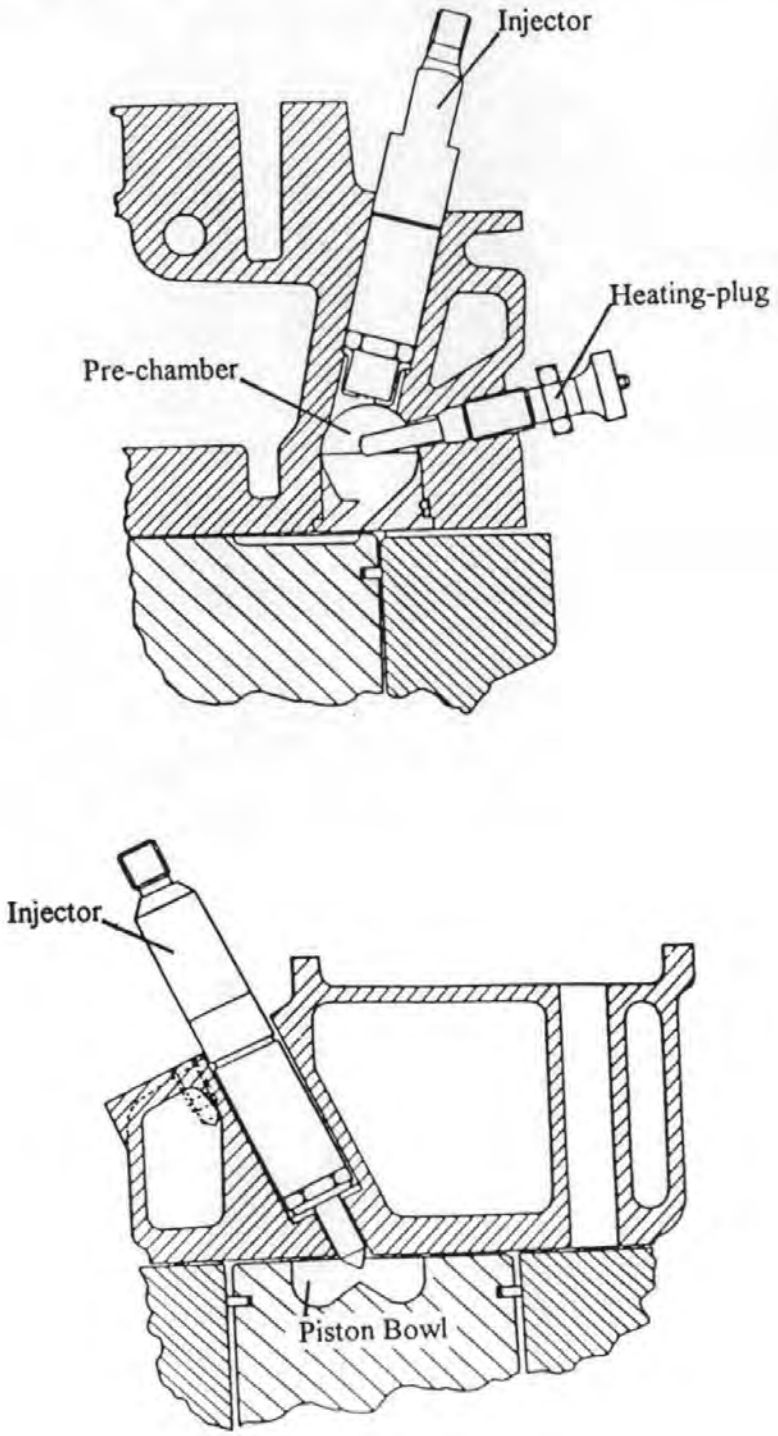


Figure 1.2 a) Indirect injection and b) Direct injection diesel injectors

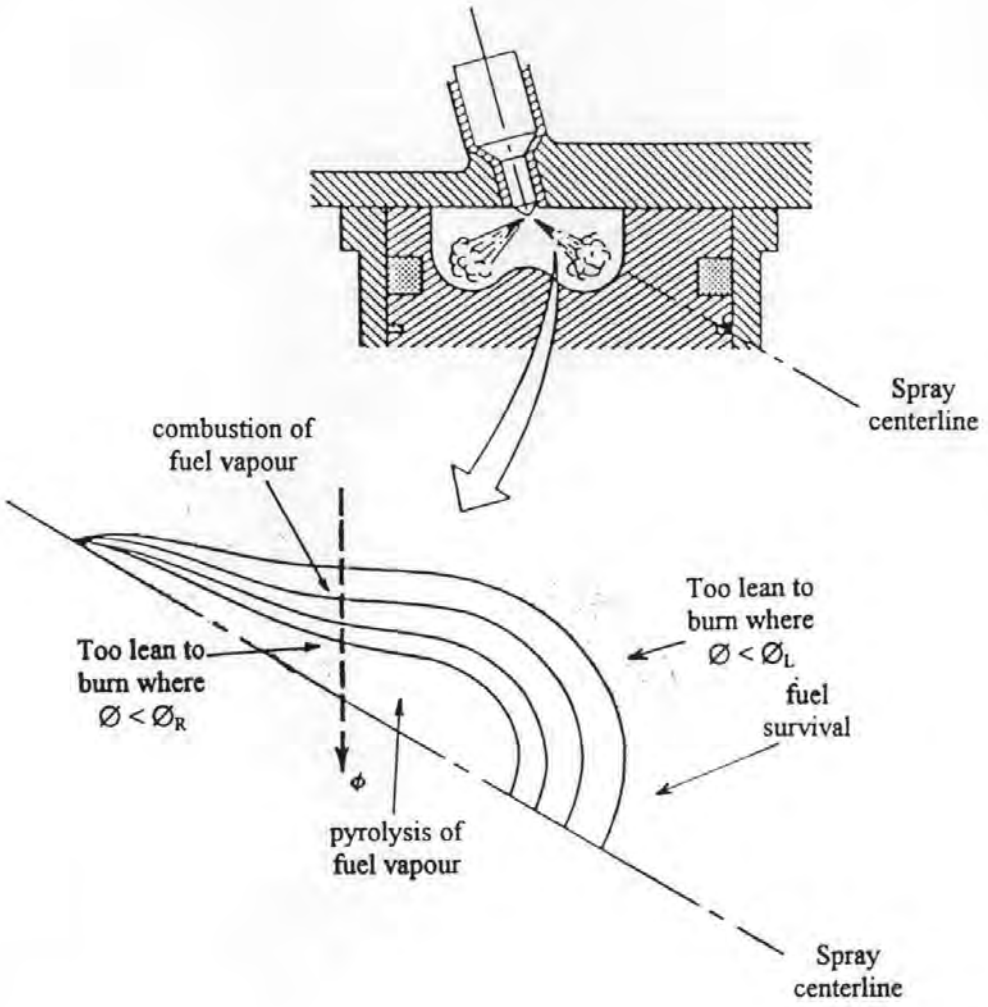


Figure 1.3. Illustration of the fuel spray distribution from a direct injection diesel showing regions of fuel survival and fuel pyrolysis

where :

$\varnothing$ air/fuel ratio

$\varnothing_R$ rich flammability limit for combustion

$\varnothing_L$ lean limit for combustion

1.6 Diesel exhaust sampling

Schuetzle (1983) describes two main approaches for the sampling of diesel exhaust: direct isokinetic sampling, and sampling once the exhaust gases have passed

through a cooling device. Dilution tunnel sampling is the most widely used example of the former system and is the current method with which regulatory emission levels are set and monitored. The aim of the dilution tunnel is to simulate the physical and chemical processes that effect exhaust gases entering the atmospheric environment from the exhaust pipe. The main components of the dilution tunnel system are shown in Figure 1.4. Exhaust gases are passed directly into a large tunnel where they are diluted with a known volume of filtered air of constant humidity and temperature. The exhaust is sampled by drawing the gases through a weighed glass fibre filter to trap out any particulate matter.

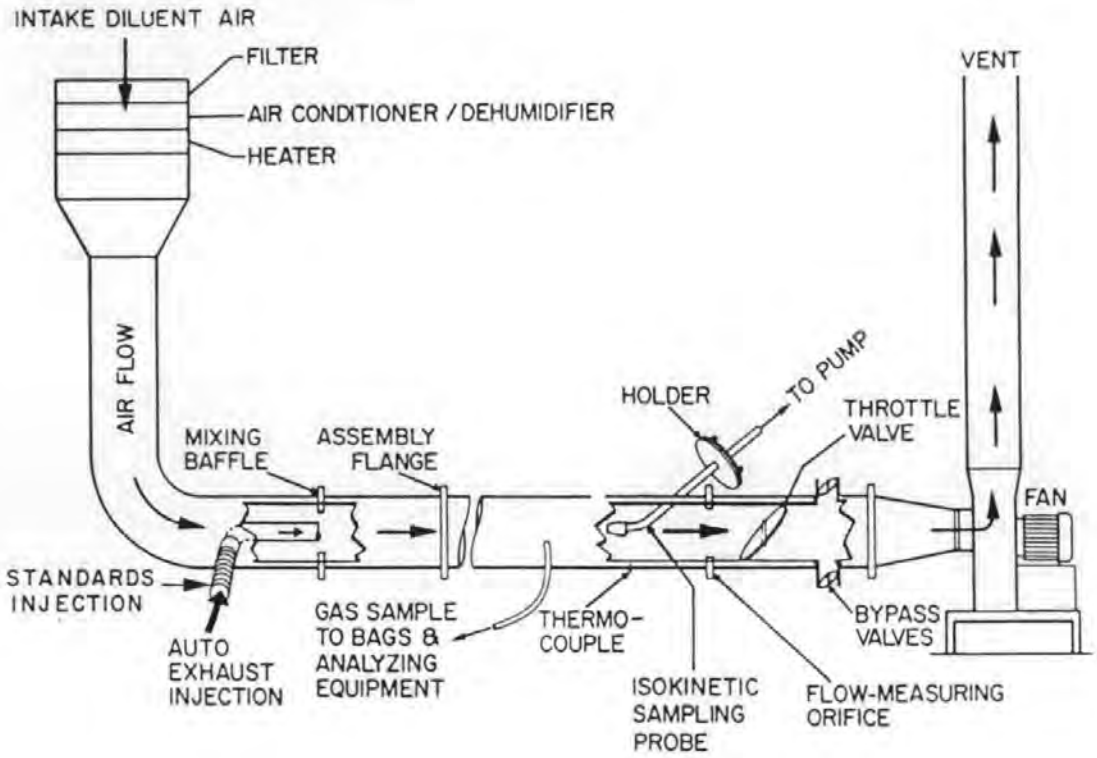


Figure 1.4 Construction of a standard dilution tunnel exhaust sampling system

Volatile hydrocarbons not adsorbed to particulate material in the exhaust, are routinely collected on traps containing organic polymeric adsorbent resins such as XAD2 and Chromosorb 102 (Schuetzle 1983, Williams et al. 1985). XAD2 has been recommended by Schuetzle because of its chemical inertness to nitrogen oxides. Nelson (1989) reported collecting polycyclic aromatic hydrocarbons (PAH) of up to 4 rings on a XAD2 resin trap maintained at 40-50°C. Williams (1985) also reported

that up to 50% of PAH containing four fused rings are in the vapour phase at diesel exhaust temperatures. These results illustrate the need for the use of resin traps in conjunction with dilution systems for the collection of PAH from diesel exhaust. A significant underestimation of the emission of these compounds may otherwise occur.

Filter sampling methods have been criticised because of the possibilities that exist for artifact formation. Sampling artifacts result from an extended exposure of the sample collected on the filter to hot reactive exhaust gases such as NO_x and ozone (O_3). The formation of artifacts may results in an underestimation of the emission rate of PAH. Pitts *et al.* (1978) were the first to identify sampling artifacts in diesel exhaust. Research by Beckman *et al.* (1989) demonstrated that the conversion of pyrene to nitro-pyrene increase with the length of time that the filter paper was exposed to the exhaust flow.

The second approach, described by Schuetzle (1983), involves the sampling of exhaust after it has been passed through a cooling system such as that used by Grimmer (1973). In this system the raw exhaust is drawn through a condenser before the cooled exhaust gases pass through a filter for particulate collection. Several condensation sampling systems have been reported in the literature (Kraft and Lies 1981).

Other methods of exhaust gas sampling have been reported. Chan *et al.* (1981) used electrostatic precipitators to sample diesel exhaust. Stenburg *et al.* (1983) developed a cryogradient system in combination with traditional filter sampling. Kruzel *et al.* (1991) sampled diesel exhaust gases close to the exhaust port using large vats of dichloromethane solvent. The exhaust was passed through three vats arranged in series cooled with water, CO_2 and liquid nitrogen respectively. The exhaust sample was concentrated after sampling by removing the dichloromethane (DCM) solvent using a Kuderna-Durnish apparatus.

This research has utilised a novel exhaust gas sampling device, Total Exhaust Solvent Stripping Apparatus (TESSA). The TESSA has been designed specifically for the analysis of organic species in automobile exhaust gases. The system consists of a stainless steel tower through which the exhaust gases are directed. A downwards counter-current flow of solvent strips organic species from the exhaust. The construction and mode of operation of the TESSA system is outlined in more

detail in Section 2.2. The TESSA system has been shown to collect volatile exhaust HCs more efficiently than conventional dilution tunnel methods without adsorbent traps (Trier *et al.*, 1988). This is essential if diesel exhaust is to be characterised accurately with respect to hydrocarbon emissions.

1.7 The nature of diesel exhaust emissions

Individual components of diesel exhaust emissions can be classified according to whether they are present in the exhaust as either gaseous, vapour phase or particulate emissions. The principal gaseous compounds present in diesel exhaust are CO_2, CO, NO_x, and SO_2. The major vapour phase component of diesel exhaust is water vapour which can react with gaseous oxides of nitrogen and sulphur in the exhaust to form nitric and sulphuric acids. Many unburned hydrocarbons (UHCs) are also present in the vapour phase at the elevated temperatures encountered in diesel exhaust emissions. Particulate emissions from diesels are a complex mixture of organic and inorganic components.

The following sections discusses the origin and chemical composition of these NO_x, SO_2, UHCs and particulates in detail. The origin of SO_2 in the emissions is discussed in conjunction with the formation of sulphate in Section 1.7.3.1.

1.7.1 Unburned hydrocarbons

The term 'hydrocarbons" is a general one which includes a wide range of organic pollutants that are primarily the result of incomplete combustion of hydrocarbons present in diesel fuel and lubricating oil Many hydrocarbons are sufficiently volatile to exist in a gaseous state at diesel exhaust temperatures. In the absence of sufficient particulate matter to bind with, PAH with up to four fused rings are present in the vapour phase of diesel exhaust in significant (Lane, 1989). Straight chain n-alkanes up to C_{18} are also present in the vapour phase in diesel exhaust as are nitrated and oxygenated derivatives of C_{10}-C_{12} hydrocarbons and two and three ringed PAH (IARC, 1989). Many hundreds of individual hydrocarbons have been identified in diesel exhaust Schuetzle, 1983; Nelson, 1989; Rogge *et al.*, 1993). These include aliphatic and aromatic hydrocarbons, that are present in diesel fuel and lubricating oil, and that have passed through the engine chemically unchanged, or that

have undergone partial oxidation to produce oxidized products such as aliphatic and aromatic ketones, quinones, aldehydes, carboxylic acids and nitro derivatives and many more (Schuetzle, 1983; Tong *et al.*, 1984b).

1.7.2 Nitrogen oxides (NO_x)

The term 'NO_x" is a general one and refers to the oxides of nitrogen; nitric oxide (NO), nitrous oxide (N_2O) and nitrogen dioxide (NO_2). NO is the primary oxide of nitrogen formed in combustion systems. NO is readily oxidised either during combustion or in the atmospheric environment to NO_2. NO in diesel exhaust may be formed from atmospheric nitrogen as thermal NO (Fig. 1.5), or from fuel bound nitrogen as 'prompt NO" (Fig. 1.6) (Pourkashani, 1992). The formation of thermal NO from molecular nitrogen is highly temperature dependent, and occurs only at temperatures greater than 1800K. At lower temperatures insufficient energy exists to break the N_2 triple bond and fix the nitrogen (bond dissociation energy 945kJ/mol; Handbook of Chemistry and Physics, 1992/3). The formation of thermal NO is also dependent on the oxygen concentration, increasing with greater O_2 partial pressures.

$$O^{\cdot} + N_2 \rightleftharpoons N^{\cdot} + NO$$

$$N^{\cdot} + O_2 \rightleftharpoons O^{\cdot} + NO$$

$$N^{\cdot} + OH \rightleftharpoons H + NO$$

Figure 1.5 Formation of thermal NO

Prompt NO can be formed in significant quantities in some combustion environments in low temperature, fuel rich conditions and short residence times. In this case breakage of the N_2 triple bond to yield reactive N atoms is catalysed by species resulting from fuel fragmentation e.g. $CH^{\cdot}$, $CH^{\cdot}_2$, $C_2H^{\cdot}$ etc.:

$$CH^{\cdot} + N_2 \rightleftharpoons HCN + N^{\cdot}$$

$$HCN + OH \rightleftharpoons CN + H_2O$$

$$CN + O_2 \rightleftharpoons NO + CO$$

$$N^{\cdot} + O_2 \rightleftharpoons NO + O^{\cdot}$$

Figure 1.6 Formation of "prompt" NO

The formation of "prompt" NO from nitrogen-containing organic compounds in the fuel is significant during diesel fuel combustion. Carbazole and its alkyl derivatives are the major nitrogen containing compounds present in diesel fuel (≈150ppm total, Williams *et al.* 1986). The extent of conversion of fuel-bound nitrogen to NO is dependent on the local combustion characteristics and the initial concentration of nitrogen bound compounds. The thermal decomposition of these compounds yields radicals such as HCN, N˙, CN˙, and NH which may undergo oxidation along reaction pathways similar to those for the formation of prompt NO (Pourkashani, 1992).

1.7.3 Diesel particulate composition

Diesel particulate matter has been defined by the EPA as any diesel exhaust effluent collected on a binderless glass filter in a dilution tunnel at temperatures below 125°F (52°C). The composition of a typical diesel exhaust particulate from DI and IDI light duty diesels are shown in Fig.1.5 (Ketcher and Morris, 1991). Diesel particulates typically contain three distinct components. These are unburned and partially burned fuel and lubricating oil components which constitute the solvent soluble organic fraction (SOF) of the particulate matter, an insoluble fraction of which soot is the major component, and sulphate and bound water. The contribution of each fraction to the total mass of the particulate matter varies greatly according to engine design and operating conditions. The contribution from the insoluble component of the particulate matter (i.e. soot) is generally greatest at high load where low air fuel ratios and high temperatures cause a greater conversion of fuel

carbon to elemental carbon (Kittelson, 1986). The contributions made by the SOF is generally more significant at low loads where combustion efficiencies are reduced due to the lower temperatures and factors such as poor fuel atomisation and fuel/air mixing and a greater proportion of the fuel survives (Hunter *et al.* 1989). The contribution of sulphate and bound water to the particulate is determined by the sulphur content of the fuel. Oxidation catalysts can increase the contribution of sulphate to the particulates (see Section 1.7.3).

1.7.3.1 Sulphate

Diesel fuels currently contain 0.1-0.2% sulphur by weight, with the maximum permissible sulphur content at present being 0.2% in accordance with EEC Directive 93/12/EEC. During combustion the organic sulphur is degraded by radicals such as H_2S, HS, S or S_2 and then oxidised via the SO radical to SO_2. Conversion of fuel sulphur to SO_2 is essentially quantitative. A small fraction of the SO_2 may be oxidised further to SO_3:

$$SO_2 + O_2 \rightleftharpoons SO_3 + O^{\cdot}$$

The reaction is exothermic and the equilibrium favours the formation of SO_3 at flame temperatures. Oxidation of SO_2 to SO_3 can take place homogeneously in the gas phase or heterogeneously on particulate surfaces. The main reaction responsible for homogenous oxidation is thought to be:

$$SO_2 + O^{\cdot} + M \rightleftharpoons SO_3 + M$$

SO_3 can combine with water vapour in the exhaust gases to form sulphuric acid vapour which can condense on the particulate as sulphate and add to the mass of the particulate. The mass of sulphuric acid is a factor of 3 larger than that of sulphur alone, and even small rates of conversions can result in a significant particulate mass. Most oxidation takes place in the gas phase with a small contribution from oxidation on the soot particles (Clarke, 1992).

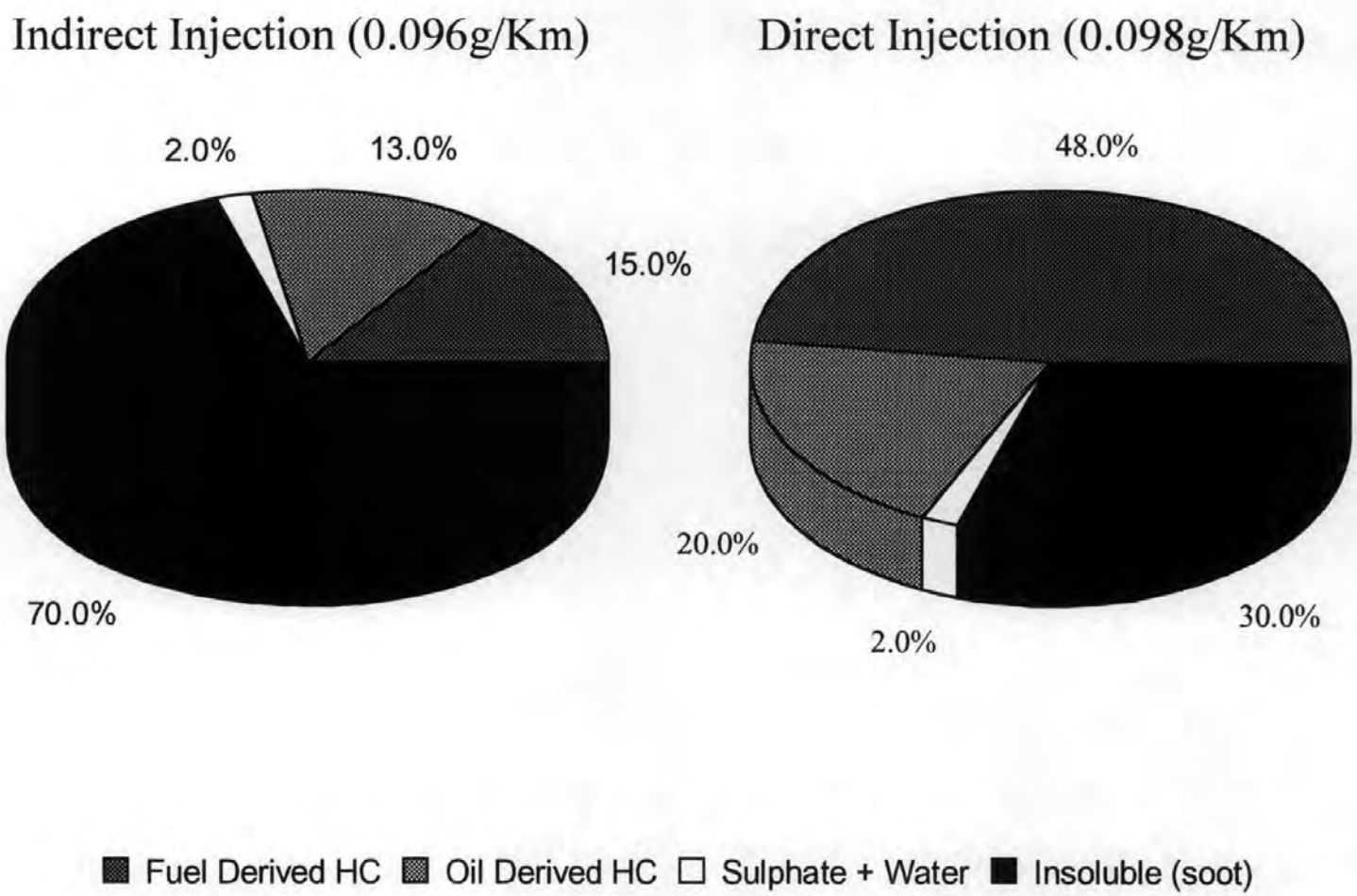


Figure 1.7 Composition of diesel exhaust particulates from 1.8L DI and IDI diesel engines

The influence of fuel sulphur to particulate emissions is well understood (Baranescu, 1988; Stradling *et al.*, 1993). For all engine types the contribution of fuel sulphur to particulate sulphate and associated bound water is linearly dependent on the fuel sulphur content with typical conversion factors of between 1% and 3% (Clarke, 1992; Stradling *et al.*, 1993). For diesel vehicles fitted with oxidation catalysts the rate and efficiency of the conversion of SO_2 in the exhaust stream to sulphate can be greatly increased and can add substantially to the mass of the particulate (Naber *et al.*, 1993; Brear *et al*, 1992). Oxidation catalysts with improved selectivity are being developed (Floysand *et al*, 1993). In an attempt to help the development of catalyst technology a reduction in fuel sulphur content to 0.05% by mass has been specified (EEC Directive 93/12/EEC). Reductions of fuel sulphur content from 0.15% to 0.05% have been shown to reduce the mass of the particulate from a diesel passenger car by 15% (Naber *et al.*, 1993) although other workers have claimed a reduction of only 2.3% for a similar decrease in fuel sulphur content (Betts *et al.*, 1992).

1.7.3.2 Insolubles (soot)

The occurrence of soot in exhaust effluents is a consequence of the incomplete combustion and reduction of the hydrocarbon fuel and occurs in almost all combustion systems. In diesel engine combustion, soot is derived predominantly from pyrolysis of diesel fuel hydrocarbons. There is a small, but significant contribution, from lubricating oil hydrocarbons (Essig *et al.*, 1990). Essig *et al.* (1990) estimated the lube oil contribution to the carbon fraction of the particulate to be between 15% and 20%. Individual fuels have different tendencies to form soot. The molecular structure of the fuels is an important parameter determining the amount and rate of soot formation. Others include the fuel/oxidant ratio, the gas temperature and the pressure. This sooting ability is often expressed in terms of a critical sooting equivalence ratio (ϕ_c).

The sooting tendency of aromatic fuels is greater than that of aliphatic fuels (Olsen and Pickens, 1984). Aromatic molecules are essential intermediates in the formation of soot, largely owing to the ability of the aromatic structure to stabilise intermediate species (Pradho and Lahaye, 1983). The thermodynamic stability of

PAH enables them to survive the high temperatures associated with diesel combustion. The degree of stabilisation increases with the size of the conjugated system (Stein, 1985). In aliphatic fuels, the initial aromatic structures have to be synthesised from non-aromatic precursors. In this situation, the rate of formation of PAH will determine the rate at which the soot nuclei are produced which in turn controls the mass emission rate of soot. Olsen and Pickens (1984) assigned numerical rankings to the sooting tendencies of individual molecules:

acetylene 0; alkenes 25-26; isoalkanes 61-70; n-alkanes 34-76
alkylbenzenes 83-91; naphthalenes 100.

The high ranking of naphthalene is a result of the ease of formation of the naphthalene radical by the facile abstraction of a hydrogen. The naphthalene radical has been identified as a key intermediate in the growth of soot nuclei (see Fig. 1.11). 1-methylnaphthalene has been reported as one of the most prolific sooting compounds (Glassman, 1988), presumably for similar reasons. Nelson (1989) has identified several of the suggested key intermediate species in the growth of large polyaromatic species (*e.g.* styrene, phenylacetylene) in diesel exhaust emissions collected on an XAD_2 resin trap.

The actual process of soot particle formation as described by Haynes and Wagner (1983), consists of two more or less separate stages:

a. nucleation/particle inception
b. growth and agglomeration

The first stage in soot production, nucleation, involves the conversion of neutral fuel molecules containing only a few carbon atoms into small nuclei containing many hundreds of carbon atoms. The nuclei are aromatic in nature and it is generally agreed that condensed polycyclic aromatic compounds are the main constituents of these particles (Lam, 1988). The early particles may have diameters as small as 2nm (Haynes and Wagner, 1981) and have a greatly increased carbon/hydrogen ratio (C/H ratio) of around 10, compared to a C/H ratio in the fuel of 0.3-0.5 (Cullis, 1986). The C/H ratio continues to increase as the nuclei dehydrogenate (age) in the high temperature flame. The carbon nuclei formed in the nucleation stage have highly

reactive surfaces and readily capture hydrocarbons in the gas-phase by physical and chemical means. This is the growth stage in the formation of soot particles. In the later stages of soot formation, particles agglomerate to form soot.

1.7.3.3 The solvent organic fraction of diesel exhaust particulates

The solvent organic fraction of diesel exhaust particulates comprises mainly unburned and partially oxidised fuel and lubricating oil components. The contribution from the two sources is influenced by engine conditions, especially with respect to load. The fuel contribution to the SOF is greatest at low power where factors such as poor fuel atomisation lowers the combustion efficiency (Andrews, 1993). Lube oil contribution is greatest at low load and high speeds where oil consumption is high but in-cylinder temperatures are insufficient to completely oxidise the oil (Essig *et al.*, 1990). Cartillieri and Tritthart (1984) investigated a range of diesel engines and found the lubricating oil contribution to the SOF to vary between 19% and 88%, whilst Hilden and Mayer (1984) found the contribution to vary between 30% and 50%. Most lube oil escapes to the cylinder through the ring gap, but contributions from leakage around the ring groove and between the ring and the liner can also be significant (Wong and Hoult, 1991; Essig *et al*, 1990; Milazo and Bidini, 1992). A small amount of oil may also enter the combustion chamber down the valve stems (Deuring, 1981).

A number of analytical techniques have been developed to estimate the SOF of diesel particulate. Traditionally, soxhlet extraction with solvent has been used to determine the composition of particulate material and remains the standard test against which other methods are compared. Cuthbertson *et al.* (1987) developed a method using gas chromatography (GC) with solid sample injection. In this method, a portion of the filter paper was inserted into the injector port of the GC and the temperature of the injector was raised isocratically. Hydrocarbons were thermally desorbed from the filter and separated on the GC column. A cut-off temperature was specified in order to distinguish between lubricating oil and fuel derived hydrocarbons. Halsall *et al.* (1987) used a purged vacuum oven sublimation technique. The SOF is determined by placing the weighed filter in an oven which is evacuated and heated to about 200°C for eight hours. The filter is then reweighed

and the weight loss is a measure of the SOF of the particulate. Thermogravimetric analysis (TGA) has in recent years become widely used for SOF determination (Abass *et al.*, 1991). In TGA analysis the filter is placed in the TGA and heated to 550°C in an inert atmosphere. The weight loss is the mass of the SOF of the particulate. Once the mass of the SOF is known air is allowed into the TGA and the residual carbon is oxidised, the loss in weight representing the carbon content of the particulate. TGA enables analysis of the continuous weight loss of the sample and has been used to determine the contribution of fuel and lubricating oil to the SOF (Abass *et al.* 1991).

1.8 Factors affecting diesel exhaust emissions

A wide variety of factors influence the amount and composition of the emissions from diesel powered vehicles. Of these, engine design and technology has the greatest influence on the emission characteristics for a given vehicle. More recently, however, it has been demonstrated that fuel quality may also have a significant influence on the emissions from modern diesels.

1.8.1 Engine design and technology

To date, the process of lowering diesel emissions in step with ever tightening emission legislation has largely been achieved through improvements in engine design and technology. Continued advances in this field will remain central to the effort to comply with future emissions legislation. The primary concerns regarding diesel exhaust emissions are with respect to NO_x and particulate emissions. A fundamental trade-off exists with respect to these pollutants in diesel combustion and the challenge to the engine designer is to develop engine technologies which simultaneously reduce emissions of both pollutants.

NO formation occurs predominantly in the lean flame region during the premixed phase of combustion, where both flame temperatures and local oxygen concentrations are high (Fig. 1.8). Particulates on the other hand are formed predominantly during the diffusion burning period. Actions designed to reduce NO_x, lower the proportion of pre-mixed combustion, and consequently have the effect of increasing the diffusion burning period thereby increasing particulate formation and

vice versa. Technologies such as turbocharging and high pressure fuel injection can, by careful calibration, improve this fundamental trade-off with minimum loss of fuel economy (Lida *et al.*, 1988; Horrocks, 1993).

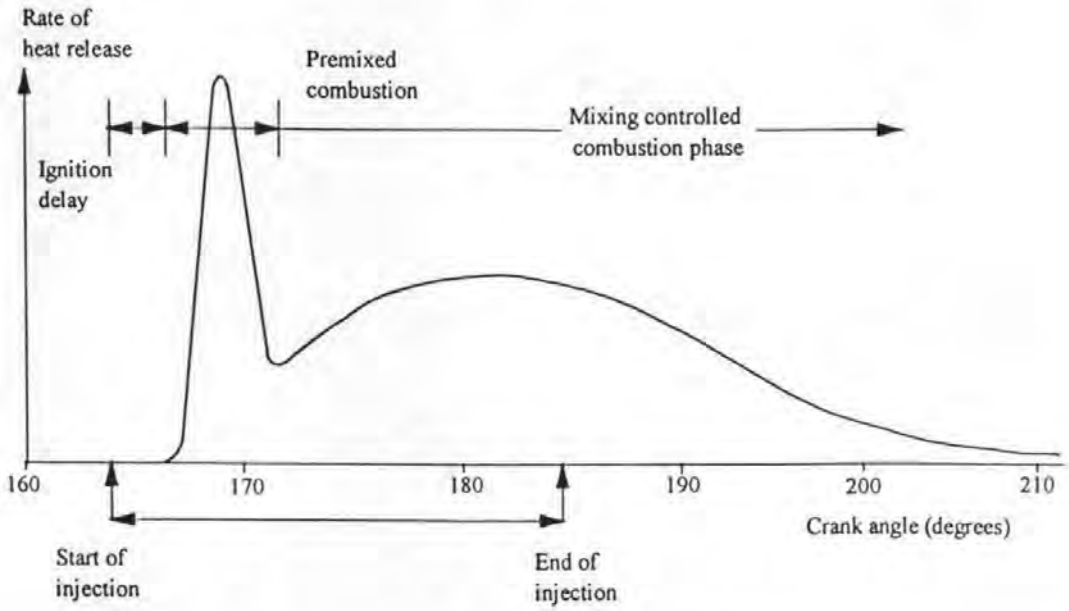


Figure 1.6 Flame temperature distribution during the diesel combustion cycle

Turbocharging has been reported to offer the best compromise in emissions reduction, (QUARG 1993) and has the added advantage of increasing the specific power output of the engine. The major contribution of the turbocharger is to reduce emissions of incomplete products of combustion. This is owing to the increased charge of air supplied by the turbocharger which facilitates a more complete oxidation of fuel hydrocarbons and particulates (Hunter *et al.*, 1989). A greater oxygen concentration also reduces the ignition delay period with turbocharged combustion. This lowers the amount of fuel injected before ignition which reduces the initial spike of heat release during the pre-mixed combustion phase. The lower temperatures counteract the effect of increased oxygen in the cylinder and the formation of NO_x is controlled.

Turbocharging, whilst advantageous from the point of view of reducing exhaust emissions and improving fuel consumption, has the disadvantage of reducing torque at low engine speeds and can also lessen engine response. For this and other

reasons, naturally aspirated engines are likely to remain in demand for the time being (Shundoh *et al.*, 1992). Technologies designed to reduce emissions from naturally aspirated diesels are also required to meet new emission limits. The main advances in this field in recent years have been in the development of new fuel injection systems and in combustion chamber design.

In DI diesels, a steady trend towards increasing fuel injection pressures has occurred. Diesel injectors designed to operate at higher pressures have been shown to reduce particulate emissions (Kato *et al.* 1989, Shundoh *et al.*, 1992). The primary effect of increasing fuel injection pressures is to enhance fuel atomisation and air entrainment in the fuel spray during the diffusion stage of combustion which improves fuel/air mixing. As with turbocharging, high pressure injection increases the initial combustion temperatures through the rapid compression of burned gases (Kobayashi *et al.* 1992). Higher flame temperatures improve the oxidation of hydrocarbons and particulates and these effects are manifest in a decrease in emissions of products of incomplete combustion. Recent research has shown that reductions in particulate emissions, through high pressure fuel injection, have not increased the emission of NO_x (Shundoh *et al.*, 1992).

The actual design of the injector in terms of the number of injector holes, spray direction and composition has been shown to have a major impact on the emission characteristics (Van Gerpen *et al.*, 1985; Corcione *et al.*, 1991). Centralised fuel injection in DI diesels has been reported to reduce emissions of NO_x by virtue of lowering swirl, and hence air-fuel mixing, during the premixed burning phase (Horrocks, 1993). Conversely, high swirl is desirable in the later stages of combustion to control HC and particulate emissions, although too large an induced swirl effect may create overlean conditions thereby increasing HC emissions (Van Gerpen *et al.* 1985). Konno *et al.* (1992) reported the use of an auxiliary combustion chamber into which fuel was injected during the main period of combustion. The flow of gases from this chamber into the main chamber created strong turbulence in the main stage of combustion. The authors reported a significant reduction in HC and particulates without an increase in NO_x.

Despite the advances that have been made, the NO_x/particulate trade-off remains and reductions in particulate emissions gained through technologies such as

turbocharging and high pressure fuel injectors, are generally paid for at the expense of small increases in NO_x emissions. Technologies aimed at improving combustion efficiency may, however, be used to offset the detrimental effect of introducing technologies aimed specifically at reducing NO_x emissions, such as retarded injection timing and exhaust gas recirculation (EGR). EGR involves directing a proportion of the exhaust gases back into the manifold of the combustion chamber. The reduced supply of oxygen lowers the rate of formation of NO_x in the cylinder. 'Hot EGR' where the temperature of the recirculated gases is kept at a high level has been shown to simultaneously reduce NO_x and particulate and HC emissions (Durnholz *et al.*, 1992). Similarly, retarded injection timing can be used to control NO_x. This has the effect of reducing the amount of fuel burned under pre-mixed conditions and lowers peak flame temperatures that occur at this stage of the combustion cycle thereby reducing NO_x emissions (Lida *et al.*, 1988).

Engine management is a comparatively new technology that offers great potential for reducing emissions. Traditionally, comparatively expensive engine management technologies have not been fitted to small diesel vehicles since the profit margin on these engines is smaller relative to the larger diesel engines. In order to meet the new legislative limits however, engine management systems are increasingly being fitted to smaller diesel engines. Engine management has enabled precise control over the supply of fuel to the cylinder to optimise the air/fuel ratio for the cleanest combustion at specific engine conditions. The rate of EGR can also be controlled in this way to optimise the trade-off between emissions of incomplete products of combustion and NO_x.

1.8.2 Exhaust gas after-treatment

Many manufacturers are turning to exhaust after treatment systems in an effort to break the NO_x/particulate trade-off which is necessary to comply with future emission limits. Three-way catalysts cannot be fitted to diesels vehicles since they require near to stoichiometric conditions to operate. Instead, attention has focused on the use of oxidation catalysts and particulate traps. Through-flow oxidation catalysts reduce emissions of unburned hydrocarbons(UHC), CO and particulate emissions by oxidation of adsorbed organics, and are the preferred exhaust after-

treatment for LDVs in Europe (Beckmann, 1992; cited by Zelenka and Herzog, 1993). Emissions of PAH have been reported to decrease with the use of flow-through catalysts (Andrews *et al.*, 1987). Oxidation catalysts have no effect on the carbonaceous centre of the particulate since this requires high temperatures for complete oxidation of the carbon to occur (550°C without a catalyst; Davies *et al*, 1993). The use of catalysts reduces the temperature required to fully oxidise UHC and CO and thus improves performance at low exhaust temperatures. Oxidation of SO_2 to sulphate can be an undesirable side-effect of the catalytic activity. The development of selective catalysts has been shown to overcome this problem (Davies *et al.*, 1993; Brear *et al.*, 1992).

Where control of diesel particulates is required the use of particulate traps is necessary. Diesel particulate traps are desirable from the position of allowing increased rates of EGR (so-called "clean EGR"). This offers benefits in terms of reduced engine wear over time and improved NO_x emission rates. Regeneration of the particulate traps at low exhaust temperatures has proved a major hurdle in their development. Various solutions to this problem have been proposed including external heating sources and addition of catalysts to the fuel.

Recent research has also focused on the catalytic reduction of NO_x emissions. Diesel combustion operates with an excess of air hence the necessity associated with this development is to achieve NO_x reduction in a net oxidising environment. The use of UHC present in diesel exhaust in conjunction with a suitable catalyst offers an elegant solution (Engler *et al.*, 1993; Konno *et al.*, 1992). However, UHC emissions from modern diesels are low and it may be necessary to intentionally increase their emission to achieve the necessary reduction of NO_x.

1.8.3 The effect of diesel fuel quality on diesel exhaust emissions

Diesel fuel quality has until recent years had comparatively little effect on the overall emissions from diesel vehicles. With the development of new ultra-low emitting diesel engines however, the relative contribution to the emissions from the diesel fuel itself will become proportionately greater. Consequently, efforts are being made to develop 'clean diesel fuels' that will contribute less to diesel emissions.

Diesel fuel quality can be specified according to a number of physical and chemical properties of the fuel. With regard to exhaust emissions, the principal fuel qualities of interest are density, cetane number, volatility, aromatics content, sulphur content and viscosity. At present no single standard governs the quality of diesel fuel in the EC with the exception of sulphur content. Sulphur contributes directly to the mass of the diesel particulate (see Section 1.6.3.1.) and has been limited to 0.3% by weight since 1975 (EC Directive 75/716/EEC). In order to comply with the more recent limits on particulate emissions, the sulphur content of diesel fuel must be reduced to 0.2% by weight by 1 October 1994 and 0.05% by 1 October 1996. In Britain specifications for automotive diesel fuel are set in British Standard, BS 2869: Part 1: 1988 (British Standards Institution, 1988). This standard is not legally enforceable. The European Committee for Standardisation (CEN) has developed a standard diesel fuel specification for introduction in 1996.

The influence of diesel fuel properties on exhaust emissions has been investigated by a number of workers (Tritthart *et al.*, 1993; Floysand *et al.*, 1993; Naber *et al.*, 1993; Betts *et al*,. 1992). Tritthart *et al.* (1993) tested advanced DI and IDI diesel engines equipped with oxidation catalyst, EGR, turbocharging and intercooling, on several commercially available fuels and over European, American and Japanese test cycles (FTP 75, FTP 72 hot; ECE 15 + EUDC cold & hot; Japan 10.15 hot). Their results show that individual fuel parameters can have significant effects on the overall emission rates from advanced diesel engines. In general the DI engine had greater emissions of HC, CO and NO_x than the IDI diesel engine. The trend was not as prominent for total particulates. Increases in both the aromatic content and density of the fuel caused an increase in total particulates and gaseous emissions of CO and HC in both engines. The trend was more noticeable for the IDI engine. Emissions of HC and NO_x for both DI and IDI engines were found to decrease with an increase in the fuel cetane number. Above a certain cetane number however, the particulate emissions from the DI engine began to increase because of a decrease in the period of lean pre-mixed burning in the combustion chamber. Due to the complex intercorrelation of fuel properties, these authors were unable to relate the emissions trends to any single fuel parameter. They concluded that fuels with cetane number >53 and density <0.835 would be advantageous in reducing emissions,

although too high a cetane number could detrimentally affect the emissions from DI diesels.

In order to investigate the effects of individual fuel parameters on diesel emissions, various workers have attempted to break the correlation between individual fuel properties. Betts *et al.* (1992) using an IDI passenger car fitted with EGR investigated the emissions from a series of 37 fuels specifically designed to decorrelate the influence of cetane number, aromatics content and density, and also of sulphur content by doping fuels with tertiary butyl disulphide. The authors concluded that density was the key property influencing the emissions of particulates. They ascribed the influence of density on emissions to an overfuelling effect causing instantaneous lower air/fuel ratios and hence less complete combustion. Cetane number and aromatics content had a statistically insignificant effect on particulate emission. Sulphur content was found to have a minor influence on particulate emissions. A decrease in sulphur content from 0.2% to 0.05% reduced particulate emissions by only 2.3%. In later tests, on the same car fitted with an oxidation catalyst (Floysand *et al.* 1993), similar fuel effects on emissions were demonstrated. However, fuel effects had much less of an effect in reducing emissions than the catalyst itself. Total emissions of HC's, CO and particulates were reduced considerably by the catalyst (59-77%, 81-95% and 23-54% respectively).

Until recently, total aromatic content was considered to be a major factor in influencing particulate emissions from diesel engines, largely because of the role of aromatic species as precursors in soot formation. More recently it as been suggested that higher soot emission rates, previously attributed to aromatic content of fuels, could equally well be explained in terms of the density of those fuels. However, total aromatic content may be the wrong parameter with which to assess the effect of aromatic species in the fuel on particulate emissions (Floysand *et al.*, 1993; Naber *et al.*, 1993). The polyaromatic content of a fuel may be a more informative measure. There is a high correlation between density and polyaromatic content, hence the overfuelling phenomenon proposed (Stradling *et al.*, 1993), may be in part, owing to a sudden increase in the polyaromatic species in the combustion chamber. Naber *et al.* (1993) also attempted to decorrelate diesel fuel parameters to study the individual effects of fuel parameters on particulate and NO_x emissions. The study was

performed on a modern IDI passenger car diesel equipped with EGR and an oxidation catalyst. The authors concluded that the main factors influencing emissions were fuel density and sulphur content in agreement with other workers (Betts *et al.* 1992; Floysand *et al.*, 1993). The authors also found that the variation in total particulates was dependent on polyaromatics content, with an increase in the polyaromatic content leading to an increase in the mass of the particulate. No distinction was made between the influence of di and tri-aromatics in this study. Mono-aromatics were found not to influence the particulate matter content of the exhaust emissions.

1.8 4 Future diesel fuel requirements

Fuel manufacturers will be hard pressed to produce diesel fuel at the refinery which can conform to increasingly stringent specifications. Whilst the quality of the refineries pool of diesel fuel will decrease in the future, the demand for diesel fuel is likely to continue to increase (Hutcheson and Van Passen, 1990; Lindsay *et al.*, 1992; Rivers *et al.*, 1993). The contradiction between the requirement, and the available oil, will almost certainly require an increased catalytic cracking, hydrogenation and desulphurization capacity on the part of the fuel producers. This however, has environmental implications in terms of additional energy consumption which equates with CO_2 emissions. In addition, diesel fuels that have undergone such treatments have been reported to be less stable (Batts and Fathoni, 1991). The effects of certain fuel parameters on diesel emissions is not yet proved (i.e. diesel aromatics). Specifying diesel fuel quality with respect to parameters, which have not been shown to reduce emissions, may simply waste resources and energy. Even so, certain countries e.g. Sweden and California have introduced specifications for PAH and aromatic content of fuels (Table 1.5).

Table 1.5. Advanced Diesel Fuel Quality Standards

Property/Specification	CARB* 1993	CEN** 1996	Sweden		
			Class 1	Class 2	Class 3
Sulphur content, (wt %max)	0.05	0.05	0.001	0.005	0.300
Aromatics, (vol % max)	10	----	5	20	----
PAH, (vol % max)	1.40	----	0.02	0.10	----
Cetane number (min)	48	49	50	47	----
Cetane index, (min)	40	46	----	----	----
Density, (kg/m^3) at 15°C	830-860	820-860	800-820	800-820	800-860
IBP °C (min)	170	----	180	180	180(10%)
95% b.pt. (°C max)	320 (90%)	370	285	295	340-370
* Reference fuel **Proposed					
CARB: California Air Resources Board; CEN: European Committee for Standardisation					

1.9 Health effects of diesel exhaust emissions

The health effects of diesel exhaust have been the focus of much research during the last decade since the original findings that diesel exhaust emissions were potentially mutagenic (Huisingh, 1978). In 1989, diesel engine exhaust was officially classified as a probable human carcinogen (IARC).

1.9 1 Health effects of diesel particulates

The main perceived risk associated with diesel emissions in the last decade has been the role of diesel exhaust particulate matter in causing pulmonary cancers. Whilst diesel emissions of noxious gasses such as NO_2 and SO_2 are a cause for concern especially for more susceptible individuals such as asthmatics, their effects tend to be short-term and reversible as opposed to diesel particulates which may persist in the lungs of victims.

Diesel exhaust particulates are readily inhaled owing to their small size (0.1-0.3μm diameter) and deposited in the unciliated regions of the lung, (Scheepers and Bos, 1992). Evidence from animal studies performed during the 1980's served to emphasise the risk to humans from diesel exhaust particulates. Recent reviews on older research however, has cast doubt on some of the assertions made in earlier studies.

Kotin *et al.* (1954) was the first to demonstrate the potential carcinogenicity of diesel exhaust particulates when he found that mice developed skin tumours in epicutaneous tests with both gasoline and diesel exhaust condensates. During the last

decade the potential carcinogenicity of diesel exhaust has been confirmed in several studies, using experimental animals (*e.g.* Mauderly *et al.*, 1986; Ishinishi *et al.* 1986). The carcinogenicity of diesel particulate matter has largely been attributed to the presence of organic species adsorbed to the surface of the particulate. This includes PAH's, some of which are known human carcinogens (e.g. benzo[α]pyrene and indeno[c,d]pyrene), and nitroarenes (e.g. 1-nitropyrene). More recently the validity of the experimental data presented in animal experiments has been questioned (Stober, 1992; Gerde *et al.*, 1991). The high concentrations that these animals were subjected to are in excess of that which workers with even a high occupational exposure to diesel exhaust would normally encounter. In addition, significant tumour rates were encountered only in animals with a high particulate burden in the lung. Recent research has shown that the induction rate of lung tumours in rats from pure carbon (carbon black) is at least as great as that for diesel soot (Heinrich *et al.*, 1990; Nikula *et al.* 1993). This, and similar evidence, has led the scientific community to recognise that genotoxic species, associated with diesel exhaust particulates, in causing cancers, is linked to the nature of the particulate, the burden in the lung and the rate and mechanism of clearance of the particle (Scheepers and Bos, 1992; Gerde *et al.* 1991). Synergistic effects with gaseous exhaust effluents has also been suggested (Scheepers and Bos, 1992). Whilst the evidence for the carcinogenic effect of diesel exhaust particulates has recently been questioned, equally recent research has concluded that air particulate matter from all sources, of less than 10μm in diameter (termed PM_{10}), may be associated with increased mortality (Pope *et al.*, 1992). In view of the fact that diesel exhaust particulate matter makes a substantial contribution to the total atmospheric particulate burden, particularly in urban areas (QUARG, 1993), the effect of diesel particulates on public health remains a considerable cause for concern.

1.9.2 Epidemiological evidence

Epidemiological data from many studies performed during the last decade have been used to evaluate the risk posed by diesel exhaust to humans. To date epidemiological evidence has proved inconclusive in evaluating this risk. In part this has been due to the difficulty in identifying populations that have received sufficient

exposure to diesel exhaust to warrant study, despite the fact that diesel engines have been in use for many decades. In addition, contributing factors to the incidence of cancer such as smoking and exposure to asbestos, are difficult to remove from the equation in order to derive meaningful results. Stober (1992) has stated that, 'the epidemiological tool is too coarse to find a reliable small effect caused by diesel exhaust."

Garshick *et al.* (1987 and 1988) in a case-study of railroad workers occupationally exposed to diesel exhaust, claimed an increased risk of lung cancer of 41% for workers exposed to diesel exhaust relative to low risk, non-exposed workers. Hansen, (1993) observed an increased mortality in truck drivers from respiratory cancer and multiple myloma, relative to other unskilled male labourers and concluded that exposure to diesel exhaust contributed to the increased lung cancer risk. Emmelin *et al.* (1993) in a case-study of dockyard workers also concluded that diesel exhaust increased the risk of lung cancer in these workers. The effect was independent of smoking habits. In contrast, Guillemin *et al.* (1992) assessed the risk posed by occupational exposure to diesel exhaust for truck drivers and demonstrated no link between exposure to diesel exhaust and lung cancer.

1.10 The origin of PAH in diesel exhaust emissions

The primary aim of the present study has been to investigate the origin of PAH in diesel exhaust emissions. This section has been devoted to a more detailed review of the possible sources of PAH in diesel exhaust.

Diesel PAH are present in diesel exhaust emissions both adsorbed to and absorbed in particulate material as part of the SOF and in a gaseous state. Longwell (1982) identified four sources for PAH in the exhaust gases of combustion systems:

1. from unburned fuel
2. from unburned lubricating oil
3. from fuel that has undergone pyrolysis but has not passed through a flame zone
4. from PAH produced during combustion (pyrosynthesised PAH)

The PAH contribution from these sources is illustrated in Figure 1.9. Unburned fuel and pyrosynthesis are the major contributors of PAH to the exhaust emissions of

diesel engines. The relative contribution of PAH from these sources has proved the subject of much debate and will be discussed in the following sections.

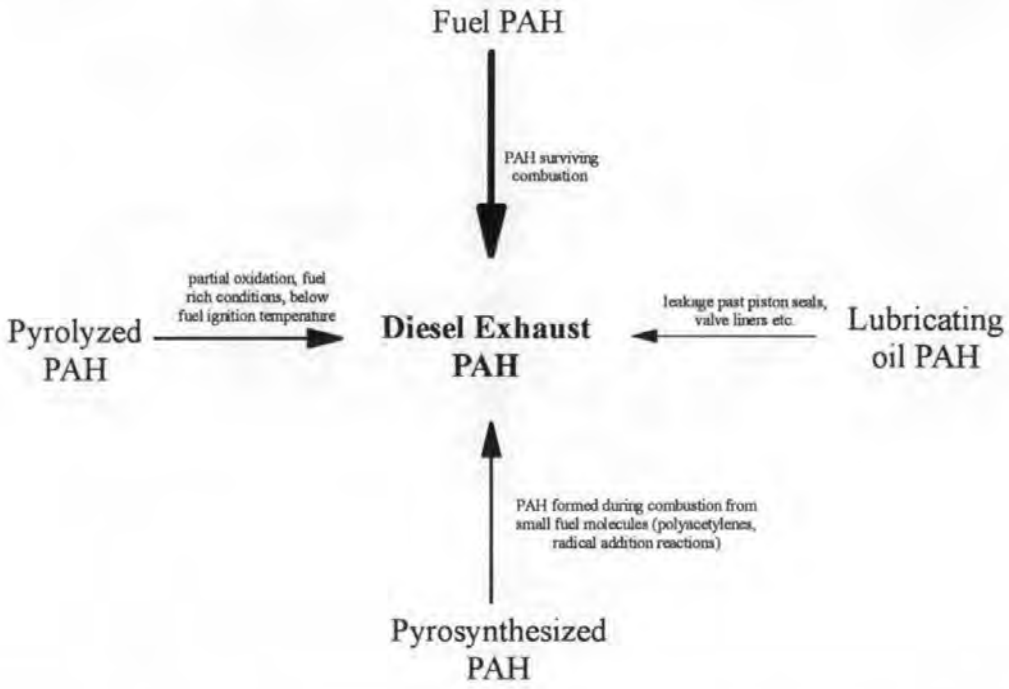


Figure 1.9 The sources of PAH in diesel exhaust emissions

1.10 1 Diesel fuel PAH surviving combustion

Diesel fuel contains a wide range of PAH. The predominant PAH in UK diesel fuels are naphthalenes, fluorenes and phenanthrenes and their alkyl homologues (Williams *et al.*, 1986). The PAH composition of the diesel fuel used in this research is presented in Section 2.2. Alkyl naphthalenes are the most abundant group of PAH in all diesel fuels followed by alkylated fluorenes and phenanthrenes. Diesel fuel contains substantial amounts of heterocyclic PAH especially sulphur containing PAH, such as dibenzothiophene and nitrogen-containing PAH, such as carbazole. Similar PAH compositions for diesel fuel, originating from different refineries and crude oil stocks, have been reported (Nelson, 1989). Examples of the structures of the major PAH found in diesel fuels are shown in Figure 1.10.

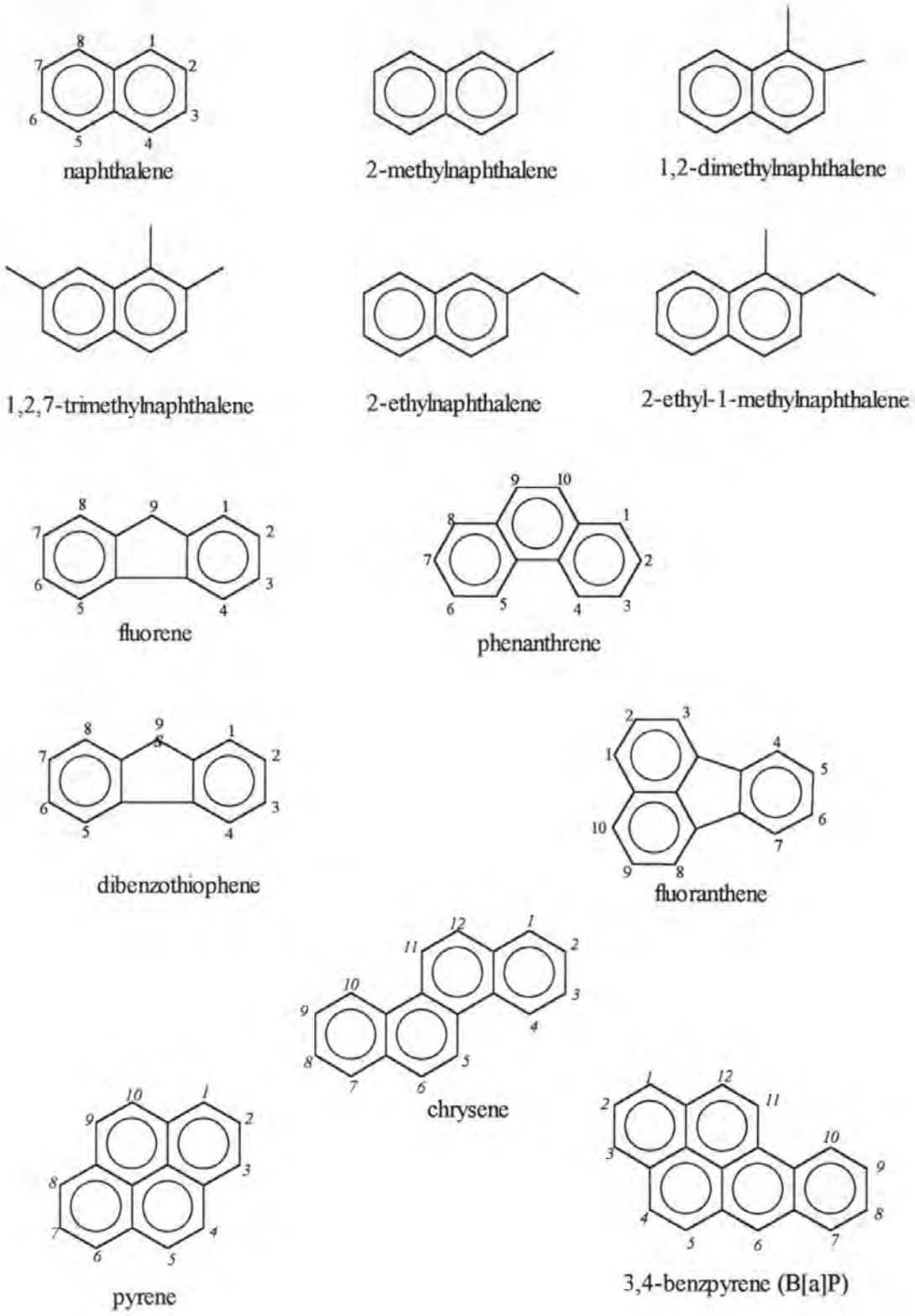


Figure 1.10 Structures of major PAH present in diesel fuel

The similarity between the composition of the fuel and the SOF of exhaust particulates with respect to PAH was noted in early research in this field and led to the conclusion that PAH in automotive exhaust were primarily unburned fuel components (Begeman and Colluci, 1970). Andrews *et al.* (1983) was the first to perform a detailed PAH analysis of both the fuel and the emissions. In that work the authors performed a mass balance on PAH consumption and emission in a four stroke single cylinder diesel and concluded that PAH in the exhaust originated primarily from unburned fuel. This result was confirmed in later work on a modern DI diesel (Williams *et al.*, 1989). The importance of the unburned fuel route to PAH emissions in the exhaust has been demonstrated by a number of other workers (Barbella *et al.*, 1989; Abbass *et al.*, 1988; Henderson *et al.*, 1984; Williams *et al.*, 1987). The results from these experiments however, do not refer strictly to fuel survival. Rather, these results refer to a total recovery of PAH and include all possible sources by which PAH may have contributed to the emissions.

The mechanisms whereby fuel may by-pass the high temperature flame zones in the cylinder, to be emitted unaltered to the exhaust, are well established. Fuel injected late in the combustion cycle from the nozzle sac (the residual sac volume), that is poorly atomised, will experience a low air/fuel ratio and may survive the combustion process. Fuel droplets that impinge on the wall of the combustion chamber will experience reduced combustion temperatures and may escape oxidation (Andrews, 1992). These engine conditions are realised predominantly when the engine is idling or at low load. High engine speeds generate overswirl and shorten the period over which combustion may occur and can also increase emissions of unburned hydrocarbons (Rao, 1993; cited Collier *et al.*, 1994)

1.10.2 Formation of PAH during combustion (pyrosynthesis)

The term pyrosynthesis refers to the process whereby PAH molecules are formed in the flame zone as a consequence of the kinetics of the combustion reaction. The pyrosynthesis of PAH during diesel combustion, occurs in high temperature zones where air/fuel mixtures are inside the flammability limits, and is a consequence of the chemical kinetic processes occurring during combustion. Polycyclic aromatic hydrocarbons may be formed from any type of hydrocarbon fuel. The specific PAH

formed, and their rate of production, will vary with fuel type and engine operating conditions. Control of PAH formed during combustion, may not be feasible, since their formation is a consequence of the chemical kinetic processes of diesel combustion. Improvements in engine design and fuel composition may lower the amount of combustion-formed PAH contributed to the exhaust, but are unlikely to eliminate this source entirely.

A large number of combustion experiments have demonstrated the propensity of PAH to be pyrosynthesised from a variety of hydrocarbon chemical classes during combustion (Badger and Spotswood, 1960; Crittenden and Long, 1973; Cole *et al.*, 1984; Lam *et al.*, 1988; Harris *et al.*, 1988; Hamins *et al.*, 1991). Virtually all the hydrocarbon types studied individually in these experiments are also present in diesel fuel. The possible pyrosynthetic routes to the formation of PAH during diesel combustion are manifold. Experiments have shown that the formation of PAH may be classified into two major pyrosynthetic pathways, distinguished according to the chemical class of the hydrocarbon precursor (Prado and Lahaye, 1983). These precursors are grouped into aliphatic and aromatic hydrocarbons. Most commercially available diesel fuels have an aromatic hydrocarbon content of between 20% and 30% (v/v). PAH constitute approximately 5-7% of the total aromatics the remainder consists primarily of substituted benzenes. The remaining 70% of diesel fuel is comprised of aliphatic hydrocarbons. Straight-chain alkanes (n-alkanes) varying in carbon number from C_9-C_{30} are the major aliphatic species present. A wide range of branched alkanes are also present (Gough and Rowland, 1990).

1.10.2.1 Formation of PAH from aliphatic hydrocarbons

In the combustion of aliphatic fuels any aromatic species produced must be formed from aliphatic precursors. There is general agreement that the dominant pathways to PAH production involve free radical routes. Other mechanisms involving ions and Diels-Alder type addition reactions have also been proposed (Barnard and Bradley, 1985). At high temperatures aliphatic hydrocarbons are cracked and dehydrogenated to smaller saturated molecules and olefins (Tosaka *et al.*, 1989). The further pyrolysis of olefins, and in particular ethylene, will produce acetylene (Crittenden and Long, 1973). Acetylenes and hydrogen are the major

gaseous species produced in the combustion of hydrocarbons, owing to their stability at high temperatures (Stein, 1985). Chain lengthening of acetylene may lead to the formation of unsaturated C_2, C_4, C_6, C_8 species which can stabilise as polyacetylenes. Alternatively, either by formation of a branched radical with ring closure or by cyclisation, unsaturated species may form an aromatic ring with a carbon side chain (Crittenden and Long, 1973).

Frenklach *et al.* (1985) proposed a detailed mechanism for the formation of an initial aromatic ring (as a phenyl radical), by the combination of acetylene (C_2H_2) units (Figure 1.11). Further combination of acetylene with the phenyl radical and sequential hydrogen abstraction results in the formation of the naphthyl radical. Aromatic radicals such as phenyl and naphthalenyl are considered to be important intermediates in the production of larger polyaromatic species. The rapidity with which these intermediates are generated determines the rate at which larger polyaromatic molecules are formed. This explains why polyaromatics (and soot) are formed more rapidly and in greater abundance from fuels containing aromatic species, since the aromatic structure is already present in these fuels to promote the growth of PAH.

1.10.2.2 Formation of PAH from Aromatic Hydrocarbons

The simplest route to the formation of polyaromatic molecules is the combination of two existing aromatic units (Stein, 1991). At high temperatures and in the presence of oxygen, hydrogen atoms are stripped from the aromatic ring thereby generating aryl radicals (Crittenden and Long, 1973; Bittner and Howard, 1981). Subsequent displacement of hydrogen atoms on an aromatic ring by aryl radicals provides a simple means of irreversibly joining two aromatic units (Pradho and Lahaye, 1983). One factor limiting the extent to which aryl radicals influence the formation of PAH, is the strength of the C-H bond in the aromatic molecule. A second, is the tendency for aryl radicals to abstract labile hydrogen atoms, rather than to add to aromatic units. Hence, labile hydrogen atoms must be consumed before arylation can become significant (Stein, 1991)

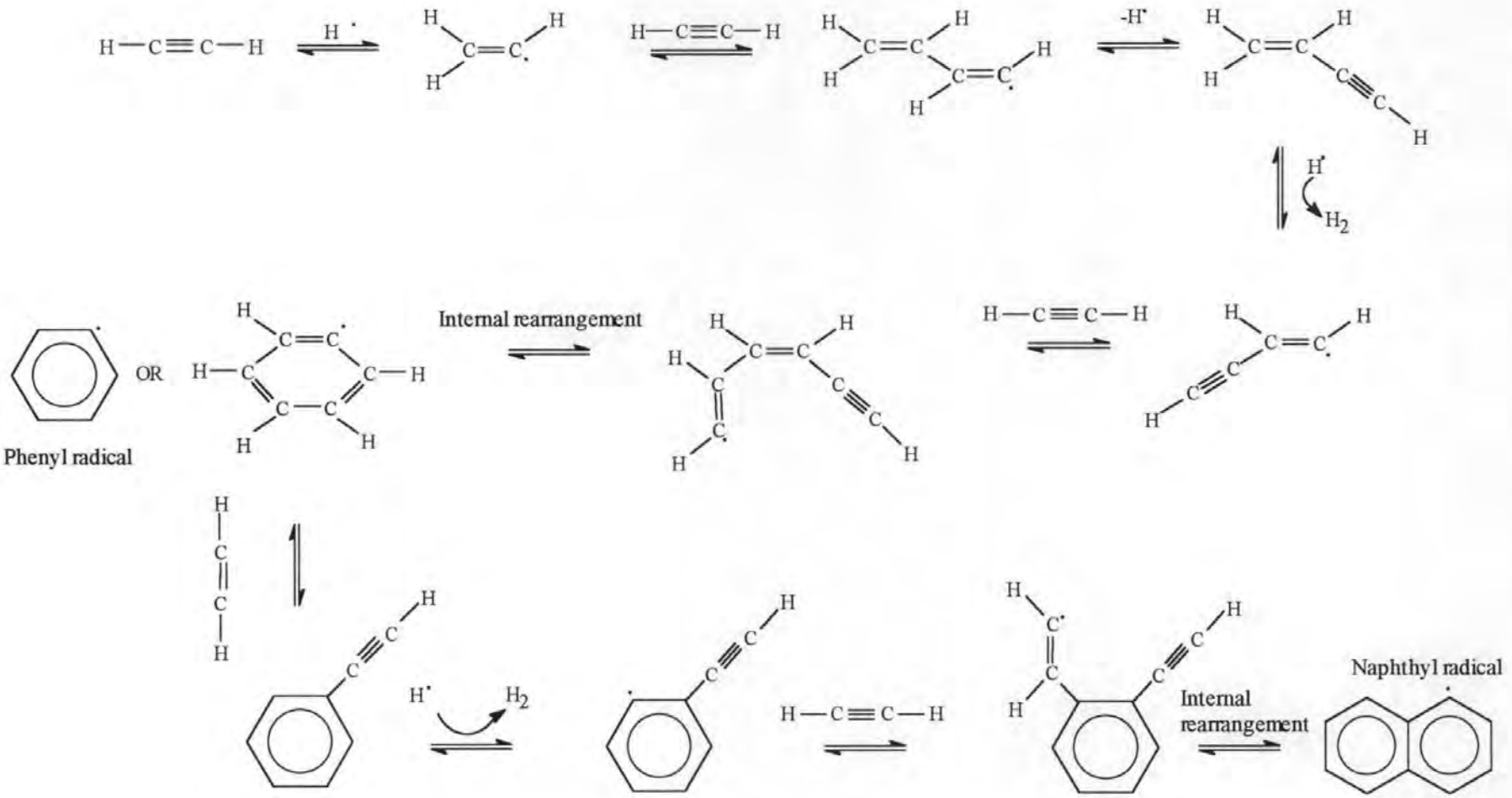


Figure 1.11. Formation of the initial aromatic ring from addition of radical acetylenic species and subsequent growth to form PAH. The formation of larger PAH from the naphthyl radical follows a similar pathway by addition of C_2 units. Adapted from Frenklach (1985).

The production of higher molecular weight PAH may also result from the reaction between aryl radicals and non-aromatic species, particularly acetylenic species (Pradho and Lahaye, 1983; Longwell, 1982). The aromatic ring is thought to aid the formation of larger polyaromatic species in this way by resonance stabilisation of key intermediate species (such as styrene and phenylacetylene) thereby preventing them from decomposing into the reactants (Prahdo and Lahaye, 1983). Addition of further acetylenic species is followed by rapid and irreversible ring closure.

The structure of the aromatic molecule itself, affects the rate of soot formation. For example, aromatics with carbon side chains are thought to be most important intermediates in the formation of larger polyaromatic species and soot (Crittenden and Long 1973) owing to the relative ease in the formation of the aryl radical. Other PAH take no part in the formation of larger aromatic species occurring as stable by-products of the aromatic growth mechanisms.

1.10.2.3 The Formation of PAH During Diesel Combustion

Combustion experiments clearly demonstrate the pyrosynthetic formation of PAH from both aliphatic and aromatic precursors (Section 1.9.2.1 and 1.9.2.2). It has been assumed that this process must also occur at the high temperatures and pressures associated with the diesel combustion process. The complexity of diesel fuel however, makes the identification of specific reaction mechanisms, leading to the formation of PAH during diesel combustion, almost impossible without the use of specialist techniques. One technique that has been widely used involves substituting normal diesel fuel with a simplified chemically-defined fuel substitute. Several diesel combustion investigations have been performed using single component fuels (Henderson *et al.*, 1984; Abbass *et al.*, 1988; Barbella *et al.*, 1989; Ciajolo *et al.*, 1992). Abbass *et al.*, (1989) used hexadecane as a fuel. A range of PAH were identified in the exhaust. Fluorene, phenanthrene and their alkyl-substituted homologues were most prevalent, although their abundance was significantly lower when compared with their concentration in diesel emissions from the combustion of normal diesel fuel. Total PAH emissions were 10% of those from normal diesel fuel. The authors concluded that the contribution of PAH from exhaust deposits on the walls of the dilution tunnel may have been responsible for PAH detected in the

exhaust. In a similar study, Barbella *et al.* (1989) used *n*-tetradecane as the fuel. A wide range of PAH were detected in the emissions, including naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes and their alkyl-substituents. These authors concluded that PAH emitted from the combustion of pure tetradecane were primarily products of combustion. The mass emission rates of the PAH from tetradecane combustion were also found to be less than the emission rate of PAH from normal diesel fuel although the actual rate of emission was not quantified. Ciajolo *et al.* (1992) investigated the effect of fuel aromaticity on diesel emissions using tetradecane and tetradecane spiked with 10% 1-methylnaphthalene. The composition of PAH in the emissions from both fuels was similar. However, the emission of all PAH was increased by the addition of 1-methylnaphthalene to the tetradecane. In this experiment pyrene, phenanthrene and alkylnaphthalenes were the most abundant PAH species in the emissions. This confirms evidence from flame studies which suggest that pyrosynthetic reactions contributing to the formation of PAH favour the presence of existing aromatic species in the fuel which act as "building bricks" in the formation of larger PAH structures (Pradho and Lahaye, 1983; Crittenden and Long, 1973). Similar conclusions were reached by Barbella *et al.* (1989). The authors observed greater emissions of larger 4 & 5-ringed aromatics such as pyrene and fluoranthene from commercial diesel fuel than from tetradecane/toluene fuel mixture.

1.10.3 Lubricating Oil

Lubricating oil has been shown to accumulate PAH as it ages (Williams *et al.*, 1989). Lubricating oil that has escaped into the combustion chamber and has survived the combustion process may in this way contribute to the PAH burden of diesel exhaust. Williams *et al* (1989) demonstrated that the contribution of oil derived unburned hydrocarbons (UHC) and PAH to diesel exhaust increase of with the age of the oil. The authors concluded that the contribution of phenanthrene, methylphenanthrene (MePa), fluoranthene and pyrene to the emissions from lube oil that was 235 hours old, was 42%, 18%, 11% and 8% respectively.

The contribution of PAH to the emissions with the lubricating oil is likely to be most significant for engine operating conditions where the lubricating oil contribution to the exhaust is significant, such as high speed and low load conditions,

or for poorly maintained and older, worn engines. For most operating conditions the lubricating oil contribution will be minor compared to PAH derived from unburned fuel, owing to the considerably greater concentration of PAH in diesel fuel relative to the concentration of PAH in lubricating oil.

1.10.4 Pyrolysed PAH

Vaporised fuel when mixed with hot combustion products can pyrolyze and oxidise and these mixtures can by-pass the flame zone and become a component of the exhaust gases. In diesel combustion, the formation of PAH via pyrolysis reactions generally takes place in fuel rich conditions outside of the flammability limits of the mixture (Figure 1.3). Dealkylation of alkyl-substituted-PAH, which leads to the formation of the parent PAH molecule (see Chapter 4) is, strictly speaking, a pyrolysis reaction (Longwell, 1982). Dealkylation has been observed in a number of experiments and is a primary source of combustion-formed PAH (Herlan, 1978; Trier *et al.*, 1990; Barbella *et al.*, 1990). The polar fraction of diesel exhaust particulates contains numerous partially oxidized PAH molecules and is a consequence of the pyrolysis oxidation of PAH during combustion. Substituted PAH species, especially ketone, quinone, carboxylic acid, ketone and nitro derivatives are abundant in diesel exhaust (Schuetzle, 1983; Rogge, 1993).

1.11 The use of ^{14}C-radiotracers in diesel emission research

The factors that control the distribution of PAH in diesel exhaust emissions are poorly understood. Little is known especially about the detailed mechanisms which lead to the formation of these compounds during combustion and the extent to which individual PAH molecules survive the combustion process and are emitted in the exhaust. Most existing diesel emission research techniques are unable to yield this kind of information. The use of radiotracers added individually to the fuel matrix can, however, yield detailed chemical information regarding the origin of PAH in diesel emissions and the fate of these compounds during combustion. Radiolabelled PAH added to the diesel fuel are, moreover, in such tiny mass quantities that their presence disturbs the combustion characteristics of the fuel little, if at all, when compared with other diesel fuel spiking techniques.

The application of the use of ^{14}C-radiotracers in the field of diesel emissions research is unique to Plymouth. Research has demonstrated the ability of the technique to yield unequivocal information with regard to the combustion of diesel fuel HCs that is unobtainable by any other technique, and which can provide a direct test of proposed theories (Petch *et al.*, 1988; Rhead *et al.*, 1990, Trier *et al.*, 1990; Tancell *et al.*, 1994). Previous experiments have investigated the combustion of aliphatic and aromatic components of diesel fuel. Petch *et al.* (1988) combusted radiolabelled ^{14}C-9-methylanthracene in a single cylinder DI 2l Petter engine and demonstrated the pyrosynthetic formation of a variety of unidentified radiolabelled products of combustion. Rhead *et al.* (1990), using the same engine, investigated the combustion of radiolabelled ^{14}C-benzene and ^{14}C-octadecane. ^{14}C-benzene was recovered in a yield of 0.08% and ^{14}C-octadecane in a yield of 0.0004%. In both cases very low levels of radioactivity were detected throughout the exhaust sample indicating the formation of small amounts of a wide range of radioactive products of combustion.

1.12 Aims of the current investigation

The aims of this research were to further develop the radiolabelling technique and to extend its application to the investigation of the combustion of specific diesel fuel HCs. The combustion of three PAH, (B[α]P, pyrene and fluorene) and one n-alkane (hexadecane) has been investigated, using ^{14}C-radiolabelled derivatives of these PAH. New radio-chromatographic techniques for the detection and quantification of radioactive products of combustion in diesel emissions have been developed and applied to the combustion of these radiotracers. The use of radiochemical specific activities has, for the first time, enabled a distinction to be made between the relative contribution of fuel hydrocarbons to the emissions from the sources of survival and pyrosynthesis. This information has given a clearer picture of the sources of individual PAH in the Prima emissions, and diesel engines in general, and the physical and chemical factors that control their relative contributions from these sources.

It is proposed that dealkylation reactions are a significant source of pyrosynthesized parent PAH in diesel emissions. This research has investigated the

diesel combustion of an alkyl-PAH with the aim of determining the extent to which this process influences diesel emissions of parent-PAH. The combustion of an alkyl-PAH, ethylphenanthrene, synthesized for this purpose, has been investigated using non-radiolabelling techniques, developed during this research, to complement the radiolabelling technique.

Chapter 2

EXPERIMENTAL METHODS

2.1 Engine facility

The engine used was a 2L direct injection Perkins Prima diesel engine mounted on a test bed and was connected by a Borghi & Saveri FA100 eddy current dynamometer which was controlled by a Test Automation Series 2000 Compact Controller. The engine specifications are presented in Table 2.1. The Prima engine is fitted in both its naturally aspirated and turbocharged form in the Rover Montego and Maestro cars and vans and was among the first high speed DI diesel engines to be fitted in passenger cars (Ketcher, 1991). The engine has also found applications in the marine field.

Table 2.1 Prima engine specifications

No. of cylinders	4
Cylinder arrangement	in-line
Cycle	Four stroke
Induction system	Naturally aspirated
Fuel injection system	Bosch EPVE pump with CAV multihole injectors
Combustion system	Direct Injection
Cubic capacity	1,994 cm^3 (122 in^3)
Power (4500rpm)	60bhp
Torque (2500rpm)	119Nm
Compression ratio	18.1:1
Nominal bore & stroke	84.5mm and 88.9mm

The diesel fuel used was a standard A2 derv. Specifications for the diesel fuel are given in Table 2.2.

2.2.PAH concentration in diesel fuel

The PAH concentration in individual diesel fuels varies considerably (Williams *et al.*, 1986). Comparatively little published data exists on the detailed composition of the PAH component of diesel fuels. Where the PAH composition of diesel fuel has been investigated, the identification and quantification of individual PAH has been limited to the major parent PAH and prominant alkyl-derivatives.

Table 2.2 Class A2 diesel fuel specifications

Class A2 diesel oil	
Density at 15°C	0.8619 Kg/l
Sulphur content	0.141 %m (510 ppm)
Kinematic viscosity at 40°C	3.493 cSt
Kinematic viscosity at 50°C)	----
Flash point (PM closed)	----
Cloud point	----
CFPP	----
SFPP	----
Pour point	----
Wax content	----
Melting point of wax	----
Carbon residue (Con) on 10% residue	----
Distillation (IP123)	----
IBP	186°C
5% volume recovered at	221°C
10% volume recovered at	236°C
20% volume recovered at	255°C
30% volume recovered at	268°C
40% volume recovered at	278°C
50% volume recovered at	288°C
60% volume recovered at	298°C
70% volume recovered at	310°C
80% volume recovered at	325°C
90% volume recovered at	347°C
95% volume recovered at	365°C
FBP	374°C
Distillate/ Residue/ Loss	98.4%Vol/ 1.4 %Vol/ 0.2%Vol
Cetane number (D613)	49.0
Hydrogen content	----
Carbon content	----
Calorific value (calculated):	
Net	42.58 MJ/Kg
Gross	45.33 MJ/Kg
Aromatics content (IP391):	
Mono	19.2 %vol
Di	9.5 %vol
Tri	2.6 %vol
TOTAL	31.3 %vol

Fuel analysis performed by BP Fuels Ltd, Sunbury

Alkyl-substituted PAH are usually quantified as a single group, because of the difficulty associated with the identification of individual isomers. Gas chromatographic retention indices (R.I) have been reported in the literature, for most of the alkyl derivatives of the major PAH in diesel fuel. There are, however, few commercially available standards to facilitate the identification process. In this research, mono, di and trimethyl derivatives of naphthalene in diesel fuel have been identified and quantified, using a combination of retention index data (Alexander *et al.*, 1983; Rowland *et al.*, 1984), and available standards. The concentrations and identity of the PAH identified in the fuel are shown in Table 2.3. Alkylnaphthalenes are the major PAH species in diesel fuel. Their isomer distribution reflects the greater stability of alkyl-substitution in the β-position, relative to substitution in the α-position. The distribution of the dimethyl and trimethylnaphthalenes in diesel fuel as demonstrated by GC/MS molecular ions are shown in Figure 2.1. Quantification was performed by GC-FID and GC/MS (Section 2.10.2).

2.3 Diesel exhaust sampling

The Prima exhaust was sampled using the TESSA sampling system developed by the Combustion Research Group at Plymouth (Petch *et al.*, 1987). The system comprises a vertical stainless steel tower, through which the exhaust gasses from the Prima are diverted. The organic components in the exhaust are removed by means of a downwards counter-current flow of solvent, which removes all solvent extractable material from the exhaust. The TESSA system has been designed specifically to sample organic species from exhaust gasses, and has the advantage over conventional filtration methods of exhaust sampling. The collection of lower molecular weight hydrocarbons is improved, without requiring the use of adsorbent traps at the exit of TESSA. This last point is readily demonstrated in the composition of the TESSA extracted samples (TES) which show a dominance of naphthalenes.

The TESSA system also benefits from reduced artifact formation compared to filtration techniques. This is owing to a combination of sampling the exhaust close to the exhaust port and the rapid solvent removal of organics species from reactive gasses in the exhaust stream.

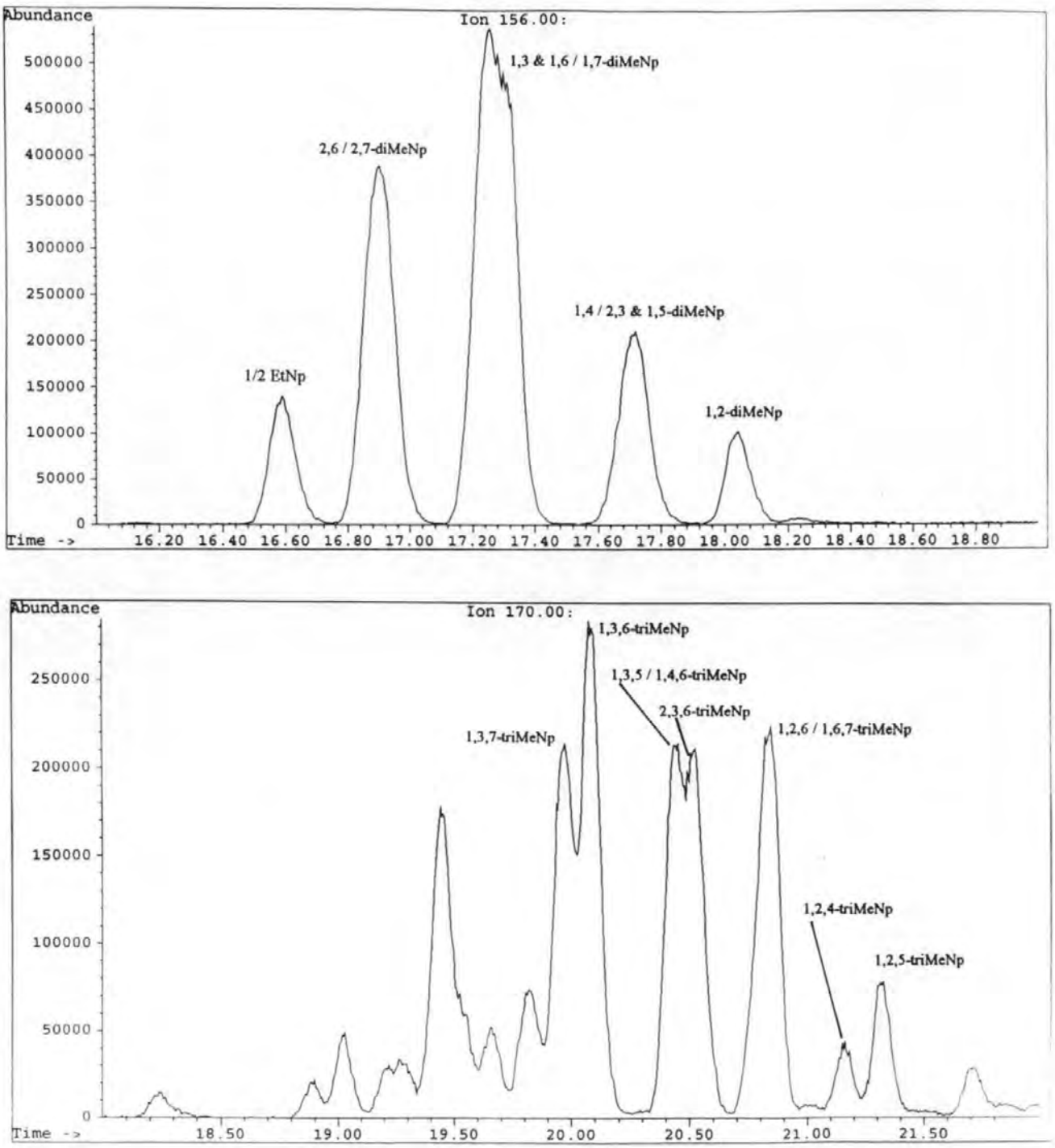


Figure 2.1 GC/MS molecular ion integration of C2-Nps and C3-Nps.

Table 2.3 PAH concentration in standard A2 diesel fuel

PAH	Concentration (ppm)
Naphthalene (Np)	1875
2-MeNp	5801
1-MeNp	3874
1 / 2-EtNp	1546
2,6 / 2,7-diMeNp	5258
1,3 & 1,6 / 1,7-diMeNp	9210
1,4 / 2,3 & 1,5-diMeNp	2708
1,2-diMeNp	1032
1,3,7-triMeNp	2083
1,3,6-triMeNp	2810
1,3,5 / 1,4,6-triMeNp	2014
2,3,6-triMeNp	1854
1,2,6 / 1,6,7-triMeNp	2633
1,2,4-triMeNp	306
1,2,5-triMeNp	702
MeEtNps*	424
MeEtNps*	356
MeEtNps*	2239
MeEtNps*	476
MeEtNps*	754
Fluorene (Fl)	774
9-MeFl	507
2-MeFl	845
1-MeFl	1058
diMeFl (total)	4313
Dibenzothiophene (DBT)	930
4-MeDBT	840
2 / 3-MeDBT	453
1-MeDBT	231
diMeDBT (total)	2756
Phenanthrene (Pa)	1255
2-MePa	1153
3-MePa	950
9 / 4-MePa	835
1-MePa	610
diMePa (total)	3752

Key: 1 / 2 indicates coeluting isomers not distinguishable.
1 & 2 indicates isomers identified but not quantified individually
* isomers not identified

Research at Plymouth has demonstrated that the formation of sampling artifacts, whilst minimised by the design of TESSA, has not altogether been eliminated (Collier *et al*, 1994). Collier *et al.* (1994) identified nitro-PAH in exhaust samples collected from TESSA. These compounds are, however, at lower levels than those encountered in filtered diesel exhaust samples collected using dilution tunnels, and confirms the efficiency of the TESSA system in reducing artifact formation

The TESSA sampling system has been designed in three separate sections and is illustrated in Figure 2.2. Exhaust sampling takes place in the centre section of TESSA, which is filled with graded glass tubing to maximise the surface area of solvent for optimum removal efficiency of organics. The glass tubing is wetted with solvent immediately prior to sampling the exhaust to minimise any possible surface catalysed decomposition of organics before they can be removed by the solvent. The upper section of TESSA is designed to condense organic species not collected by the solvent and contains copper tubing through which cooled water (4°C) is pumped. The condensed organics are collected after sampling by rinsing TESSA with solvent. The solvent/sample eluent is collected at the base of TESSA in large conical flasks (5L) which contains distilled water (1L) to facilitate a separation between the aqueous methanol layer and the DCM layer in which the organic exhaust components from the exhaust are dissolved. The solvent used for sampling is a mixture of dichloromethane and methanol (1:1) and was chosen for optimum removal efficiency of organics from the exhaust. Dichloromethane samples the non-polar and moderately polar species in the exhaust whilst the methanol samples more polar compounds. The solvent is delivered to the tower from reservoir a pressurized to 1bar at a precisely controlled rate of flow to ensure that the sampling efficiency remains constant between samples over any length of time. The pressure-controlled delivery of solvent has eliminated variations in flow rate which were experienced with the previous gravity fed system.

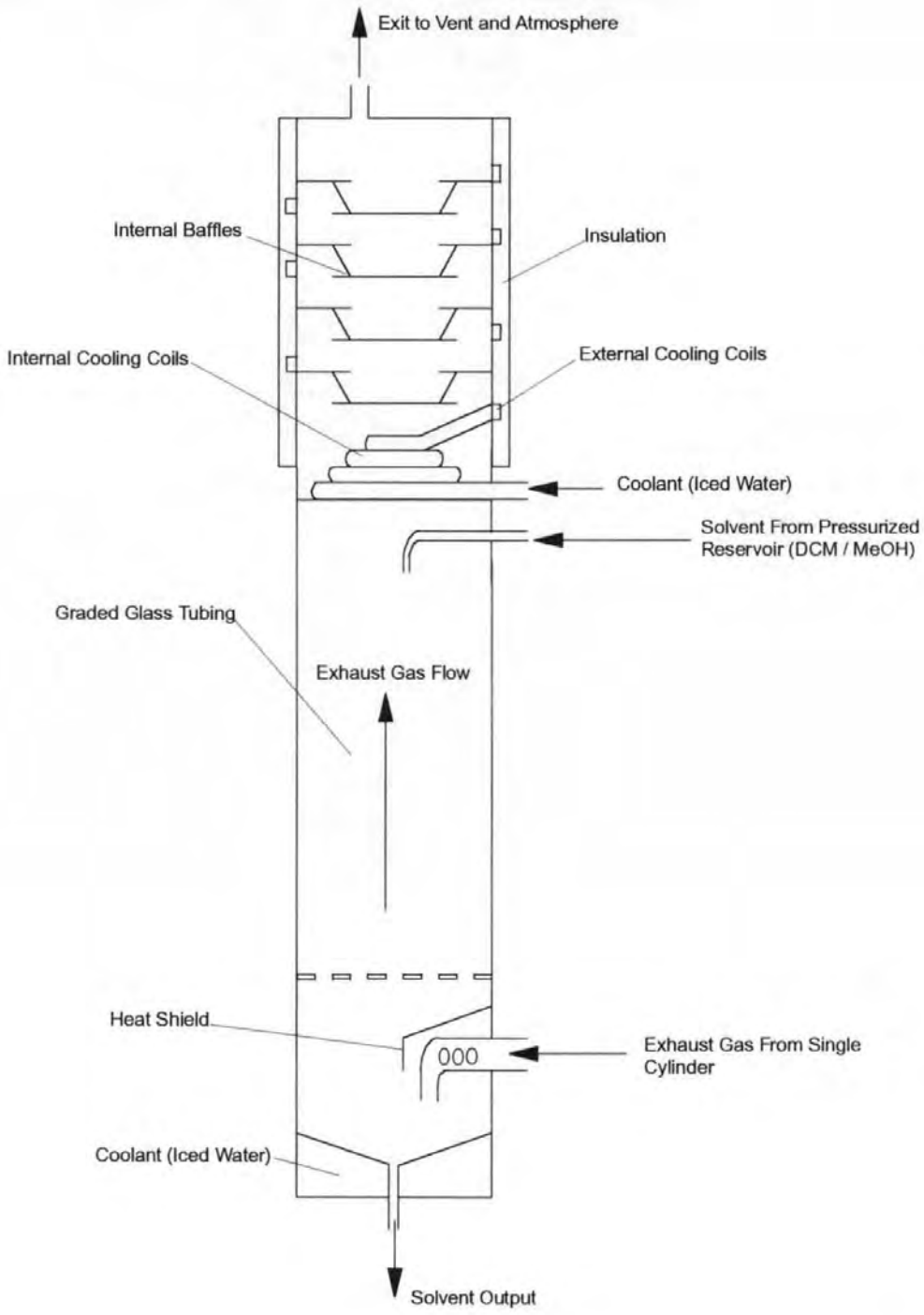


Figure 2.2 The TESSA sampling system

The capacity of the TESSA system is such that the exhaust gasses from one cylinder only may be sampled. The problem has been overcome, by splitting the exhaust manifold between the third and fourth exhaust ports and inserting a two-way monocle plate which can be used to divert exhaust gasses from the cylinder either to TESSA or to exhaust (Figure2.3a and 2.3b).

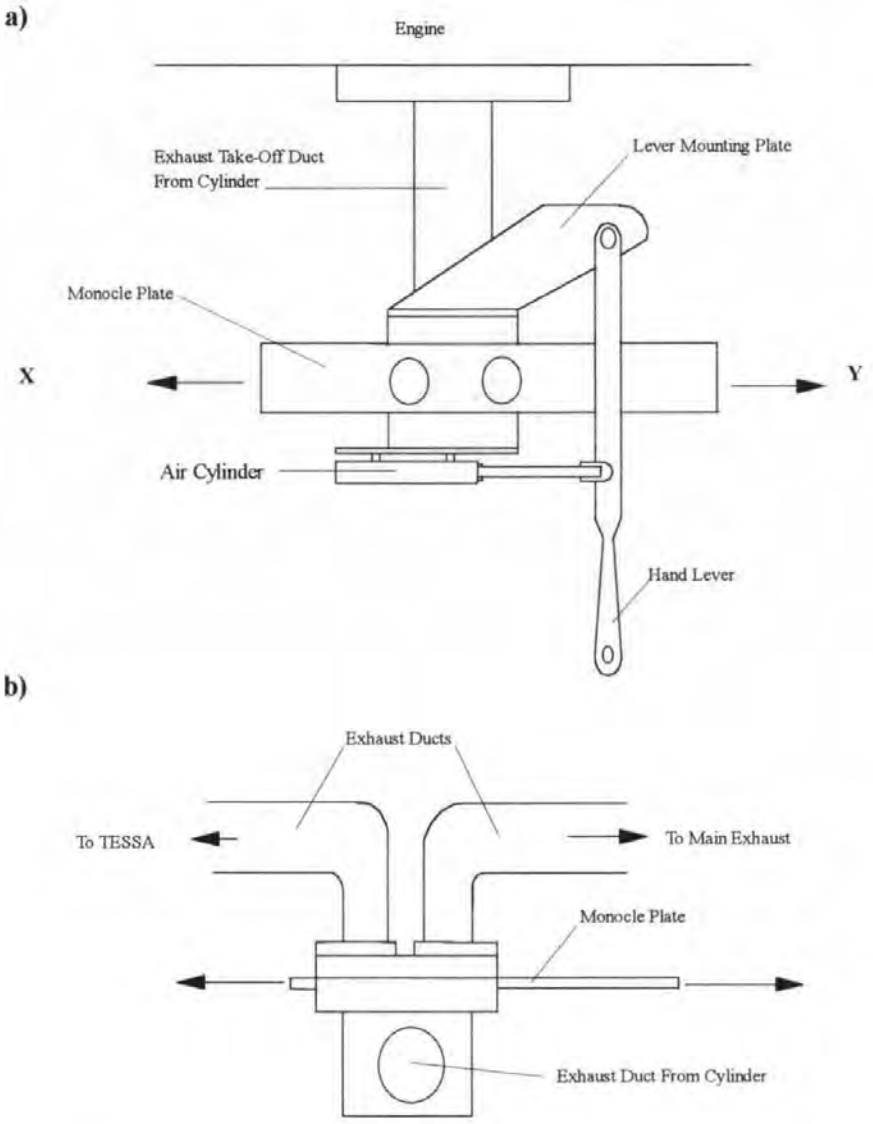


Figure 2.3. Schematic view of exhaust transfer valve showing a) Plan, with top part removed, and b) Elevation along line XY.

2.4 Materials and reagents

All solvents were of HPLC grade (Rathburn) and were used as received. Ultra-pure water was obtained from a Milli-Q system (Millipore). PAH standards, Np, biphenyl; 2-ViNp; 1 & 2-MeNp; 1,2 1,3 1,4 1,5 1,6 1,7 and 2,6-diMeNap, 1,3,5-triMeNp; Fl; 1-MeFl, DBT, Pa; 3 & 9-MePa; Fa; Py; Ch and B[α], (Aldrich) were of greater than 98% purity. 1,2,4- 1,2,5- 1,2,6- 1,3,6- 1,3,7- and 2,3,6-triMeNp were obtained from Professor S. Rowland (University of Plymouth). d_8-Np, d_{10}-Pa and d_{12}-Ch internal standards (Aldrich) were greater than 98% pure.

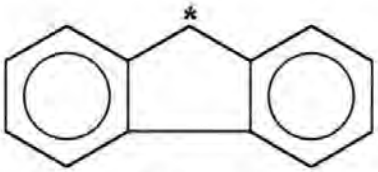
All glassware was soaked in Decon 90 (5%) for 24 hours and was rinsed thoroughly with tap water, distilled water and Milli-Q water. Before use, all glassware was rinsed twice with DCM. Silica and alumina adsorbents, glass fibre filter papers and magnesium sulphate drying agent were soxhlet extracted for 12 hours with DCM.

Reagents used in the synthesis of EtPa (viz: nitrobenzene, aluminium chloride, acetylchloride, hydrazine, triethylene and triethyleneglycol) were obtained from Aldrich and were of a purity greater than 98%.

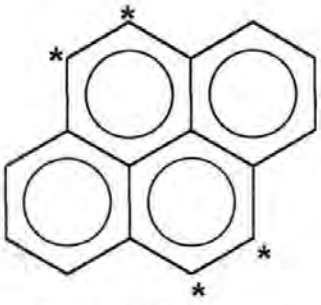
2.5 Radiochemical preparation

[7,10-^{14}C]B[α]P, [4,5,9,10-^{14}C]pyrene (Amersham International) and [9-^{14}C]fluorene (Sigma) were received dissolved in toluene. [1-^{14}C]hexadecane (Amersham International) was received dissolved in hexane. The structure and position of the ^{14}C-label in each of the radiochemicals is shown in Figure 2.4. All radiochemicals were of greater than 98% radiochemical purity and had specific activities of 248μCi/mg, 277μCi/mg, 88μCi/mg and 250μCi/mg respectively. Radiochemicals were stored under the manufacturers recommended conditions of 5°C in the dark. Under these conditions the chemicals are relatively stable, but will, however, continue to degrade at between 1% and 5% per year. It was therefore necessary to confirm both the radiochemical purity and specific activity of the radiochemicals prior to each experiment. Radio-HPLC chromatograms illustrating the radiochemical purity of the three radiolabelled-PAH are displayed in Figure. 2.5. The specific activity of a radiochemical is defined as the quantity of radioactivity per

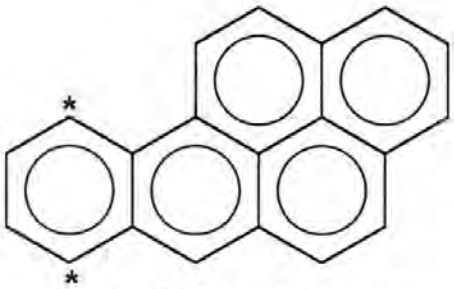
unit mass of chemical and is determined in units of μCi/mg or MBq/mg, where 1Ci is equivalent to 3.7×10^{10}Bq and 1Bq is equivalent to a single disintegration each second.



[9-^{14}C]fluorene



[4,5,9,10-^{14}C]pyrene

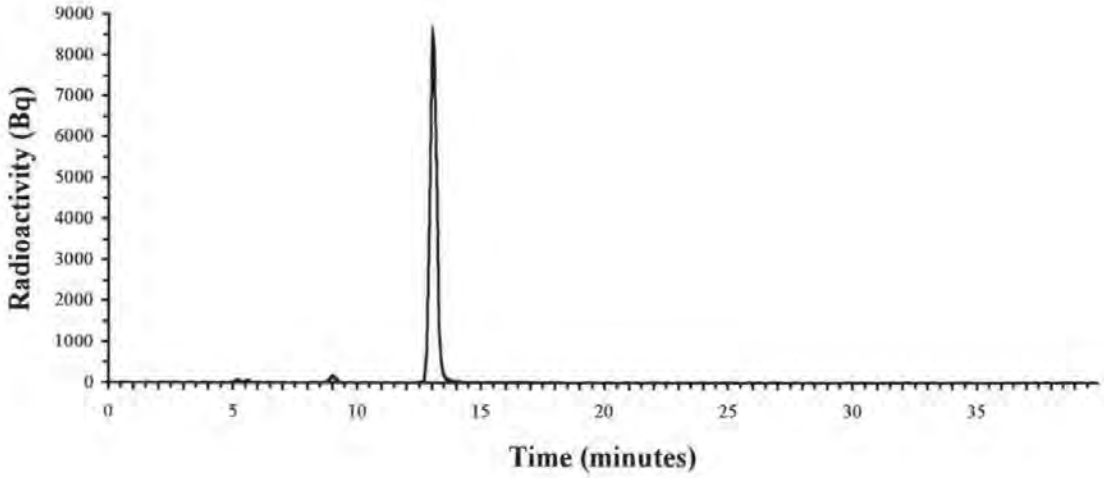


[7,10-^{14}C]benzo[a]pyrene

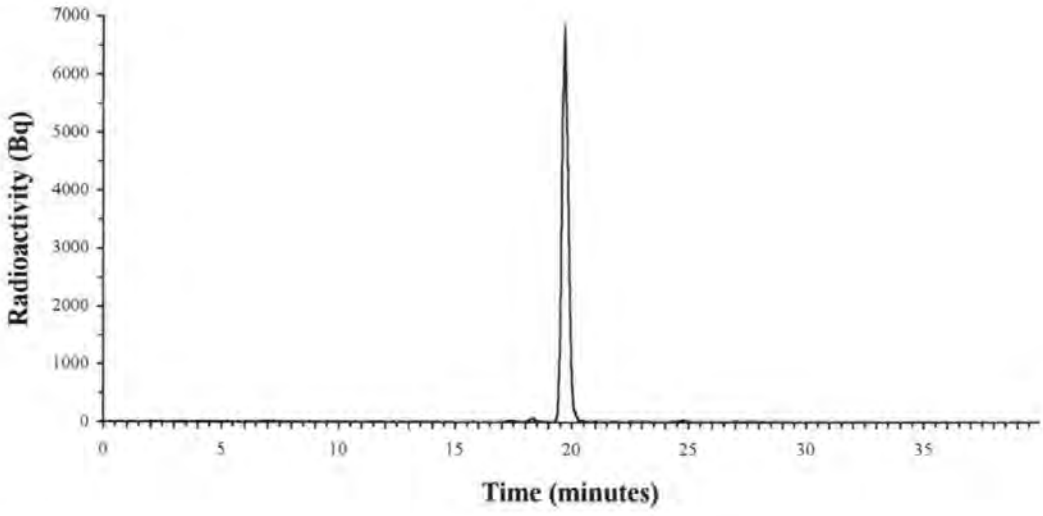
[1-^{14}C]hexadecane

Figure 2.4. Structures of selected ^{14}C-radiolabelled hydrocarbons used in this research. The positions of the ^{14}C-radiolabels are designated by *.

a)



b)



c)

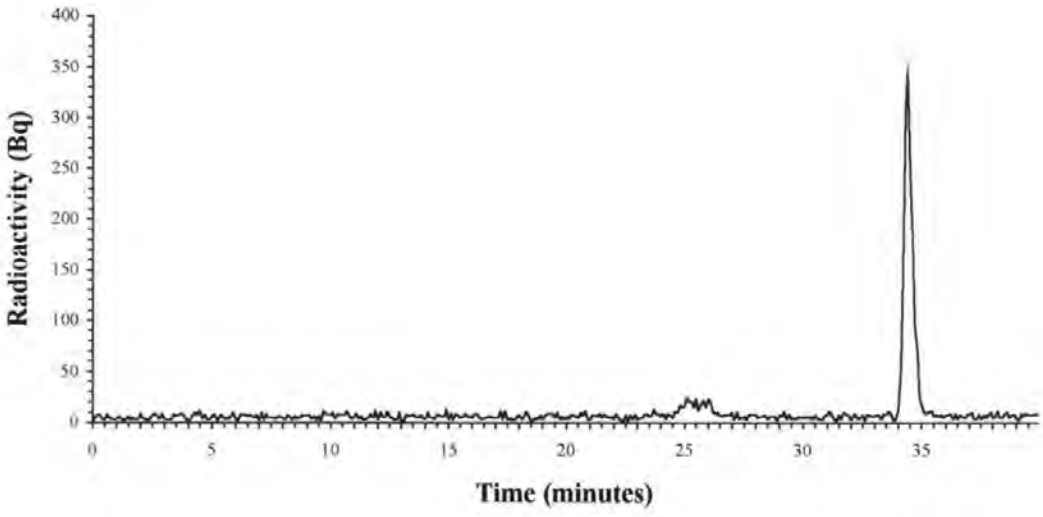


Figure 2.5 Radiochemical purity of a) [9-^{14}C]-fluorene b) [4,5,9,10-^{14}C]-pyrene and c) [7,10-^{14}C]B[α]P

An aliquot of each solution (10µl), was removed from each stock radiochemical and was made up to 1ml in toluene or hexane. The total mass of the chemical (both labelled and unlabelled) in the solution was determined by GC analysis, and the radioactivity by liquid scintillation assay. The specific activity, in units of µCi/mg, was determined from this information. The radiochemical purity was assessed using reverse-phase HPLC with radiodetection (see section 2.9.3.1). An aliquot of the stock (100µl) was taken and the solvent removed by nitrogen purge. The residue was redissolved in ACN and analysed by reverse-phase HPLC. The calculated specific activities and radiochemical purities are given in Table 2.4. In all cases the figures are in good agreement with the manufacturers values.

Table 2.4 Specific activity and radiochemical purity of radiotracers

Radiochemical	Specific Activity (µCi/mg)		Radiochemical Purity (%)	
	Received	Determined	Received	Determined
[7,10-^{14}C]B[α]P	248	250 +/- 4	>98	96
[4,5,9,10-^{14}C]pyrene	277	-------	>98	98
[9-^{14}C]fluorene	88	90 +/- 1.2	>98	95
[1-^{14}C]*n*-hexadecane	250	245 +/- 5	<98	96

To simulate, as closely as possible, the normal chemical and physical processes taking place in the engine, the radiochemical was dissolved in a diesel fuel matrix in preparation for introduction into the combustion cylinder. This necessitated the removal of the solvent from the radiochemical. An aliquot of the radiochemical, (approximately 100µCi) was taken, and the solvent evaporated by nitrogen purge in a fume cupboard at ambient temperature. The residue was redissolved in a known volume of diesel fuel (450µl to 500µl).

The total amount of radioactive precursor dissolved in the diesel fuel was determined by liquid scintillation assay. An aliquot of the solution (3 × 10µl) was removed and was made up to 1ml in toluene. The dilution ensured that the radioactivity in the solution to be counted did not exceed the counting capacity of the scintillation counter. An aliquot (3 × 25µl) of each of the three dilutions was

counted. The radioactivity in the diesel fuel matrix was determined as an average of the three values.

2.6 Introduction of the radiotracer

Owing to the limited exhaust sampling capacity of TESSA, it was required that the radiochemical be introduced in its entirety into the single cylinder sampled by TESSA. The system developed by Trier *et al.* (1990) was used with minor modifications in this research.

The introduction of the radiotracer to the single cylinder had been achieved by modifying the high pressure line connecting the fuel pump to the injector so that it incorporates two parallel lines for part of its length (Figure 2.6). One of the lines was fitted with an access plug through which the radiotracer was injected. The two lines are connected at either end by two three-way valves. The valves are air-actuated and are remotely controlled. Only one line was active at any one time (i.e. would carry fuel to the injector), allowing the inactive line to be filled with the radiotracer dissolved in the fuel. By switching the valves, the off-line section containing the radiotracer becomes the active line during sampling and the radiotracer was introduced into the single cylinder. The pressure in the fuel injector lines is approximately 600 bar. The maximum working pressure of the three-way valves is 600bar. The pressure in the fuel lines is at the upper working range of the valves, with the consequence that their replacement was necessary at several times during the study.

The supply of fuel to each cylinder is determined by the pressure in the lines connecting the pump with the injectors. Any variation in the volume of the fuel line would affect the pressure in the line and hence the volume of fuel supplied to the cylinder and the pattern of injection of fuel into the cylinder. This could affect the emission characteristics of the cylinder, hence it was necessary to maintain the volume of the altered fuel line as close as possible to that of the original lines. In practice, the volume of the modified injector line between the high pressure pump and the injector is within 10% of that of the unaltered lines connecting the pump with the injectors of the three remaining cylinders.

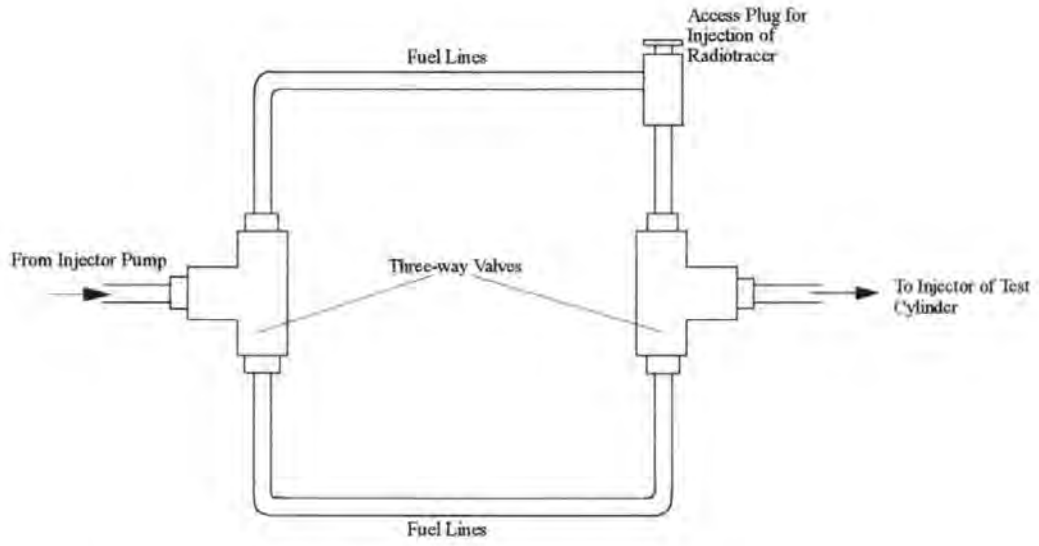


Figure 2.6 Modification of high pressure fuel lines for radiochemical injection.

2.7 Radiochemical injection procedure and diesel exhaust sampling using TESSA

The engine was conditioned for 1 hour at high speed and load and then at the engine conditions to be investigated for 15 minutes prior to exhaust sampling. After the conditioning period, the engine was stopped and the radiotracer was injected into the off-line section via the access plug. Ideally the radiotracer would be introduced into the off-line section while the engine is running, however, in tests using non-radioactive fuel, engine vibration caused small amounts of fuel to spill from the fuel line, consequently it was necessary to load the radiotracer after the engine had been stopped. The engine was then restarted and conditioned for a further 2 minutes at the engine test conditions. The exhaust sampling procedure was as follows:

1. Solvent is allowed to run through TESSA for 20 seconds to wet all of the glass surfaces.

2. The exhaust port is switched so that the exhaust gases from the single cylinder exit through TESSA.

3. After 5 seconds, the three-way valves were switched to introduce the radiotracer into the cylinder.

4. The exhaust was sampled for between 10 and 30 seconds depending on speed and load.

5. After the sampling period the three-way valves were switched to their original configuration. After a further 5 seconds the exhaust port to TESSA was closed and the remaining solvent in the reservoir was allowed to run through TESSA.

The sampling time has been minimised to maximise the specific activity of radioactive products in the exhaust, which has benefits for the subsequent analytical procedures. For the engine conditions of speed and load at which radiotracer experiments have been conducted in this research (2500rpm / 50Nm and 3000rpm / 10Nm) , fuel consumption is such that the total volume of the injector line (≈700μl) will be introduced into the cylinder in the order of a few seconds. A further advantage of the short sampling time is that duplicate and triplicate engine samples may be conducted before significant changes in the conditions of sampling, e.g. humidity of ambient air, can take place.

2.8 Evaluation of PAH recoveries

The use of several preparative HPLC stages in the sample preparation required that losses resulting from the various analytical stages be evaluated. Recoveries for PAH were evaluated using internal and external standards. Deuterated PAH (d_8-Np, d_{10}-Pa and d_{12}-Ch) were used as internal standards. Their loss was evaluated using GC/MS by molecular ion integration. Quantification of PAH recoveries using external standards was performed using GC. The recoveries of PAH were evaluated using external standards by simulating the whole sample-preparation with a standard mixture of PAH. For all PAH, there was good agreement between the recoveries calculated by internal and external standards. For PAH with more than 3-fused rings recoveries were greater than 90%. The greatest losses were, as expected, associated with naphthalene and varied between 30% and 50%. Typical recoveries for representatives of the major PAH present in diesel fuel measured by external standard calibration are shown in Table 2.5.

Table 2.5 PAH recoveries

PAH	Recovery (%)
naphthalene	60 +/- 10
1-MeNp	75 +/- 8
2,6-diMeNp	81 +/- 10
2,3,5-triMeNp	92 +/- 4
fluorene	84 +/- 8
1-MeFl	85 +/- 8
dibenzothiophene	90 +/- 8
phenanthrene	94 +/- 5
3-MePa	96 +/- 4
fluoranthene	95 +/- 5
pyrene	94 +/- 4
chrysene	99
benz[α]pyrene	98 +/- 1

2.9 Isolation and concentration of exhaust sample from TESSA

Exhaust samples collected from TESSA, were contained in methanol:DCM (ca. 2l). Deuterated naphthalene (d_8-Np), phenanthrene (d_{10}-Pa) and chrysene (d_{12}-Ch) were added as internal standards to the samples prior to work-up. The procedure for isolating the exhaust extract involved two stages. First a separation between the methanol and DCM was achieved by adding excess water. The DCM layer containing the exhaust extract, was removed by liquid/liquid partition in a separating funnel (5l) and was dried with anhydrous sodium sulphate. The aqueous methanol layer was extracted with DCM (3 × 50ml) and the washings combined. The sodium sulphate was removed by vacuum filtration and the DCM removed by reduced pressure rotary evaporation and the exhaust sample transferred to a glass vial where the remaining solvent was evaporated and the residue redissolved in hexane (500µl). The analytical work-up procedure is outlined in Figure 2.7.

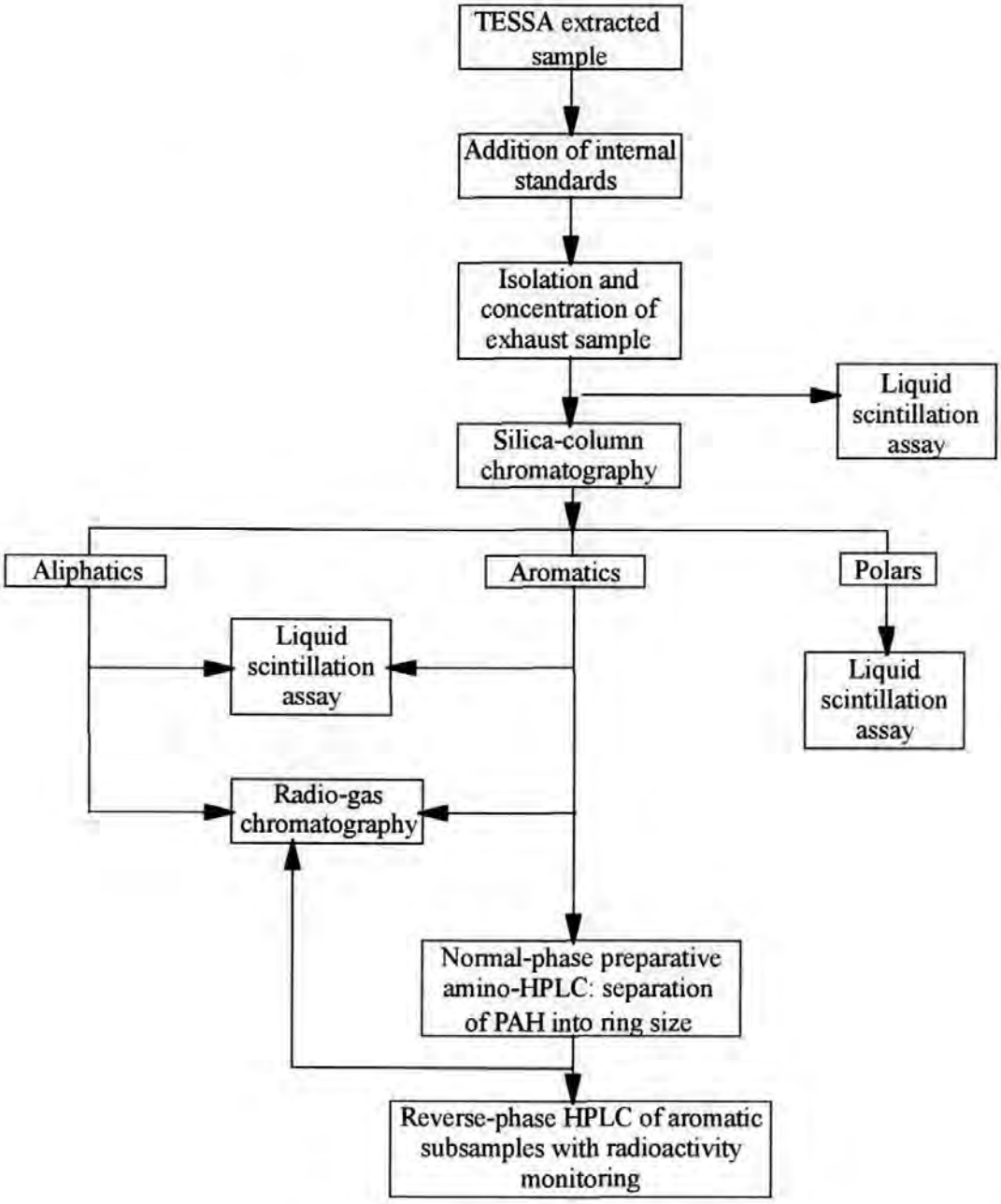


Figure 2.7 Analytical procedure for the work-up and analysis of ^{14}C-labelled diesel exhaust samples

2.9.1 Sample clean-up and preliminary fractionation by silica column chromatography

Various procedures have been employed in the separation into fractions of complex environmental samples such as diesel exhaust. Adsorption chromatography on gravity-flow open columns with alumina and silica oxides has

been widely used to achieve a chemical class separation of diesel fuels and diesel exhaust samples (Peterson *et al.*, 1983; Cookson *et al.*, 1984; Williams *et al.*, 1986; Westerholm *et al.*, 1988; Nelson, 1989; Gotze *et al.*, 1991;). The separation is simple and inexpensive but suffers from two distinct disadvantages. Firstly, the highly adsorptive nature of these materials can cause catalytic degradation of sample components and irreversible sample adsorption (Later *et al.*, 1985). Secondly, the reproducibility of the separation is highly dependent on the moisture content of the adsorbent and consequently materials need to be stored under carefully controlled conditions (Later *et al.*, 1985). The former problems can be eradicated to a large extent by deactivation of the adsorbent with a known percentage of water. Later and co-workers (1985) found the optimum activity for silica to be between 5-8% (w/w). In recent years solid-phase extraction (SPE) has replaced silica and alumina column chromatographic separations for many applications (Obuchi *et al.*, 1984; Garrigues and Bellocq, 1989; Theobald, 1985; Bundt *et al.*, 1991). SPE provides an extremely rapid separation mechanism with a wide variety of stationary phases available and good reproducibility between cartridges.

Several commercially available SPE cartridges were evaluated in this research. Silica SPE cartridges produced separations of the exhaust extract similar to that obtained by traditional silica column chromatography, however this separation was not routinely used owing to plasticiser contamination of the aromatic fraction. Reverse-phase SPE using a C_{18} stationary phase and acetonitrile water mobile phases eliminated the problem of plasticisers but reduced the efficiency of the aliphatic/aromatic separation with respect to high molecular weight PAH (e.g. B[α]P) and the light n-alkanes ($< C_{14}$).

Other chemical class separations of diesel exhaust reported in the literature include isolation of PAC from alkanes and polar PAC using liquid/liquid partition with dimethylsulphoxide (DMSO) (Natusch and Tomkin, 1978), and by gel permeation chromatography (Bechtold *et al.*, 1985). Preparative HPLC using nitro (Ruckmick and Hurtubise, 1985) and amino (May and Wise, 1984) bonded silica stationary phases have also been used to isolate aromatics from various environmental samples.

2.9.2 Experimental method for silica column chromatography.

Preparation of the silica adsorbent was performed according to the procedure of Later et al. (1985). The silica was cleaned by soxhlet extraction with dichloromethane for 24 hours before being fully activated at 185°C for 8-12 hours. Immediately prior to the separation, the silica was deactivated by injecting a weighed amount of Millipore grade water, equivalent to 5% by weight of the adsorbent, and homogenising for 1 hour on a mechanical shaker. Columns were slurry packed with a mixture of silica in hexane. The ratio of adsorbent to sample weight was not less than 100:1.

A solvent gradient of 2 column void volumes each of hexane, hexane/diethylether (10:1) and DCM/methanol (1:1) was used to elute aliphatics, non-polar PAH and heterocycles, and polar compounds respectively. The efficiency of each fractionation was verified by GC and, where required, by GC/MS. Gas chromatograms of the aliphatic and aromatic fractions of diesel fuel are shown in Figure 2.8. Each fraction was concentrated by rotary evaporation and transferred to a preweighed vial. Solvent was gradually removed by nitrogen purge at ambient temperature and the residue was redissolved in a known volume of solvent (DCM or ACN) for GC and HPLC analysis.

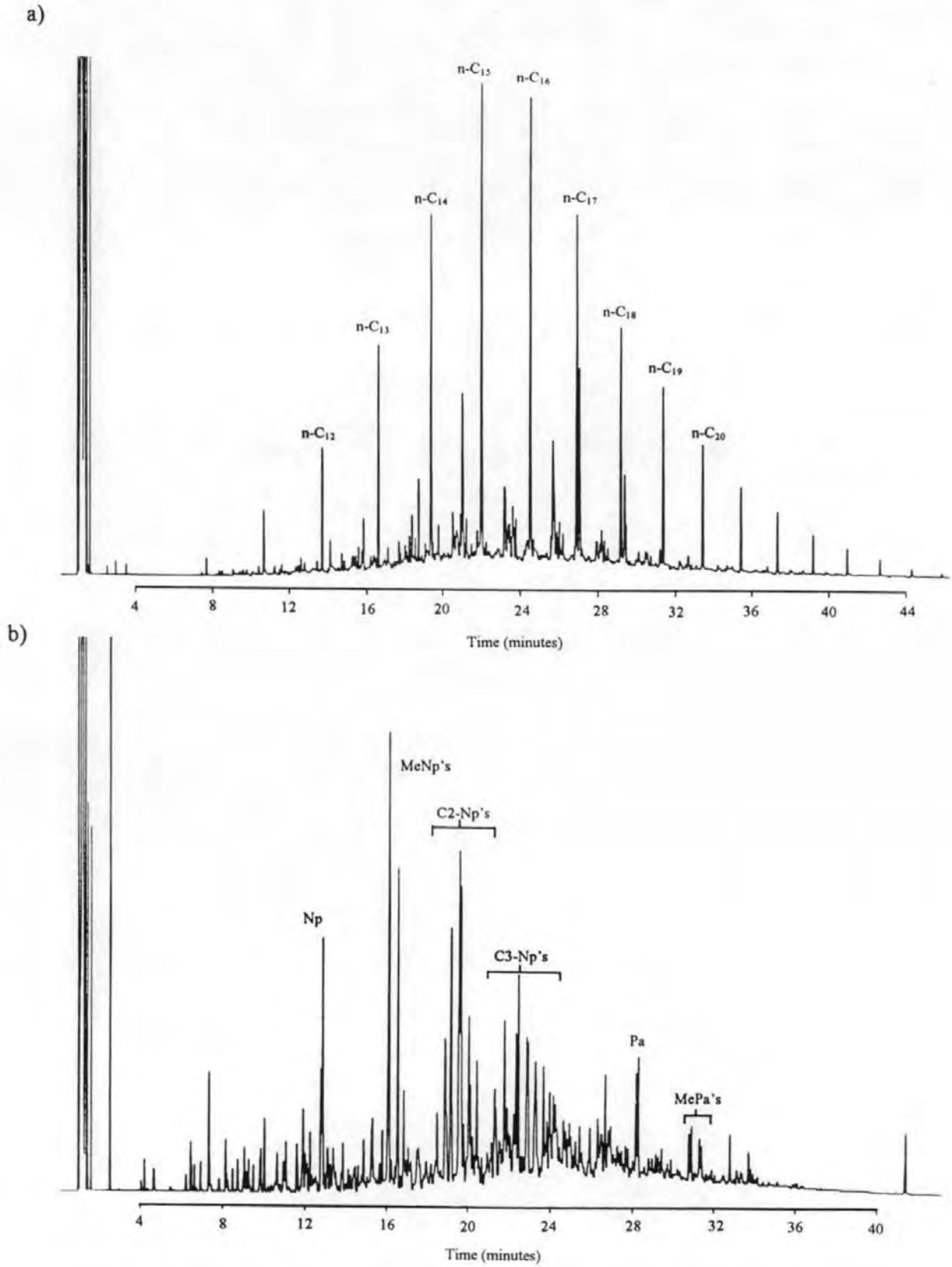


Figure 2.8 Gas chromatograms of a) the aliphatic and b) the aromatic fraction of a typical diesel exhaust sample
(see section 2.11.1 for experimental conditions)

2.10 High performance liquid chromatography

High performance liquid chromatography in both normal and reverse-phase modes, is a powerful technique for the analysis of PAH and their derivatives. HPLC is the preferred chromatographic method for non-volatile PAH and thermally unstable PAH which are not amenable to separation by GC (Fetzer *et al.*, 1986). Analytical reverse-phase HPLC (RP-HPLC), offers unique selectivity for the separation of PAH isomers (Wise and Sanders, 1985). Highly selective HPLC-detectors such as ultra-violet (UV), fluorescence and diode array UV detectors also have unique selectivity for isomeric PAH and have been widely used (Nielson, 1979; Fetzer *et al.*, 1986; Lafleur *et al.*, 1987; Wang *et al.*, 1988; Hansen *et al.*, 1991). The size and shape of the PAH molecule affects the π-electron energy levels in the molecule and determines the energy of the electronic transitions within the molecule. UV and fluorescence detectors exploit this property for their selectivity. A variety of other detectors have been used in HPLC including, refractive index (RI) detectors, thermal conductivity detectors, and electrochemical detectors. These are universal detectors which will respond to most analytes and are generally not used as detection methods for the analysis of PAH. The combination of mass spectrometric (MS) detection with HPLC is a comparatively new development and is finding increasing use in the field of PAH analysis (Singh *et al.*, 1993). Microbore HPLC-MS has been reported for the analysis of PAC (Novotny *et al.*, 1984) and offers separations that are comparable to GC with the advantages of MS detection.

2.10.1 A review of semi-preparative normal-phase HPLC for the isolation of PAH from environmental samples

One of the major advantages associated with HPLC is its ability to be used as a fractionation method for other chromatographic or spectroscopic techniques. In PAH analysis, NP-HPLC is routinely used as a fractionation step prior to analytical RP-HPLC. Their combined use can achieve separations of complex mixtures such as diesel exhaust, that are comparable to GC. Sonnefeld *et al.* (52) reported the combined use of reverse and normal-phase HPLC in a single analytical procedure for the analysis of PAC in diesel exhaust. Claessens and Van Beuren

(1987) used an off-line two-dimensional HPLC procedure for the determination of PAH, which consisted of normal-phase fractionation on silica followed by RP-HPLC on a C_{18} stationary phase. A similar experimental procedure was used by Marcomini *et al.* (1986) for the isolation of PAH from sediment extracts. The isolation of PAH in diesel exhaust and their direct determination by coupled HPLC-GC has been reported (Davies, 1987; Ostman *et al.*, 1992; Kelly *et al.*, 1992 and 1993). The reported advantages of coupled LC-GC are increased sensitivity, reproducibility and ease of operation compared to equivalent off-line systems.

Normal-phase preparative HPLC procedures have been used widely to achieve a separation of aromatic HCs according to ring-size. The majority of these separations have utilised alkylamine bonded silicas, -(RNH_2) (Ostman and Colmsjo, 1989; Grizzle and Slablotny, 1986; Pullen and Scammells, 1988; Cookson *et al.*, 1984). Other silica-bonded stationary phases that have been used to emulate this separation include diamine -$R(NH_2)_2$ (Grizzle and Thompson, 1982), nitro -(NO_2) (Ruckmick and Hurtubise, 1985), diol -$(OH)_2$, cyanopropyl -(RCN) and nitrile -(CN) (Chmielowiec and George, 1980), and 2,4-dinitroanilinopropyl (Grizzle and Thompson, 1982). Separation of PAH according to the number of fused aromatic rings by gel-permeation chromatography has also been reported (Fernandez *et al.*, 1988). Size exclusion was found to predominate although the structural characteristics of pericondensed and catacondensed PAH were found to influence the elution order.

2.10.1.1 Normal-phase HPLC using underivatised silica

Preparative HPLC using underivatised silica as stationary phase, has been widely used to fractionate environmental samples such as whole diesel exhaust (Schuetzle, 1983; Marcomini *et al.*, 1986; Claessens and Van Beuren, 1987). The separation is similar to that achieved by silica column chromatography. However the efficiency and reproducibility of the separation is greater and continuous monitoring of the eluent enables a more precise fractionation of the exhaust into chemical classes. The adsorption characteristics, and hence the mode of separation on silica, is governed by the strength of the Lewis acid-type interaction of the analyte with the silanol groups -(SiOH) on the surface of the silica. For those

compounds most abundant in diesel exhaust the usual order of elution, as measured by the capacity factor (k'), is saturated hydrocarbons < olefins < aromatic hydrocarbons < nitro-PAH < esters < aldehydes < ketones < alcohols < amines < amides < carboxylic acids. The degree of interaction between sample components and the silica is much greater than with the amino-bonded silica phase and hence analysis times are much increased.

2.10.1.2 Experimental method for normal-phase HPLC using underivatised silica

The system used for semi-preparative silica HPLC comprised of a quaternary pump (Perkin Elmer series 410 LC pump) equipped with UV/VIS and refractive index detectors in series, (Merck-Hitachi L-4200 UV/VIS spectrophotometer and Knauer 198 R.I. detector) and manual injector (Rheodyne 7125) fitted with a 1ml sample loop. The refractive index detector was used to monitor the elution of aliphatics and was particularly useful for multiple separations of diesel fuel into aromatic and aliphatic fractions. This compound class does not possess a chromophore and hence cannot be monitored with UV/VIS detection. In separations of whole diesel exhaust, where aromatics only were of interest, a backflush valve was incorporated into the system and allowed polar material concentrated at the head of the column to be swept-off by the reverse flow of solvent. This reduced analysis time and helped to extend the life of the column by minimising irreversible sample adsorption. A schematic representation of the system used for semi-preparative HPLC is shown in Figure 2.9.

A solvent gradient was used for all separations of whole diesel exhaust and consisted of: hexane (5 mins) changed to 100% DCM over 20mins and held (10 mins), changed to 100% ACN over 20mins and held (20mins). A flow rate of 2ml/min was used and could not be increased to reduce analysis times owing to the instability that this created in the response of the radioactivity monitor. Figure 2.10 illustrates a typical silica-HPLC separation of diesel exhaust monitored by UV/VIS at 254nm. Fractions were collected manually and were concentrated by reduced pressure rotary evaporation. At the end of each analysis, a reverse solvent gradient was performed which maintained the reproducibility between separations.

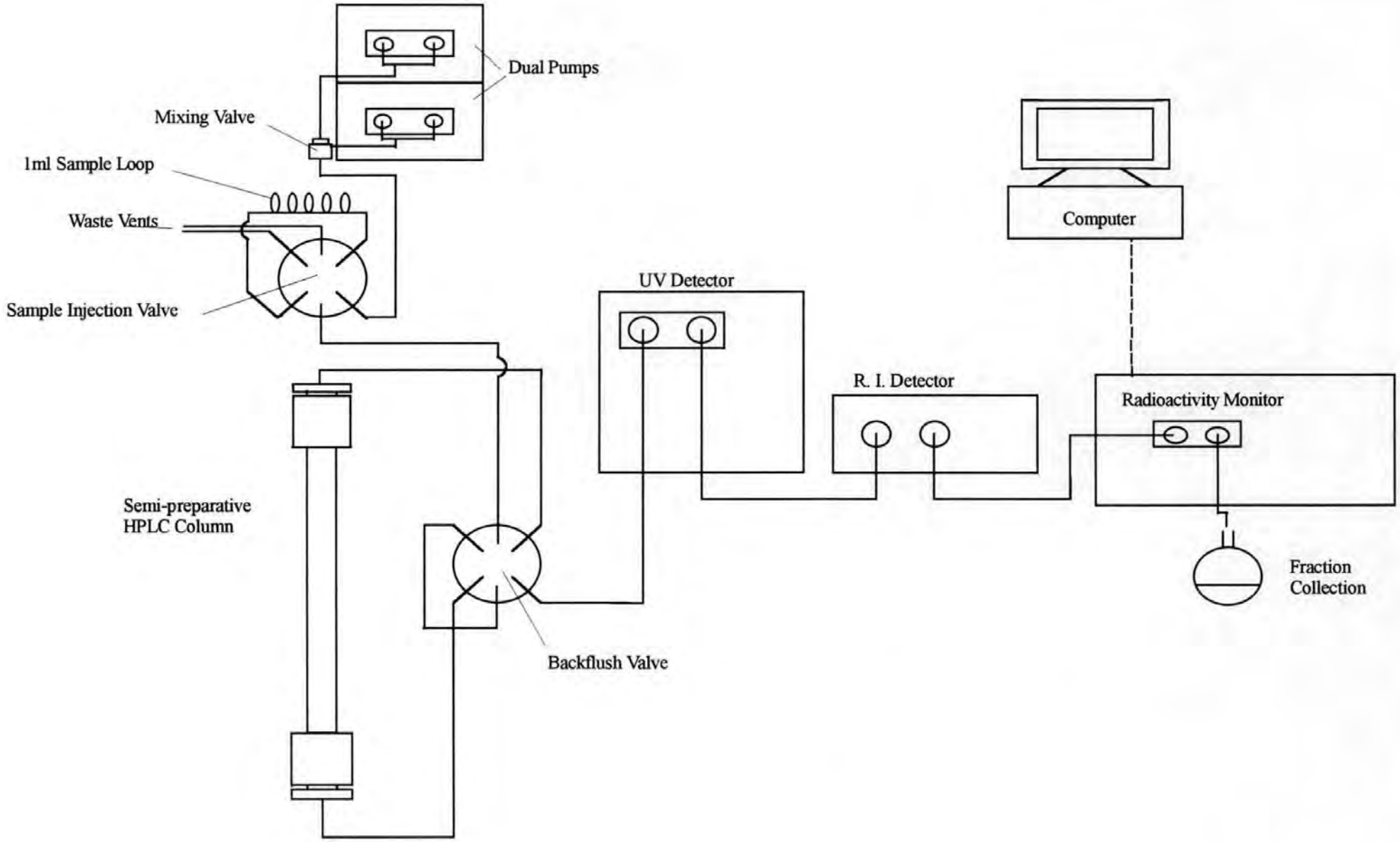


Figure 2.9 Schematic representation of the radio-HPLC system used for preparative HPLC (for experimental conditions see section 2.10.1.2.)

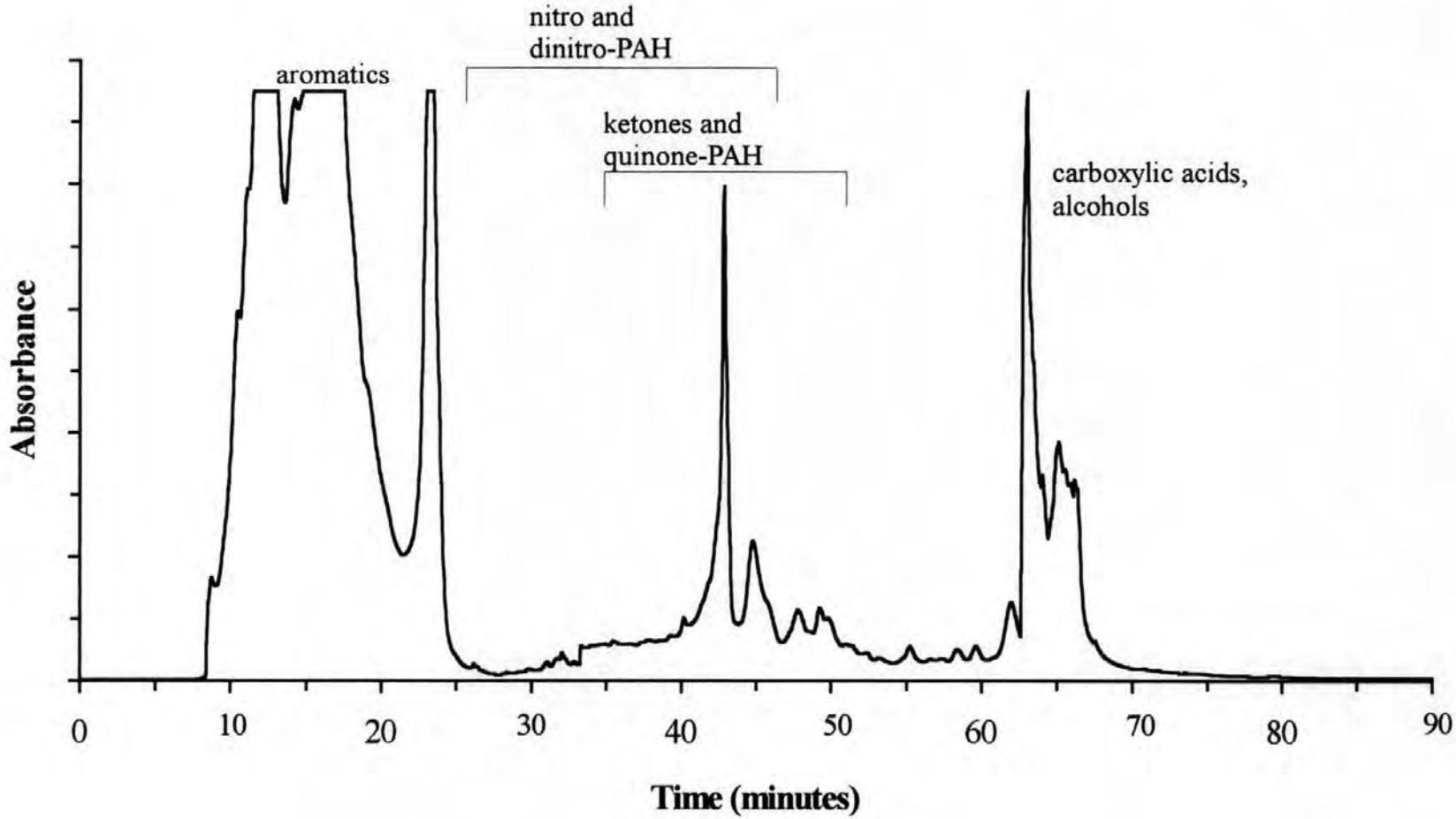


Figure 2.10 Semi-preparative silica-HPLC separation of diesel exhaust (see section 2.10.1.2 for experimental conditions)

2.10.1.3 Normal-phase HPLC using an amino-bonded silica stationary phase.

The separation, described originally by Wise *et al.* (1979) using an aminosilane stationary phase, has been most widely used to produce a ring-size separation of aromatics (Cookson *et al.*, 1984; Grizzle and Slablotny, 1986; Pullen and Scammells, 1988; Ostman and Colmsjo, 1989). The mode of separation is dependent on a charge-transfer type interaction between the delocalized π-electrons of the aromatic system and the lone pair of electrons on the nitrogen (Wise, 1977). The separation is essentially unaffected by alkyl substituents, although alkyl-PAH elute slightly before the parent unsubstituted PAH, possibly due to shielding by the substituent group which reduces the interaction between the π-electrons and the amine. The degree of interaction increases with the number of delocalized π-electrons, with the effect that larger aromatics are retained for a greater time on the column. Hence, pyrene with 8 pairs of π-electrons elutes before chrysene which has the same number of aromatic rings but 9 pairs of π-electrons. Synder and Schunk (1982) proposed a model for the retention mechanism on amino-bonded stationary phases.

Aminosilane phases and bonded-silica phases in general, are not deactivated by small amounts of water, in contrast to unmodified silica and alumina. These phases also require relatively small volumes of solvent to re-equilibrate between analyses.

One disadvantage associated with alkylamine stationary phases in the analysis of petroleum products however, is the tendency to form Schiff bases with carbonyl groups. Over a period of time the column is gradually deactivated with a consequential loss of selectivity and capacity. This effect has been observed in this research. The conversion of the Schiff base back to the amine and carbonyl functionalities occurs readily in aqueous acid conditions and is facilitated by using the column in the reverse-phase mode with water as mobile phase (Karlesky *et al.*, 1981). Karlesky *et al.* (1981) reported that 125 column void volumes of water were required to complete the conversion back to the amine and carbonyl.

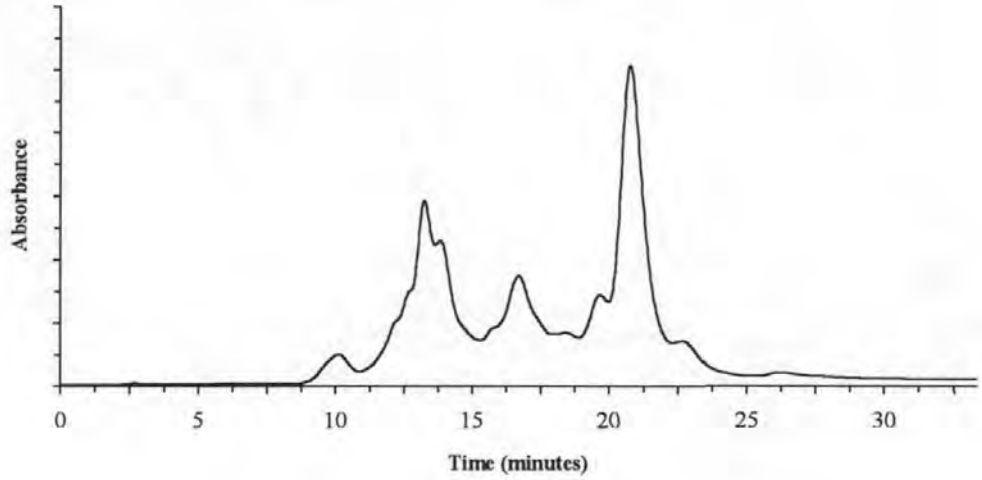
2.10.1.4 Experimental method for the separation of aromatic hydrocarbons into ring size using an amino-bonded silica stationary phase

Preparative HPLC was performed using dual pumps (Merck-Hitachi L-6200A intelligent pump and L-6000 LC pump) equipped with UV/VIS detector (Merck-Hitachi L-4200 UV/VIS spectrophotometer) and manual injector (Rheodyne 7125) fitted with a 1ml sample loop. Separations were performed using a semi-preparative column (10mm × 250mm) packed with amino bonded silica. A variety of commercially available aminosilane phases exist. In this research three phases have been tested, Spherisorb (5μm), Techsphere (5μm, HPLC Technology), Nucleosil (5μm). HPLC columns were slurry packed with 2-propanol at 8,000psi using an air-driven liquid pump.

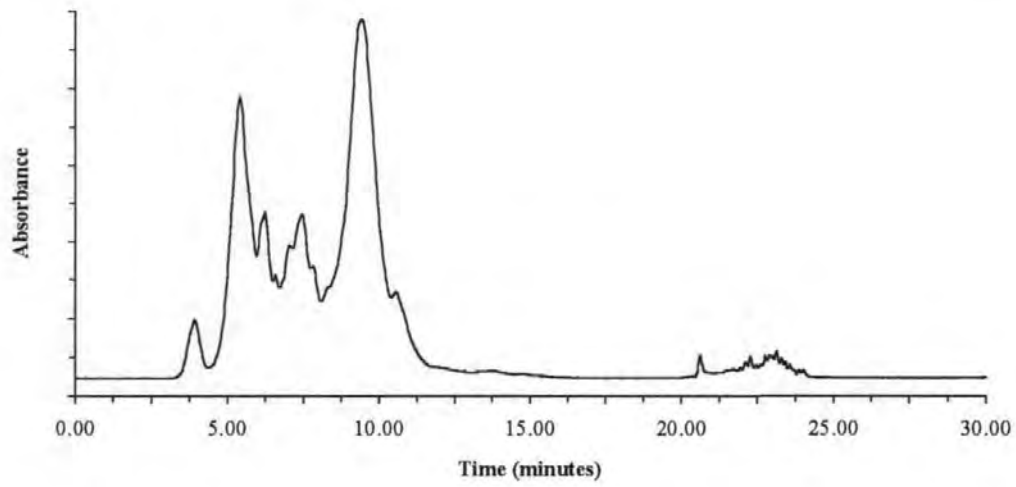
The columns demonstrated essentially identical separations of diesel fuel aromatics as shown in Figure 2.11. The retention characteristics for all phases were similar, however, the capacity factors of the three phases varied considerably. This difference is due to variations in the efficiency of derivatisation of the silica substrate in the various manufacturing processes, and is measured in terms of carbon loading. No data was available for the carbon loading of the three columns.

The separation was monitored by UV absorbance at 254nm which provides nearly universal detection for PAH. The solvent elution programme consisted of hexane isocratic for 25 minutes to 50% dichloromethane after 35 minutes at a flow rate of 2ml/min. Fractions were collected manually in round bottomed flasks (100ml). The solvent was removed using reduced-pressure rotary evaporation and the residue was then transferred to glass vials, where it was redissolved in DCM or toluene (500μl), for GC and GC/MS analysis. An aliquot (100μl) was removed for reverse-phase HPLC analysis. The DCM solvent is not miscible with the water/acetonitrile mobile phases used in reverse-phase HPLC and was removed by nitrogen purge. The residue was redissolved in acetonitrile (100μl) for reverse-phase HPLC analysis.

a)



b)



c)

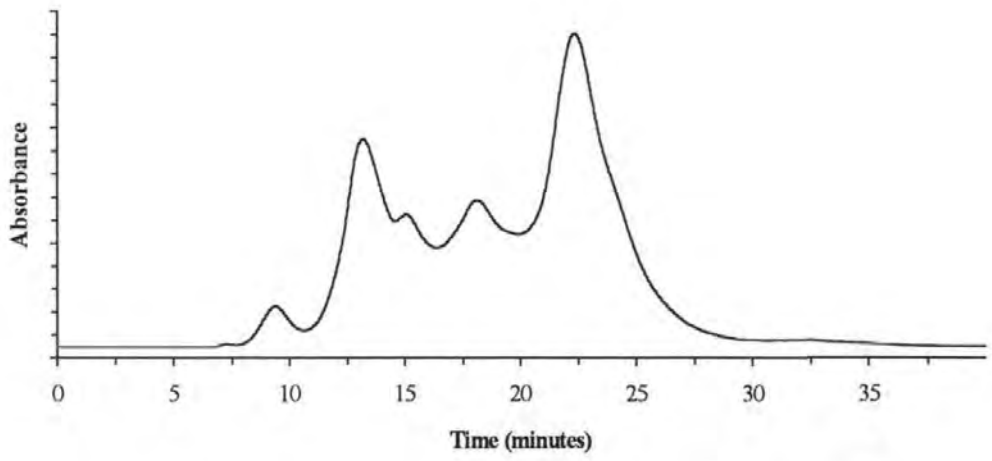


Figure 2.11 HPLC separation of diesel exhaust aromatics using a) Spherisorb-NH_2 b) Techsphere-NH_2 and c) Nucleosil-NH_2 stationary phases

The reproducibility of the separation between analyses was maintained by passing DCM (50ml) through the column after each analysis and then reconditioning the column with hexane for 20 minutes prior to the next analysis. After long periods of storage it was found necessary to recondition the column by washing with a succession of eluents of decreasing polarity in a reverse step gradient (methanol, acetonitrile, dichloromethane and hexane).

A typical exhaust aromatic sample from TESSA weighed about 5mg. Semi-preparative HPLC enabled the total sample to be fractionated in one step without overloading the column. The radioactive products in the exhaust were present at very low levels, close to the analytical limits of detection of the HPLC-radioactivity monitor. There was great benefit therefore, in being able to fractionate the total exhaust aromatics in a single procedure since this enabled sufficient radioactivity to be concentrated in a single aromatic subsample to be above the instrumental limits of detection in the subsequent reverse-phase radio-HPLC analysis.

Each fractionation yielded five subsamples comprised of monoaromatics, naphthalenes and alkyl derivatives, a fraction containing fluorenes and dibenzothiophenes, phenanthrenes and alkyl homologues and a fraction containing PAH with more than four rings. The efficiency of each fractionation was confirmed by GC and GC/MS analysis of each subsample and is demonstrated in Figure 2.12. which shows gas chromatograms of the individual aromatic subsamples obtained by fractionation of diesel fuel.

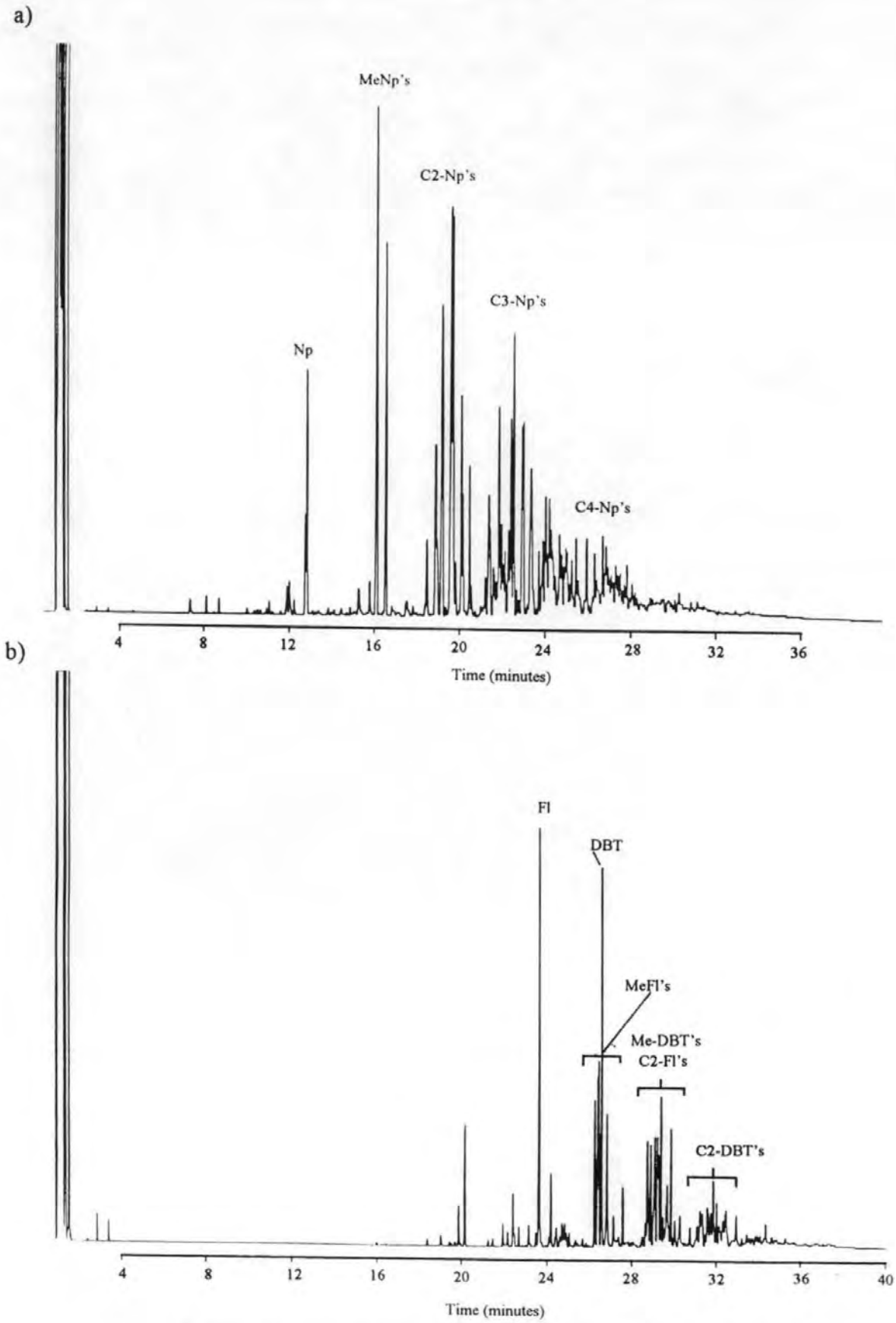


Figure 2.12 Gas chromatograms of aromatic subsamples of diesel exhaust obtained from normal-phase amino-HPLC illustrating

a) 2-ringed aromatics (naphthalenes) and **b) fluorenes and dibenzothiophenes**

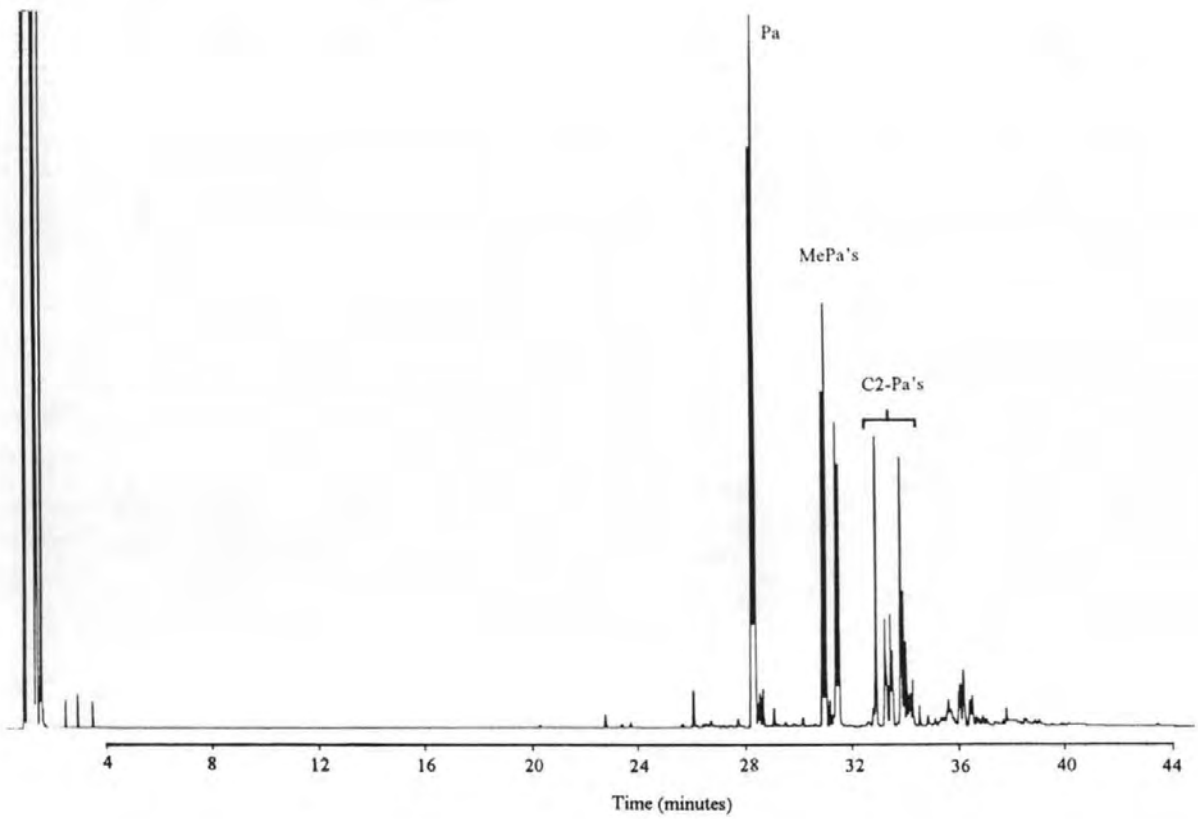


Figure 2.12c Gas chromatogram of the 3-ringed aromatic subsample of diesel exhaust obtained from normal-phase amino-HPLC fractionation

2.10.2 Reverse-phase HPLC

HPLC used in the reverse-phase mode is a powerful analytical technique for the determination of PAH in environmental samples. RP-HPLC is most widely used with monomeric and polymeric octadecysilane (C_{18}) stationary phases. Tetraphenylporphyrin based silicas, and silicas bonded with multidentate phenyl groups have also been applied to the separation of PAH (Kibbey and Meyerhoff, 1993; Jinno *et al.*, 1990). Monomeric C_{18} phases are prepared using monofunctional silanes, their reaction with the silica substrate results in a single moiety on each derivatised surface silanol (Sander and Wise, 1990). Polymeric C_{18} phases are prepared from the reaction of trifunctional silanes with silica in the presence of water. This generates extensive cross-linking to form polymers on the surface of the silica (Sander, 1990). The stationary phase of polymeric C_{18} phases differs to that of the monomeric C_{18} phase in having a rigid, well defined surface structure maintained by the extensive crosslinking between the functional groups.

Retention of PAH in RP-LC proceeds according to the number of fused rings and the degree of alkylation. Highly alkylated PAH elute with unsubstituted-PAH of considerably larger size in contrast to normal-phase HPLC separations. The mode of separation is dependent on the degree of interaction between the solute and stationary phase, and the solute and mobile phase. In RP-LC, hydrophobic interactions between the non-polar solute and polar mobile phase partitions the solute into the stationary phase. Decreasing the polarity of the mobile phase by increasing the percentage of the organic solvent, reduces the retention of the solute.

Once the solute has been partitioned into the stationary phase, the elution order and retention of the individual solutes is determined by the interaction between the two. In general, the polymeric phases are superior to the monomeric phases in the separation of PAH, particularly with regard to the separation of isomeric and alkyl-substituted PAH (Sander and Wise, 1987). The latter is an important consideration in the analysis of diesel fuels which are dominated by alkyl-PAH. The rigid structure of the polymeric phase is thought to be more sensitive to the structure of the PAH. The planarity of the solutes in particular has been shown to determine the retention characteristics on polymeric C_{18} phases (Wise and

Sander, 1985). It is thought that planar PAH molecules penetrate deeper into the rigid surface structure of the polymeric phase and are retained longer.

2.10.2.1 Experimental method for the reverse-phase HPLC analysis of aromatic subsamples

RP-HPLC separations were performed using a Supelcosil LC-PAH column (Supelco Inc., 25cm × 4.5mm I.D.), with 5μm octadecylbonded silica as stationary phase. The stationary phase was polymeric (Wise and Sander, 1993). Instrumentation comprised of dual pumps (Merck-Hitachi L-6200A intelligent pump and L-6000 LC pump), equipped with UV/VIS and fluorescence detectors in series (Merck-Hitachi L-4200 UV/VIS spectrophotometer and Merck-Hitachi F-1050 fluorescence spectrophotometer). Samples dissolved in ACN were injected into a mobile phase of ACN/H_2O at a flow rate of 1ml/min. The volume of sample was 40μl and this was introduced into a 100μl sample loop connected to a manual injector (Rheodyne 7125). A solvent gradient was used with an initial composition ranging from ACN/H_2O (60/40) for analysis of 2 ring PAH samples, to an initial composition of ACN/H_2O (80/20) for samples containing 4 & 5-ringed PAH. A linear solvent gradient to 100% ACN over 20 minutes and 10 minutes respectively, was used for the various PAH fractions. All mobile phases were degassed by helium purge for 20 minutes prior to their use. This was particularly necessary when using fluorescence detection since dissolved oxygen strongly quenches the fluorescence signal.

Retention times for PAH were reproducible and were used to identify PAH by comparison with the retention times of standards. The fluorescence detector was operated at excitation (λ_{ex}) and emission (λ_{em}) wavelengths of 365nm and 427nm respectively for detection of B[α]P, and λ_{ex} = 320nm and λ_{em} = 430nm for detection of pyrene. The selectivity of the fluorescence detector enhanced the response to the PAH of interest whilst suppressing that of other compounds eluting in this fraction. PAH were quantified using linear calibration graphs, ($r^2 > 0.999$ for all PAH) constructed from duplicate and triplicate injections of standard PAH solutions.

2.10 3 Radioactivity measurement

Three methods of radioactivity measurement were utilised in this study, radio-HPLC, radio-GC and scintillation counting. The first two are on-line measurement systems whilst scintillation counting is an off-line counting technique. Radio-HPLC has been the major detection system used in this research. Radio-GC has been used for radiolabelled n-alkane analysis. Static scintillation counting has been used as a confirmatory technique for quantification purposes.

2.10.3.1 HPLC radioactivity measurement

All HPLC analyses were performed with simultaneous on-line radioactivity measurement. The HPLC radiodetector used was a Berthold LB 505 C-1 radioactivity monitor, equipped with a yttrium glass, solid scintillant measuring cell (150µl cell volume) and dual monitoring circuits for simultaneous measurement of ^{14}C and ^{3}H isotopes.. ^{14}C radioactivity measurement was performed in the high energy window. The internal amplifier settings describing the energy range of the window were 70mV for the lower level (LL) and 900mV for the upper level (UL) of the window. Noise and luminescence events were detected, and compensated for, using a coincidence circuit with a resolution time of 100 nanoseconds. The lower energy level (LL) of the high energy window used for ^{14}C measurement, was set to exclude luminescence and phosphorescence events. The radiodetector was remotely controlled from a PC. Data handling and manipulation was performed using a Berthold HPLC programme. This allowed manual and automatic integration of radiopeaks, for quantification purposes. The quantity of radioactivity associated with a radiopeak was calculated using the following formulae:

$$\text{Radioactivity (µCi / Bq)} = \frac{\text{integrated counts (I)} \times \text{flow rate (F, ml/min)}}{\text{cell volume (V, ml)} \times \text{counting efficiency (E)}}$$

The total number of counts in a given radio-peak was determined by manual integration. The counting efficiency of the radioactivity monitor was determined as 65% by repeat, reverse-phase analyses of a solution of ^{14}C-pyrene, the precise activity of which had been determined by liquid scintillation assay (section 2.9.3.2). The counting efficiency was found to vary marginally with the composition of

mobile phase according to the percentage water content (Figure 2.13). The level of background noise was determined prior to each analysis and background subtractions were performed in the subsequent quantification.

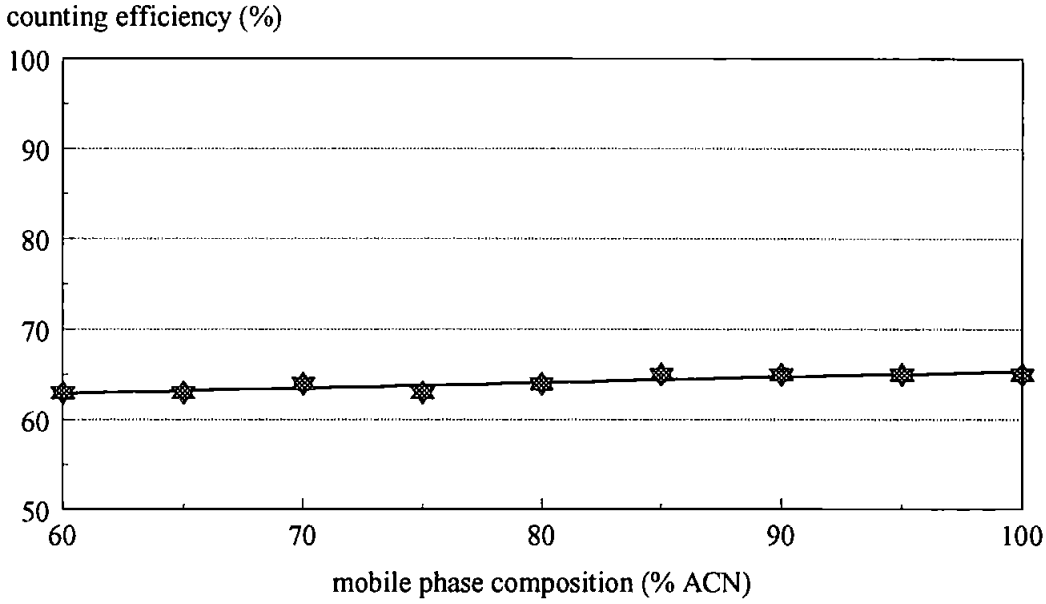


Figure 2.13 Variation in the counting efficiency of the HPLC radioactivity monitor with mobile phase composition.

2.10.3.2 Radioactivity measurement by static liquid scintillation counting

The method of radioactivity measurement using off-line, static scintillation counting offers the highest sensitivity and greatest accuracy of the radioactivity detection systems used in this research. This is owing to the longer residence times that radioactive sample components may spend in the measuring cell when compared with radio-GC and radio-HPLC detection systems, where the length of time a radioactive sample component can spend in the measuring cell is determined by the flow rate of the mobile phase. Owing to the high accuracy of the technique, liquid scintillation counting was used to calibrate the GC and HPLC radioactivity monitors used in this research.

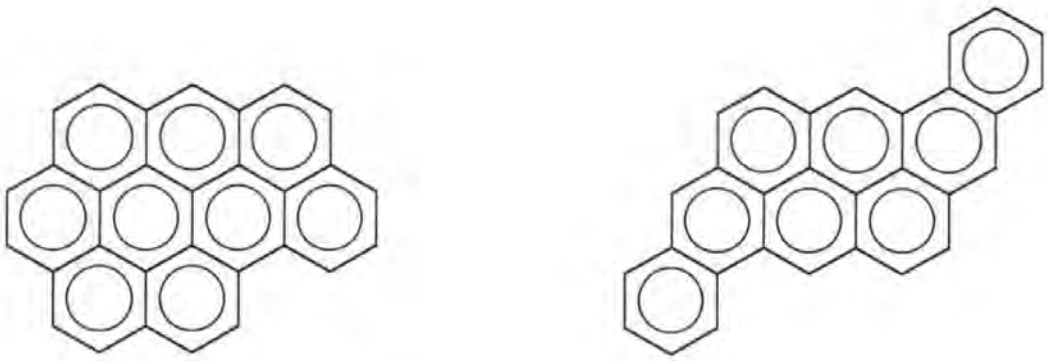
The major disadvantage associated with liquid scintillation counting is the limited resolution afforded by the technique. Extensive, pre-fractionation of the sample is required to achieve resolution comparable to the flow-through radio-GC

and radio-HPLC continuous monitoring systems. This degree of pre-fractionation is labour intensive.

Liquid scintillation counting was performed using a Phillips PW4700 Liquid Scintillation Counter. Measurement of ^{14}C β-emissions was performed using the high energy window. The discrimination settings of the window were, LL = 40KeV and UL = 160KeV. The maximum energy of β-emissions from ^{14}C nuclei is 0.156MeV. These settings ensured that all β-particles from ^{14}C disintegrations would be counted. A sample/scintillant ratio of 10:1 was determined as the minimum before the counting efficiency of the liquid scintillant was affected. The volume of samples to be counted was usually less than 100µl and were dissolved in 2ml of scintillant. The scintillant used was 2-(4'-tert-butylphenyl)-5-(-4-"-biphenyl)1,3,4-oxydiazole (5%) in toluene. Samples were counted for 5 minutes or until 40,000 counts were registered.

2.11 PAH analysis by gas chromatography

Gas chromatography is ideally suited to the analysis of complex mixtures owing to its extremely high resolution. It has been widely used in the analysis of PAC in diesel exhaust (Tong *et al.*, 1984; Henderson *et al.* 1984 & 1988; Cartellier and Tritthart, 1984; Williams et al., 1986). GC is most suited to the analysis of small PAH, since the main prerequisite is that the molecule be volatile in the temperature range used. For most GC applications, this limits the range of PAH that may be analysed to those PAH containing up to 8 fused aromatic rings (molecular mass range < 350). The degree of condensation markedly affects the volatility of PAH. Less condensed PAH may be readily analysed by GC whilst more highly condensed PAH with the same number of carbons are often not amenable to analysis by GC (Fetzer, 1989). Naphtho[8,1,2abc]coronene ($C_{30}H_{14}$) for example, cannot be analysed by GC except with the use of high-temperature applications, whereas pyranthene ($C_{30}H_{16}$) can be readily analysed by GC (Figure 2.14). Recently, the high temperature GC analysis of PAH with relative molecular masses of up to 450 has been reported (Bemgard *et al.*, 1993).



Naphtho[8,1,2abc]coronene pyranthene

Figure 2.14 Structures of Naphtho[8,1,2abc]coronene and pyranthene

The compatibility of GC with element specific detectors also makes GC the preferred chromatographic method, for the analysis of heterocyclic PAH, particularly nitrogen and sulphur-containing PAH. The FID is the most widely used detector in GC because of its universality of response. It is the detector of choice for the GC analysis of hydrocarbons. The detection limits of the FID are however, comparatively high and its response to certain heterocyclic PAH, is poor compared to certain selective detectors. Where sensitivity to these compounds is required, flame photometric detectors (FPD) and thermionic specific detectors are used. The FPD detector is sensitive to sulphur and phosphorus containing compounds whilst the thermionic detector responds to nitrogen containing compounds. The response of both detectors is far superior to the FID for these compounds. Both flame photometric and thermionic specific detectors have been used to analyse for sulphur containing thiophenes and nitrogen containing carbazoles in diesel fuel, (Williams *et al.*, 1986). Other detectors that have been used in combination with GC for the analysis and detection of PAH include the electron capture detector (Grimsrud and Valkenburg, 1984) and the mass spectrometer (MS).

GC in combination with mass spectrometry (GC/MS) is a most powerful tool in the analysis of complex mixtures, and has been extensively used for the identification of PAH in diesel emissions (Peterson *et al.*, 1983; Henderson *et al.*, 1984; Tan, 1988; Farrar-Kan *et al.*, 1991; Lowenthal *et al.*, 1994). For most PAH analysis, GC/MS is used in the electron impact ionisation mode. Negative and

positive ion chemical ionisation techniques (NICI and PICI) are widely used in the analysis of polar, substituted PAH and to distinguish isomeric compounds (Oehme, 1985; Bayona *et al.*, 1988). GC/MS combines the high resolution of capillary GC with the molecular structure information provided by MS and often can lead to the complete identification of individual PAH. PAH are well suited to analysis by MS. The extensive π-electron delocalisation induces high stability in PAH. The mass spectra of PAH reflect this stability and contain an intense molecular ion and few fragment ions (Josefson, 1983). Alkyl-PAH, like the parent molecule, also generate clear mass spectra, dominated by a molecular ion, but with major fragment ions corresponding to the loss of the alkyl substituent also present in the mass spectra.

2.11.1 GC-FID analysis of PAH

GC analysis were performed on a Carlo Erba HRGC (model 5300) equipped with FID detection and on-column injection. The GC was fitted with a DB-5 (J & W Scientific,) capillary column (30m × 0.32mm I.D., 0.25μm film thickness). Hydrogen, at a flow rate of 2ml/min was used as carrier gas and nitrogen was used as make-up gas at a flow of 30ml/min. The detector was maintained at a temperature of 320°C. Peak detection and integration was performed using a Shimadzu, C-R3A integrator. A temperature gradient was used and varied in its initial oven temperature according to the sample solvent. For most GC analysis the sample solvent was DCM, and an initial oven temperature of 40°C was used. This was raised linearly to a final temperature of 300°C at 5°C/min and held at 300°C for 10 minutes. Where toluene was used as the solvent the initial oven temperature was 110°C. Toluene was the preferred solvent for GC analysis of samples containing higher molecular weight PAH such as the 4 and 5 ringed PAH fractions. This was owing to the improved chromatography of later eluting PAH and reduced GC analysis times. High boiling point solvents such as toluene and xylenes have been reported to improve both the FID response and chromatography, of high molecular weight PAH in their analysis by GC using a splitless injection technique (Brindle and Li, 1989; Trevelin *et al.*, 1992).

Identifications of PAH by GC were performed using the linear retention index systems of Lee *et al.* (1979) and Vassilaros *et al.*(1982) with naphthalene,

phenanthrene, chrysene and B[α]P as internal standards. Retention Indices were based on duplicate or triplicate injections and were compared with the literature data. Quantification of PAH by GC was performed using linear calibration graphs (R^2 not less than 0.999) constructed from the means of duplicate and triplicate injections of standard PAH solutions. Relative response factors for all of the major parent PAH, and representative isomers of their alkylated derivatives in diesel fuel were determined. The FID response to phenanthrene was taken as unity. Response factors were found to vary from 0.8 for naphthalene to 1 for B[α]P. This was in good agreement with the literature data (Tong *et al.*, 1984; Blanco *et al.*, 1992). The use of on-column injection avoided the problems of discrimination of higher boiling PAH that other injection techniques introduced.

2.11.2 GC/MS analysis of PAH

GC/MS used in the EI mode was employed routinely to confirm peak identifications performed by GC, and for quantification purposes. Two GC/MS systems were used in this research. GC/MSD was performed using a Hewlett Packard 5890 series II gas chromatograph equipped with a Hewlett Packard 7673 autosampler and Hewlett Packard 5970 series mass selective detector (MSD). The MSD was operated in the scan mode with an ionizing potential of 70eV and an ion source temperature of 300°C. The GC was operated in the splitless injection mode with an injector temperature of 250°C and was fitted with an OV-1 (0.32mm × 12m) capillary column. The temperature programme was from 40°C to 300°C at 5°C/min and held at 300°C for 20 minutes.

GC with high resolution MS was performed using a Carlo Erba Strumentazione HRGC interfaced to a Kratos MS25 mass spectrometer. A DB-5 (J & W Scientific, 30m × 0.32mm I.D., 0.25μm film thickness) capillary column was installed in the GC. The ion source temperature was 230°C and the ionizing potential was 40eV. Cold on-column injection and He carrier gas were employed throughout.

2.12 Radio-gas chromatography

Preliminary radio-GC investigations were performed on the system developed by Petch *et al.* (1988) which was based on the design of Wels (1977). In this system, the eluent from the FID is diverted upwards into a glass column, where a downward flow of 2-phenylethylamine (10%) in 2-methoxyethanol absorbed the $^{14}CO_2$. The system however, demonstrated poor resolution and a low collection efficiency of the $^{14}CO_2$ gas. Several commercially available radio-GCs were investigated for their applicability in diesel emission research.

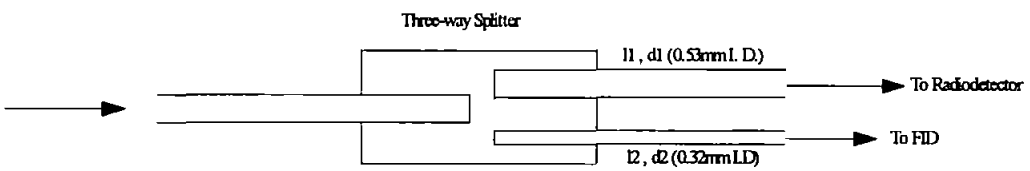
The main difficulty associated with the use of radio-GC systems in this research is the ability to introduce sufficient radioactivity to the detector to be above instrumental limits of detection (LODs). TESSA exhaust samples generally have low specific activities. The difficulties associated with introducing sufficient radioactivity to be above the instrumental limits of detection that are encountered in radio-HPLC analyses, are accentuated in radio-GC by the lower sample loading capacity of GC columns compared with HPLC columns. The difficulties are exacerbated by the fact that only a portion of the sample is counted in radio-GC analysis, whereas the whole sample is measured in radio-HPLC analysis. The problem has been overcome to a great extent through the use of large diameter GC columns which have greater sample loading capacities and shorter exhaust gas sampling times which have increased the specific activities of the exhaust samples.

2.12.1 Experimental method for the radio-GC analysis of diesel exhaust samples

GC analyses were performed using a Chrompak 9000 gas chromatograph, equipped with on-column injection, and FID detector. A temperature programme was used and consisted of an initial oven temperature of 50°C raised linearly at 5°C/min to 300°C which was held for 10 minutes. Two columns were evaluated in this research; a SPB5 borosilicate glass column (Supelco, 0.75mm I.D. × 60m) with a nominal sample loading capacity of 100-150 μg, and a DB5 megabore column (J&W Scientific, 0.53mm I.D. × 30m, 0.25μm film thickness) with a nominal sample loading capacity of 50μg. The separation of the aromatic fraction of diesel fuel, (1μl injection volume, 150mg/ml sample concentration) performed using the

borosilicate glass column is shown in Figure 2.15. The Figure illustrates that peak resolution is retained despite the high sample loading. The carrier gas was a mixture of Argon/Methane (95:5) at a flow rate of 20ml/min and 8ml/min for the SPB5 glass column and the DB5 megabore column respectively. The detector temperature was 320°C.

A schematic illustration of the radio-GC system is shown in Figure 2.16. To improve resolution a retention gap was created at the column inlet using a length of deactivated capillary tubing (50cm), as described in the literature (Grob, 1982; Grob and Grob, 1983). Press-fit connectors (Jones Chromatography) were used to join the two lengths of capillary tubing. The eluent was split between the two detectors in a ratio of approximately 10:1. The split is governed by the back-pressures in the two lines exiting the splitting device, and may be determined using a simple calculation:



$$\frac{1}{10} = \frac{m_1}{m_2} = \frac{\rho_1 . A_1 . V_1}{\rho_2 . A_2 . V_2} = \frac{\pi/4 . D_1^2 . V_1}{\pi/4 . D_2^2 . V_2}$$

where: ρ_1 & ρ_2 are the density of the carrier gas (kg/m^3)

V_1 & V_2 are the velocities of the carrier gas in the two lengths of tubing exiting the splitter (m/sec)

m_1 & m_2 are the mass transport rates of the carrier gas in the tubes (kgm/sec)

D_1 & D_2 are the diameter of the tubing to the FID (0.32mm) and the radiodetector (0.53mm) respectively.

l_1 & l_2 are the length of tubing connecting the splitter with the FID and the radiodetector, and need to be determined.

Since $\rho_1 = \rho_2$ & $\pi/4$ is the same for both flows:

$$\frac{1}{10} = \frac{D_1^2.V_1}{D_2^2.V_2} \quad \Rightarrow \quad \frac{V_1}{V_2} = \frac{1}{10} \times \frac{0.53^2}{0.32^2} = 0.27$$

Assuming an equal pressure drop across the two pieces of tubing:

$$\frac{\Delta P}{\Delta P} = \frac{f.(1/5).\rho_1.V_1^2.(l_1/D_1)}{f.(1/5).\rho_2.V_2^2.(l_2/D_2)} = \frac{V_1^2.l_1.D_2}{V_2^2.l_2.D_1} = 1$$

where: ΔP is the pressure drop and is the same for both,

f is the coefficient of friction and is the same for both

Now, $V_1/V_2 = 0.27$, $\therefore$

$$1 = 0.27 \times \frac{l_1.0.53}{l_2.0.32} \quad \Rightarrow \quad l_1/l_2 = 0.27 \times \frac{0.32}{0.53} = 0.16$$

$\therefore$ the ratio of $l_1:l_2 \approx 6:1$

This means that for 50cm length of tubing connecting the splitter with the furnace, a piece of tubing approximately 3m long connecting the splitter with the FID is required to achieve a 10:1 split using this diameter tubing.

In practice, back-pressure generated by the oxidation furnace reduced the ratio, (although the manufacturers claim the furnace generates negligible back-pressures). This required that an additional flow of make-up gas was plumbed in after the splitter. Deactivated capillary tubing was used to connect the splitter with the FID and furnace. The oxidation furnace was operated at an internal temperature of 700°C using activated copper as catalyst. The external temperature was 70°C and did not interfere with temperature programming. A drying tube was fitted between the gas chromatograph and the radioactivity detector to remove moisture vapour from the FID effluent gasses, which would otherwise quench the scintillations during counting. The drying tube is primarily responsible for the reduced chromatographic efficiency of the radio-GC system.

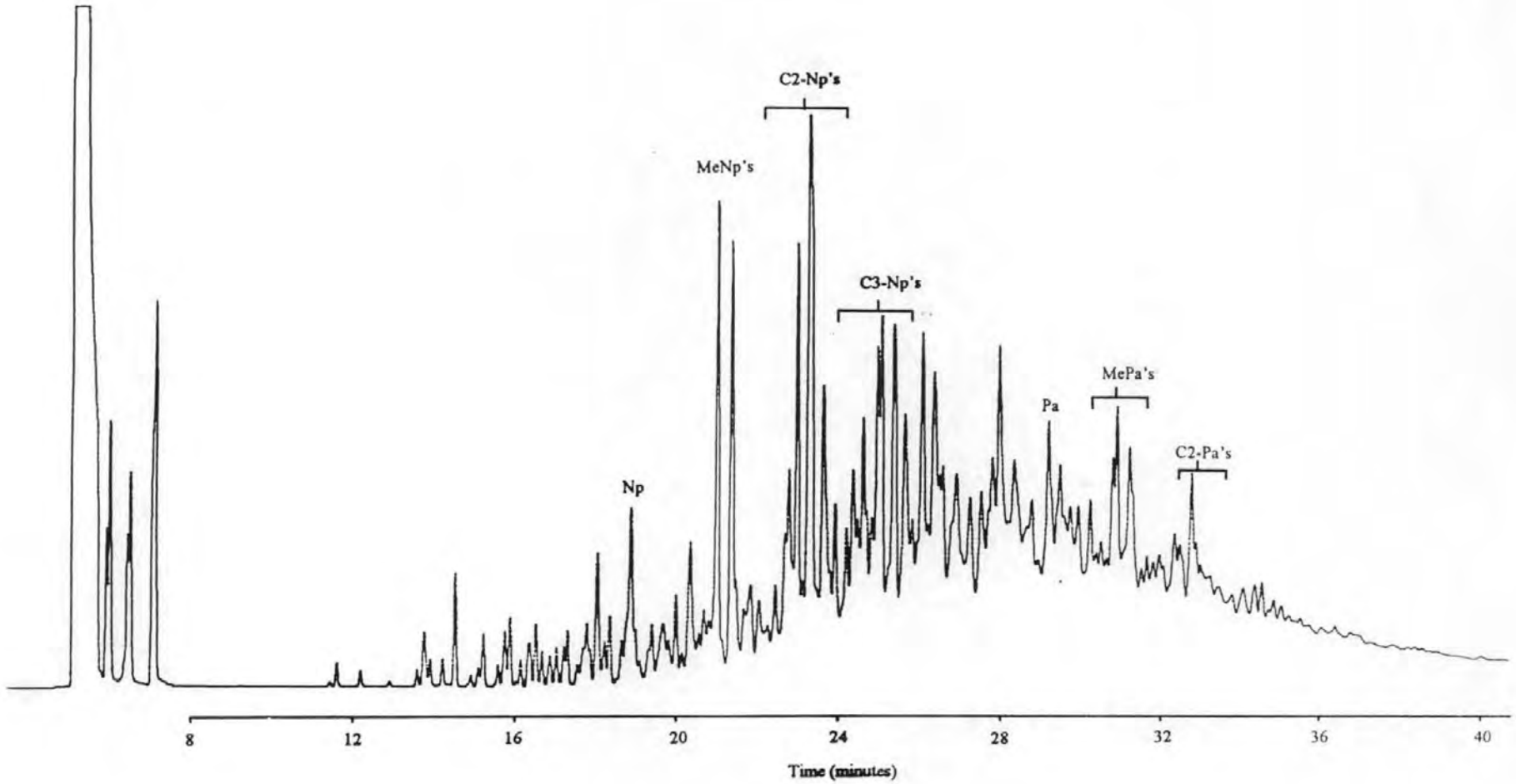


Figure 2.15 Gas chromatogram of the aromatic fraction of diesel exhaust separated on the 0.75mm I.D borosilicate glass column. Sample loading 150µg. (For chromatographic conditions see section 2.12.1)

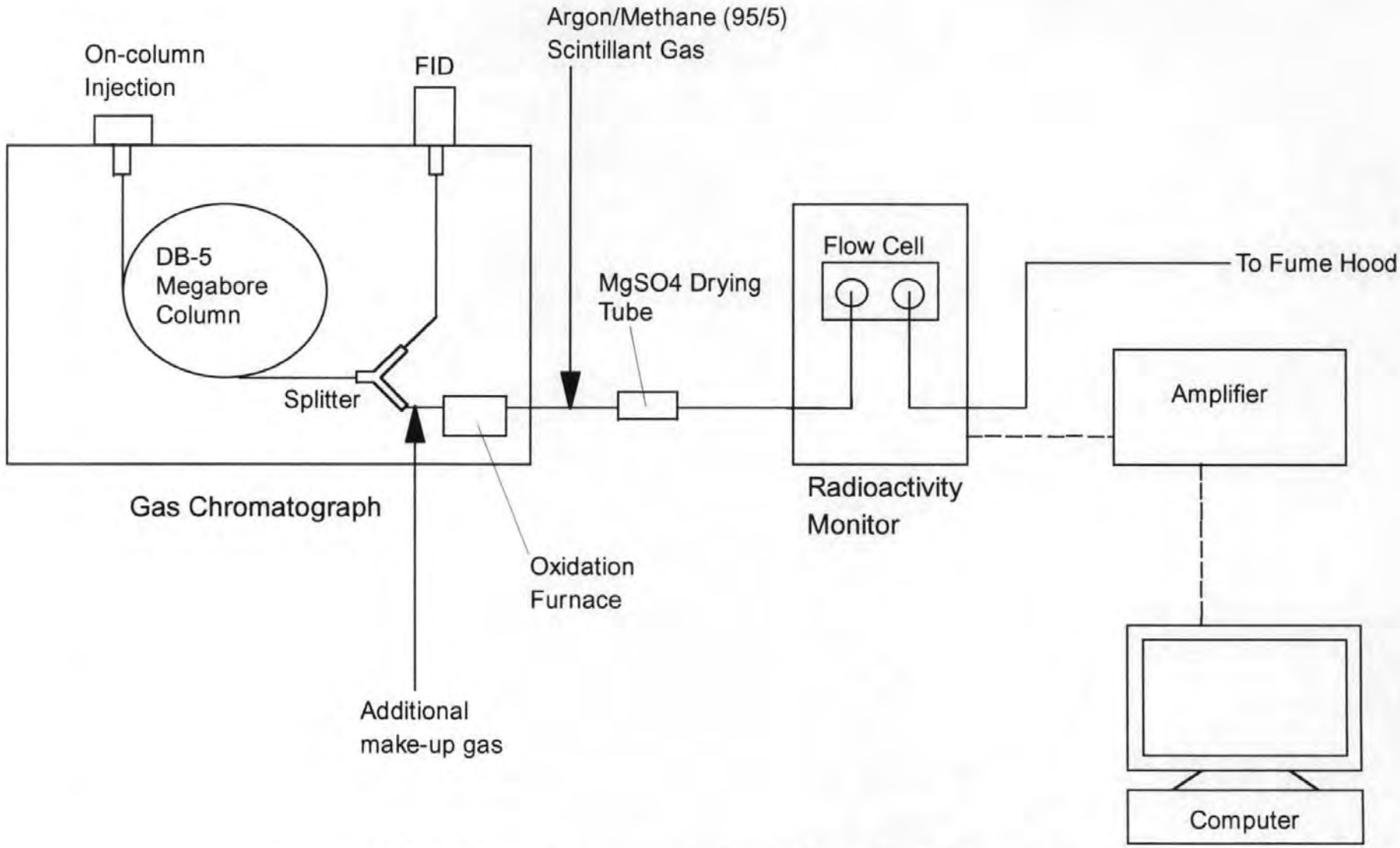


Figure 2.16 Schematic representation of the radio-GC system

Radioactivity measurement was performed using a Lablogic, GC RAM radiodetector. The scintillant gas was a mixture of argon/methane (95:5). This was also used as the GC carrier gas. Ideally helium would be used as carrier gas, since it demonstrates superior chromatography. The counting efficiency of the GC radiodetector was >80% and is greater than that of the HPLC radioactivity monitor owing to the improved mixing scintilllant gas and the $^{14}CO_2$, compared with the liquid-solid interactions in the HPLC radioactivity monitor. The Radio-GC demonstrated background levels of less than 3cpm. The limit of detection was taken as 3×S/N and determined as 10cpm (although the radio-GC has not been used for quantitative work in this research owing to limited access to the instrument).

2.13 Determination of PAH in used lubricating oil

Used lubricating oil has been shown to accumulate unburned diesel fuel hydrocarbons, including PAH as it ages (Williams *et al.*, 1989), and this can contribute to the burden of these compounds in the exhaust. The concentration of PAH in the used oil will affect their contribution to the exhaust from used oil. It is necessary to evaluate this contribution. The determination of PAH in crude, heavy oil distillates usually proceeds by a preparative HPLC stage to isolate the aromatic fraction of the oil, followed by GC-FID and GC/MS identification of PAH (Palmentier *et al.*, 1989; Matsuzawa *et al.*, 1990; Ostman and Colmsjo, 1989). Lamprecht and Huber (1992) reported a two-dimensional HPLC technique with column switching and fluorescence detection for the determination of B[α]P in oil distillates. The analysis of PAH in used oils is, however, complicated by the composition of the used oil.

Used lubricating oil is a complex mixture of hydrocarbons, additives, carbonaceous particles and heavy metals. The mixture is kept homogenous by a variety of detergents and dispersants such as succinimides, succinate esters and alkylphenol amines (Liston, 1992), which may constitute up to 2-15% by weight of the oil (Vazquez-Duhault, 1989). The high additives and suspended particles content precludes the direct chromatographic analysis of used lubricating oil, owing to the fact that carbonaceous particles and high molecular weight additives will deposit at the head of the chromatographic column. This can impair column

performance. It is necessary to remove the additives and suspended particles and isolate the base oil hydrocarbons from this mixture prior to GC analysis. Dialysis is routinely employed to this end. The base hydrocarbons pass freely through the dialysis membrane whereas high molecular weight species, comprised of additives and suspended particles (usually > 1000 daltons) are trapped. A second method employed in the recovery of base hydrocarbons from lubricating oil, utilises organic solvents that dissolve the base oil and cause the dispersant additives and suspended particles to flocculate and settle. The procedure has been termed 'extraction-flocculation' (Reis and Jeronimo, 1988; 1990).

2.13.1 Experimental method for the clean-up of used lubricating oil

The method for extracting the base oil hydrocarbons from used lubricating oil is that based on the method outlined by Reis and Jeronimo (1988) with minor modifications in solvent volumes. D_8-Np, D_{10}-Pa and D_{12}-Ch were added to the used lubricating oil prior to the extraction procedure to evaluate PAH losses. 2-propanol with 10g/L potassium hydroxide (10ml) and hexane (1ml) were added to used lubricating oil (ca. 0.5g). The KOH acts to destabilise the electrically stabilised dispersion generated by the polar solvent, and improves the flocculation of additives (Reis and Jeronimo, 1988; 1990). The solution was homogenised in an ultrasonic bath for 5 minutes and then allowed to stand for 30 minutes. The mixture was filtered using pre-extracted glass fibre filters (Whatman GF/F). Excess water (20ml) was added to the solution which was then extracted with hexane (3 × 10ml). Occasionally, on addition of water, the propanol solution would emulsify. Addition of aqueous KOH resulted in the formation of a gelatinous white precipitate, which was thought to consist of additives that had not been precipitated by the propanol. The precipitate was removed by filtration. The hexane extracts were combined and concentrated by rotary evaporation to a small volume (ca. 1ml). The extract was transferred to a preweighed vial and the remaining solvent removed by nitrogen purge. The residue was redissolved in 1ml of hexane for preparative silica-HPLC to isolate the aromatic fraction which was then analysed by GC and GC/MS.

The procedure was applied to a used oil sample (≈80hrs old). Gas chromatograms of the aromatic and aliphatic fractions of the "cleaned" oil are shown in Figure 17a and b. The aliphatics fraction obtained from silica-gel column chromatography accounted for 88% of the total oil by mass, and the aromatic fraction 8% of the oil by mass. The remaining mass was presumably made-up of polar material which had remained adsorbed to the silica column. PAH were quantified by GC/MS integration of their molecular ions. A range of PAH were detected in the aromatic fraction of the used lube oil that were not present in virgin oil. These comprised all of the major diesel fuel PAH including naphthalene, fluorene, dibenzothiophene, phenanthrene and their alkyl derivatives, and also fluoranthene and pyrene. The distribution of PAH in the oil was changed relative to the fuel so that phenanthrene (13ppm) and its methyl (100ppm total) and dimethyl (120ppm total) substituted homologues were most abundant. Naphthalenes, fluorenes and dibenzothiophenes were present in lower abundance. In the aliphatic fraction of the used oil, a series of *n*-alkanes ranging from *n*-C_{15} to *n*-C_{22}, which were absent in the virgin oil, were identified. These results confirm the conclusions of other research that diesel fuel accumulates in the lure oil as it ages (Williams *et al.*, 1989).

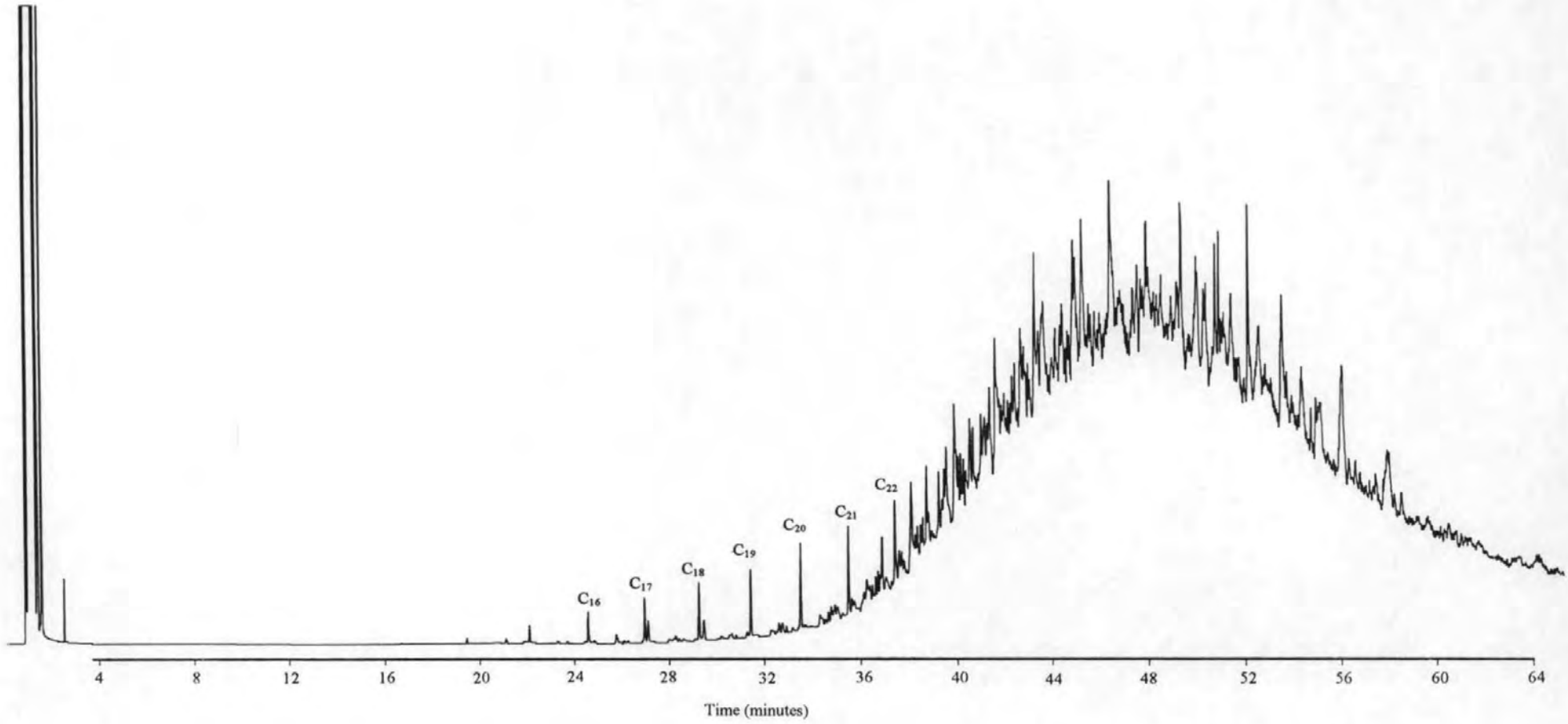


Figure 2.17a Gas chromatogram of the aliphatic fraction of used lubricating oil after the clean-up procedure

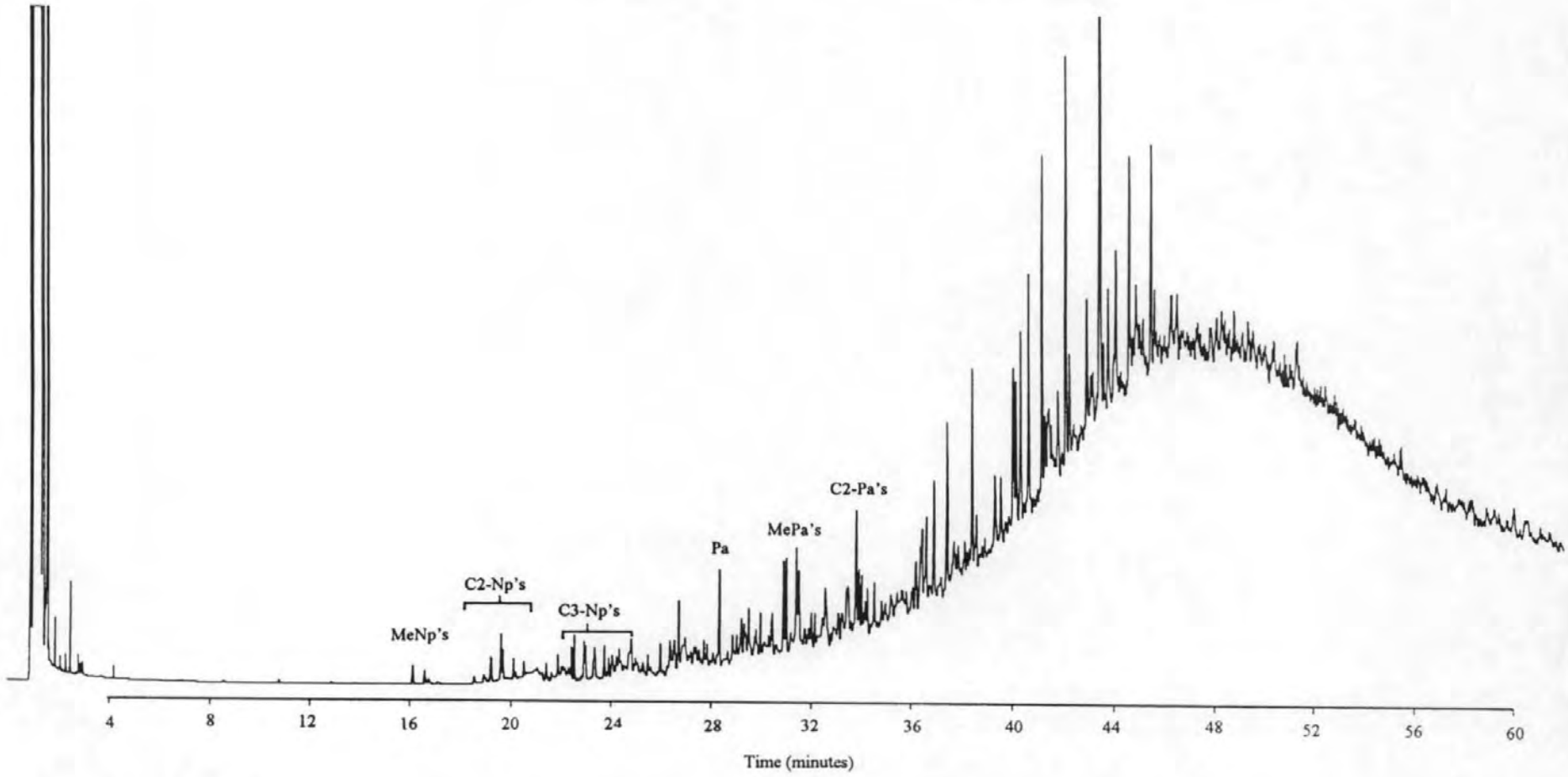


Figure 2.17b Gas chromatogram of the aromatic fraction of used lubricating oil after the clean-up procedure

Chapter 3

COMBUSTION of ^{14}C-LABELLED DIESEL FUEL HYDROCARBONS in the PERKINS PRIMA DIESEL ENGINE

3.1 Introduction

Much debate exists concerning the origin of organic species in diesel emissions. The primary sources for organic species in the emissions are from fuel survival, pyrosynthesis and lubricating oil carry over (Longwell, 1982; Williams *et. al.*, 1989). This research has focused on the use of radiotracers added to the fuel prior to combusion to investigate the relative contributions from these sources of organic species in the emissions. The radiotracer technique, developed in Plymouth, can yield unequivocal information with regard to the relative contribution of specific components to the emissions from these sources, that is unavailable by any other technique.

Of particular interest to both the environmental scientist and to the engine manufacturers are the emissions of PAH which are a hazard to human health owing to their carcinogenicity (IARC). Diesel engines are significant contributors to the atmospheric burden of PAH especially in urban areas (Stenburg, 1985). It is desirable therefore to understand the mechanisms which are responsible for the presence of PAH in diesel emissions and the relative contribution of PAH from these sources.

This research has involved investigation into diesel combustion of three ^{14}C-radiolabelled PAH and one radiolabelled n-alkane:

[9-^{14}C]fluorene

[4,5,9,10-^{14}C]pyrene

[7,10-^{14}C]B[α]P

[1-^{14}C]hexadecane

These species were chosen as representative PAH compounds with different ring size and structure type. Hexadecane was chosen because earlier work in the group had suggested that aliphatic hydrocarbons might be a source of aromatic products of combustion (Rhead *et al.*, 1990). A major aim of the investigation was to determine unequivocally the degree of survival of individual fuel components (rather than recoveries reported elswhere in the literature). Fluorene and pyrene are major parent PAH species in diesel fuel at concentrations of 770ppm and 120ppm respectively. B[α]P is a minor constituent of diesel fuel (< 1ppm) but has been classified by the

IARC (IARC, 1989) as a probable human carcinogen. With the exception of ^{14}C-B[α]P, the experiments were performed in duplicate.

3.2 Experimental

3.2.1 Engine conditions

Radiotracer experiments were performed at identical conditions of speed and load to facilitate comparisons between combustion of all HCs investigated. The engine was operated at an engine speed of 2500rpm and an engine load of 50Nm. The power output at these engine conditions was 13KW, equivalent to approximately half of full power, and simulates a period of high speed driving such as may be found on a motorway. The combustion process at these engines conditions is at its most efficient and emissions of fuel unburned hydrocarbons (UHCs) from the Prima diesel engine are correspondingly at their lowest (Collier, 1994).

3.2.2 Contribution of fuel HC to the emissions from lubricating oil

The degree to which lubricating oil contaminants influence the exhaust composition depends on both the concentration of contaminants in the oil and extent of the lube oil carry over to the exhaust. In this research, the lubricating oil contribution to diesel emissions was quantified by gas chromatography, using a method similar to that outlined by Cuthbertson (1987). The average molecular mass of the lubricating oil was significantly greater than that of the fuel. Hydrocarbons contributed to the exhaust from either source were identified according to their retention times using gas chromatography. The aliphatic fraction of the lubricating oil, usually the most prevalent part of the oil, was undetected in the exhaust samples collected by TESSA from the Prima during this research. It was concluded, that for this engine under the stated conditions, lubricating oil carry over to the exhaust was negligible.

3.2.3 Assessment of the relative contribution to diesel emissions of HCs from fuel survival or pyrosynthesis using radiochemical specific activities of fuel spiked HCs

Fuel survival and pyrosynthesis are the two major sources of hydrocarbons in the Prima emissions. The relative contribution from these sources was evaluated in this research using the radiochemical specific activities of HCs added to the fuel. The specific activity of a radiochemical is defined as the quantity of radioactivity per unit mass of material and is measured in units of μCi/mmol or Bq/mmol. Calculation of the specific activity of a compound in the exhaust required that the both the mass of hydrocarbon and the quantity of associated radioactivity, was determined.

The specific activity of the radiochemical spiked in the fuel was reduced during sampling owing to dilution from the unlabelled HC present in the fuel. The mass of the unlabelled hydrocarbon contributed by the fuel was quantified from its concentration in the fuel, the rate of fuel consumption and the sampling time and an average specific activity for the radiochemical entering the test cylinder was determined. The difference in the specific activity between the radiochemical in the fuel and in the emissions was used to establish whether pyrosynthesis was contributing to the exhaust burden of the HC, in addition to that from fuel survival. Constant specific activities for the hydrocarbon in the fuel and in the emissions would indicate that its sole source in the emissions was as a result of survival. A decrease in the specific activity, owing to dilution of the radiochemical by the pyrosynthesized nonlabelled hydrocarbon, would indicate that the hydrocarbon was being formed as a result of pyrosynthetic reactions occurring in the combustion chamber.

Unlike other quantification procedures, the use of radiochemical specific activities does not require that losses, owing to the analytical procedure, be evaluated, since these losses will occur equally to both the labelled and nonlabelled hydrocarbon. The ratio of the labelled to the nonlabelled hydrocarbon is expected to remain constant regardless of the number of analytical procedures the sample has passed through.

3.2.4 Introduction of the radiotracer into the fuel just prior to combustion

The method for introducing ^{14}C-radiotracers into the Perkins Prima diesel engine has been developed to mimic as far as is possible the normal operation of the engine (Trier *et al.*, 1991) and is described in more detail in Chapter 2. (section 2.5). The chemical reactions taking place within the combustion chamber should be unaffected by the spike. One limitation however, is the introduction of a mass of material associated with the radiochemical, that is in excess of the mass of the HC that would be contributed from the fuel under normal circumstances. In order to distribute the excess hydrocarbon burden from the radiochemical, over the maximum possible volume of fuel during the injection procedure, the volume of spike introduced into the fuel line was made as large as possible. In practice this volume was limited to about 560µl by the volume of the injector line between the high pressure injector and the cylinder.

This problem was most apparent for the combustion of ^{14}C-B[α]P. 91µCi of B[α]P dissolved in 500µl of fuel was introduced into the cylinder and had associated with it 366µg of material. The concentration of B[α)]P in the spiked fuel (732µg/ml) was much in excess of the concentration of B[α]P in normal diesel fuel (0.89µg/ml). The extent to which this mass of B[α]P has affected the combustion process in the chamber is difficult to gauge. We have assumed that it has not significantly altered the combustion process because the mass of the B[α]P spike is still small compared to the other components of the fuel. The problem is less acute in the combustion of the ^{14}C-fluorene and ^{14}C-pyrene radiotracers. Their concentration in the spiked fuel was 2.6mg/ml and 0.86mg/ml, compared to a normal concentration of 0.77mg/ml and 119mg/ml respectively, in unspiked fuel.

3.3 Results

3.3.1 Diesel combustion of [7,10-^{14}C]B[α]P

The preliminary stage in the analysis of the ^{14}C-B[α]P in the emissions was the fractionation of the exhaust sample by semi-preparative HPLC using underivatised silica. Five fractions were collected and comprised a fraction

containing PAH and heterocyclic PAH, and four fractions containing exhaust components of increasing polarity. The radioactivity present in each fraction was determined by liquid scintillation counting and is presented in Table 3.1 as a percentage of the original radioactivity.

Table 3.1. Radioactivity present in each of the five fractions of B[α]P exhaust collected from preparative silica-HPLC.

	^{14}C-B[α]P	Exhaust fraction				
	in fuel	aromatics	2	3	4	5
Radioactivity (μCi)	91	0.036	0.0032	0.0028	0.001	0.007
Radioactivity as a % of the original	100	0.04	0.0038	0.0003	0.0013	0.008

The bulk of the radioactivity isolated in the exhaust (≈75%) was concentrated in the aromatic fraction. Minor amounts of radioactivity were present in the four remaining polar fractions. Radioactive products of combustion present in the polar fractions were not identified since the levels of radioactivity were well below the limits of detection of the HPLC radioactivity monitor. The radioactivity associated with these fractions was almost certainly owing to partially oxidised ^{14}C-B[α]P species. GC/MS analyses of the less polar fractions 2 & 3, which corresponds to nitro and aldehyde derivatives, failed to identify individual compounds, with the exception of 9-fluorenone, owing to the poor detection limits of the instrument for these compounds .

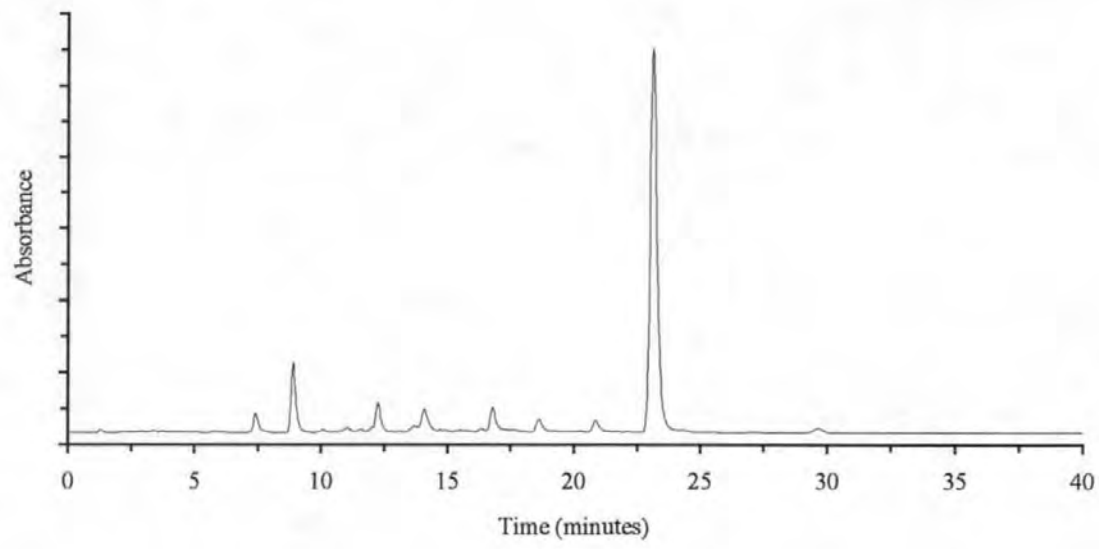
The aromatic fraction isolated by silica-HPLC, was further fractionated by normal-phase HPLC using an aminosilane column. Four aromatic subsamples were collected. Each subsample was analysed by reverse-phase radio-HPLC, with UV and fluorescence detection. A single radio-peak was detected in the subsample containing four and five ringed PAH (Figure 3.1). The identity of the radio-peak was confirmed as that of ^{14}C-B[α]P, by comparison of its retention time, with the retention time of the B[α]P mass peak, monitored by fluorescence. Triplicate injections of a B[α]P standard established the retention time for B[α]P. The slight difference in retention times between the mass and radioactive peaks was owing to the delay period between the fluorescence and radioactivity detectors connected in

series. Integration of the radio-peak indicated that the ^{14}C-B[α]P survival, was equivalent to 0.04% of the original radioactivity.

A B[α]P survival of 0.04% is substantially less than the recovery of B[α]P quoted in research by Williams *et al.* (1989). In their research, the authors sampled a 4L DI Perkins diesel engine at a similar power output, and recovered >3% of the original mass of B[α]P consumed. These figures represent a total recovery of B[α]P from all sources including pyrosynthesis, as opposed to just B[α]P survival. A B[α]P survival of 0.04% is, however, more in line with the recoveries quoted for other PAH of between 0.03% and 0.3%, in the same research. Our figure of 0.04% survival is also in better agreement with the results of Henderson (1984) where, in experiments spiking diesel fuel with 10g/L B[α]P greater than 99% of the B[α]P was combusted. In both cases however, no distinction between the relative contributions from lubricating oil and pyrosynthetic reactions could be made. Williams and Swarin (1979) investigated B[α]P emissions from 13 diesel, petrol and catalyst equipped petrol cars. Mass emission rates for B[α]P were determined, however, no analysis of the fuel concentration of B[α]P was performed and hence the recovery of B[α]P could not be assessed.

The contribution of B[α]P to the emissions from pyrosynthetic sources was determined by measuring the variation in the specific activities of B[α]P in the fuel and in the exhaust sample. This required that the mass input of B[α]P to the test cylinder was established. The concentration of B[α]P in the fuel could not be determined reliably by GC/MS of unfractionated fuel, owing to its low concentration. Instead, quantification was performed using RP-HPLC analysis of the B[α]P aromatic subsample of diesel fuel, with fluorescence detection. The fluorescence detector was operated at excitation (λ_{ex}) and emission (λ_{em}) wavelengths of 365nm and 427nm. This enhanced the response to the B[α]P whilst suppressing that of other compounds eluting in this fraction and aided integration. B[α]P was quantified from a linear calibration graph, ($r^2 > 0.999$) constructed from duplicate and triplicate injections of standard B[α]P solutions.

a)



b)

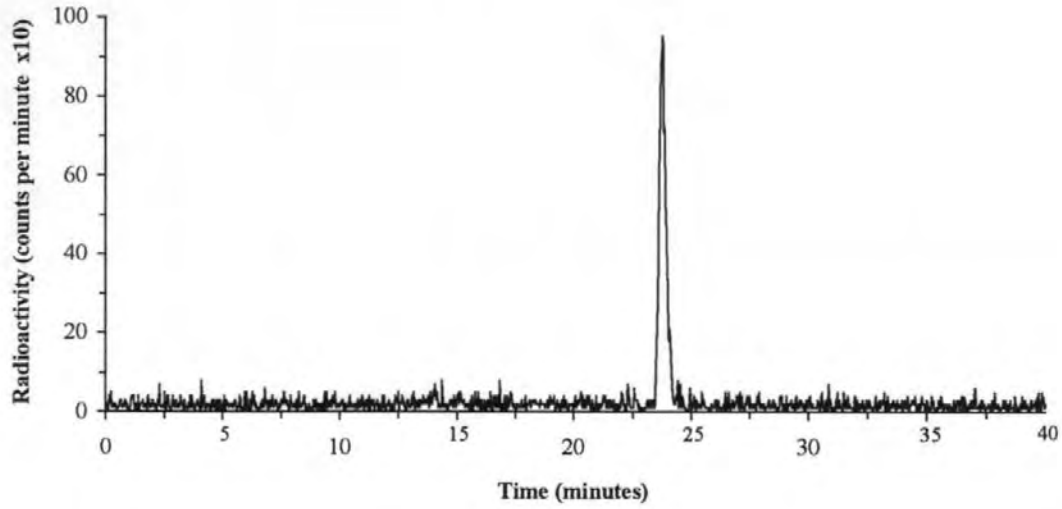


Figure 3.1 HPLC analysis of 14C-B[α]P exhaust subsample showing a) fluorescence chromatogram and b) radioactivity chromatogram (for chromatographic conditions see Section 2.10.2.1)

The concentration of B[α]P in the fuel was found to be 0.85ppm, in agreement with the figure quoted by Williams *et al.* (1986) of < 1ppm. Owing to the low concentration of B[α]P in diesel fuel, the mass of B[α]P contributed from the fuel in the 10 second sampling period was a fraction of the mass of B[α]P associated with the radiochemical. The reduction in the specific activity of the B[α]P radiochemical was, therefore, negligible in the 10 second sampling period and hence was ignored. The specific activity of B[α]P in the exhaust was also quantified using fluorescence detection and was determined as 200μCi/mg +/- 10%. This compares with a specific activity of B[α]P in the fuel of 248μCi/mg. It was concluded that the majority of B[α]P in the exhaust (≈80%) is owing to the survival of the B[α]P in the fuel. There is a small contribution of B[α]P from pyrosynthesis (<20%).

Trier *et al.* (1990) concluded that 4 and five ringed PAH including B[α]P in the emissions originated almost entirely from pyrosynthetic reactions in the combustion chamber since these compounds were present in only trace amounts in the fuel. The extent of pyrosynthesis was not established. Williams *et al.* (1989), also found tentative evidence for the pyrosynthetic formation of 4 & 5-ringed PAH, including B[α]P, from smaller 2 and 3 ring PAH precursors. In later research, Abbass *et al.* (1989) concluded that the pyrosynthetic contribution to diesel exhaust PAH was, at most, 5% of the total PAH exhaust burden. A detailed kinetic mechanism for the formation of B[α]P has been proposed by Badger and Novotny (1963) from the results of pyrolysis experiments. The results from such studies are not directly applicable to diesel combustion owing to the low temperatures at which pyrolysis studies take place, and the difference in combustion conditions. However, the suggested kinetic route is in agreement with the key features of later kinetic models proposed to account for PAH formation (Crittenden and Long, 1973; Frenklach, 1985).

3.3.2 Combustion of [9-^{14}C]fluorene.

100μCi and 120.5μCi of [9-^{14}C]fluorene, dissolved in diesel fuel (≈550μl), were introduced into the Prima in two separate engine runs. The exhaust was sampled for 25 seconds for each engine run. The whole exhaust samples were

fractionated using silica-column chromatography into aliphatic aromatic and polar fractions according to the method described in Chapter 2 (section 2.8.1.1). The radioactivity, measured by scintillation assay, recovered in the aliphatic, aromatic and polar fractions after silica-column chromatography is shown in Table 3.2.

Table 3.2 Radioactivity present in the fractions of fluorene exhaust

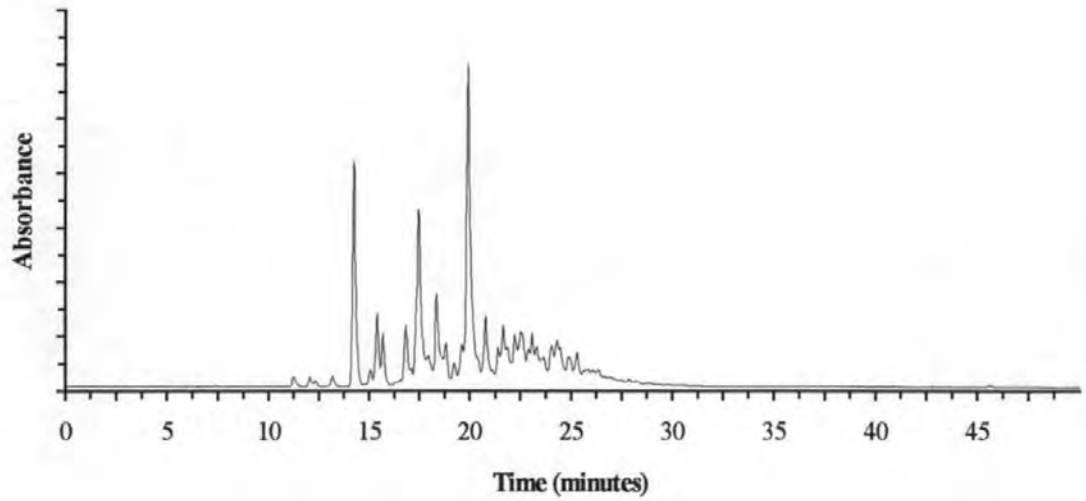
	^{14}C-Fl in fuel	Exhaust fraction		
		aliphatics	aromatics (^{14}C-fluorene)	polar
Radioactivity (μCi)	100 & 120	nd	0.75 & 1.19	0.05 & 0.07
Average activity (as a % of the original)	100	nd	0.87 +/- 0.1	0.06 +/- 0.01

nd: not detected

The aromatic fractions were further separated according to ring size by preparative HPLC on an aminosilane column. Analysis of each subsample by reverse-phase HPLC with radio-detection identified a single radioactive product present in the fluorene subsample. UV and radioactivity chromatograms for the HPLC analysis are shown in Figure 3.2. The peak (retention time 14mins 32seconds) represents the major radioactive product in the emissions and was identified as ^{14}C-fluorene by comparison with retention time of the fluorene mass peak from the UV chromatogram. The radioactivity associated with ^{14}C-fluorene in the exhaust was equivalent to a survival of 0.77% and 0.97% in the duplicate engine runs.

The specific activity of ^{14}C-fluorene in the emissions was determined by GC quantification of the mass of fluorene, and liquid scintillation assay of the associated radioactivity in the fluorene subsample, and was established as 16μCi/mg and 13.8μCi/mg in the duplicate exhaust samples. This compares with values for the specific activities of ^{14}C-fluorene in the fuel of 20.8μCi/mg and 19.7μCi/mg respectively (based on a fuel concentration of fluorene of 770ppm determined by GC/MS molecular ion integration). These results indicate that the major source of fluorene in the exhaust was as a result of survival (73.5% +/- 2.5%). A significant proportion of fluorene in the emissions however, (26.5% +/- 3%) was formed during combustion.

a)



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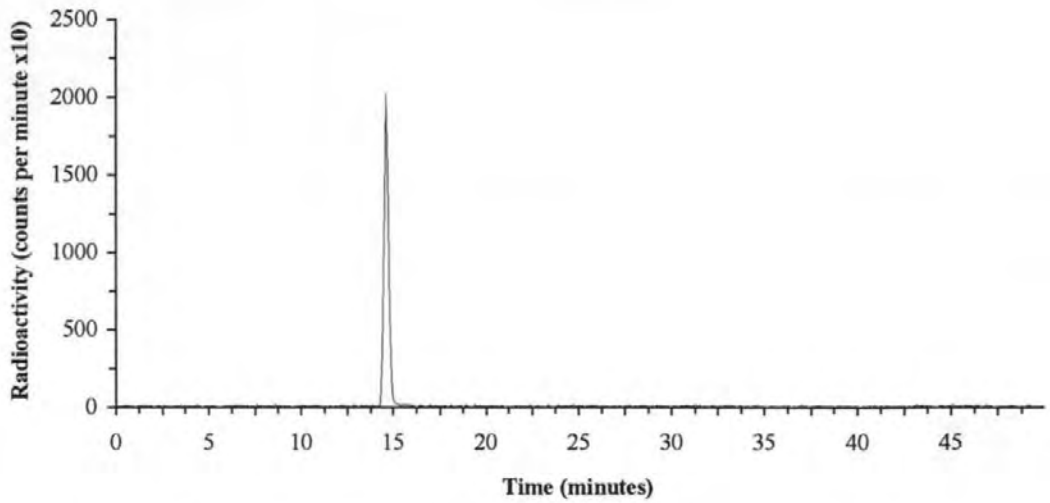


Figure 3.2 HPLC analysis of ^{14}C-fluorene exhaust subsample showing a) UV chromatogram and b) radioactivity chromatogram (for chromatographic conditions see Section 2.10.2.1)

3.3.3 Combustion of [4,5,9,10-^{14}C]pyrene

113.6μCi and 110μCi of [4,5,9,10-^{14}C]pyrene was introduced into the test cylinder of the Prima in duplicate engine runs. The exhaust was sampled for 30 seconds. The whole exhaust sample was extracted and concentrated and was then fractionated into aliphatic, aromatic and polar fractions on a silica-column. The radioactivity present in each of the three exhaust fractions is presented in Table 3.3.

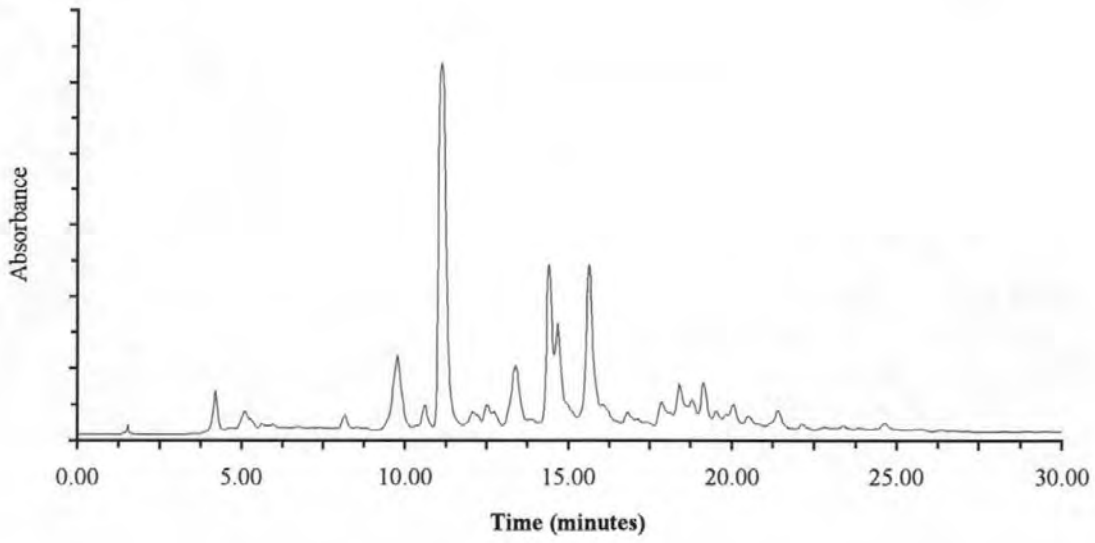
Table 3.3 Radioactivity present in the fractions of pyrene exhaust

	^{14}C-Py in fuel	Exhaust fraction		
		aliphatics	aromatics (^{14}C-pyrene)	polar
Radioactivity (μCi)	113.6 & 110	nd	0.20 & 0.18	0.10 & 0.08
Average activity (as a % of the original)	100	nd	0.17 +/- 0.1	0.08 +/- 0.01

A portion of the aromatic fraction was further separated into ring-size subsamples by preparative HPLC using an aminosilane column. Each aromatic subsample was analyzed by reverse-phase HPLC with either UV or fluorescence detection. A single radio-peak was detected in the 4 and 5-ringed aromatic subsample (Figure 3.3). This was identified as ^{14}C-pyrene surviving combustion, by comparison with retention times. Integration of the radio-peak established the extent of ^{14}C-pyrene survival as 0.18% and 0.16% of the original radioactivity introduced in the duplicate engine runs. The radio-HPLC results were confirmed by radio-GC analysis (Figure 3.4). A single radio-peak was detected in the exhaust sample with a retention time that corresponded with that of a ^{14}C-pyrene standard.

The amount of pyrosynthesized pyrene was assessed from the specific activities of the radiochemical in the fuel and in the exhaust. The concentration of pyrene in the fuel was determined as 115ppm, by GC analysis of the corresponding fuel aromatic subsample. The specific activity of ^{14}C-pyrene in the fuel was found to be 71.2μCi/mg and 67μCi/mg. This compared with a specific activity for pyrene in the exhaust of 20.4μCi/mg and 19.2μCi/mg. It was concluded, that the major contribution to pyrene in the emissions for this experiment was from pyrosynthesis (71% +/- 1%). The contribution from fuel survival constituted the remainder of pyrene in the exhaust (29% +/- 1%).

a)



b)

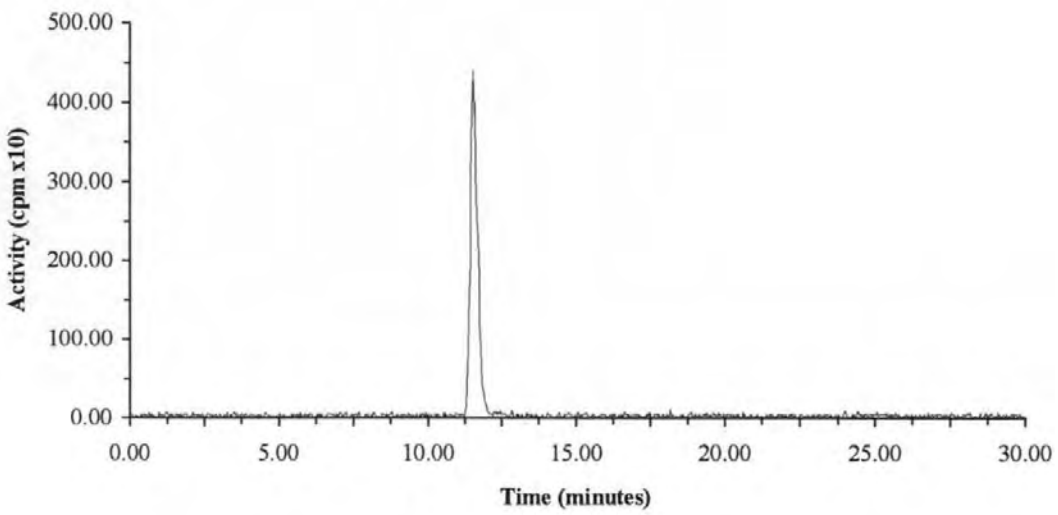


Figure 3.3 HPLC analysis of ^{14}C-pyrene exhaust subsample showing a) UV chromatogram and b) radioactivity chromatogram (for chromatographic conditions see Section 2.10.2.1)

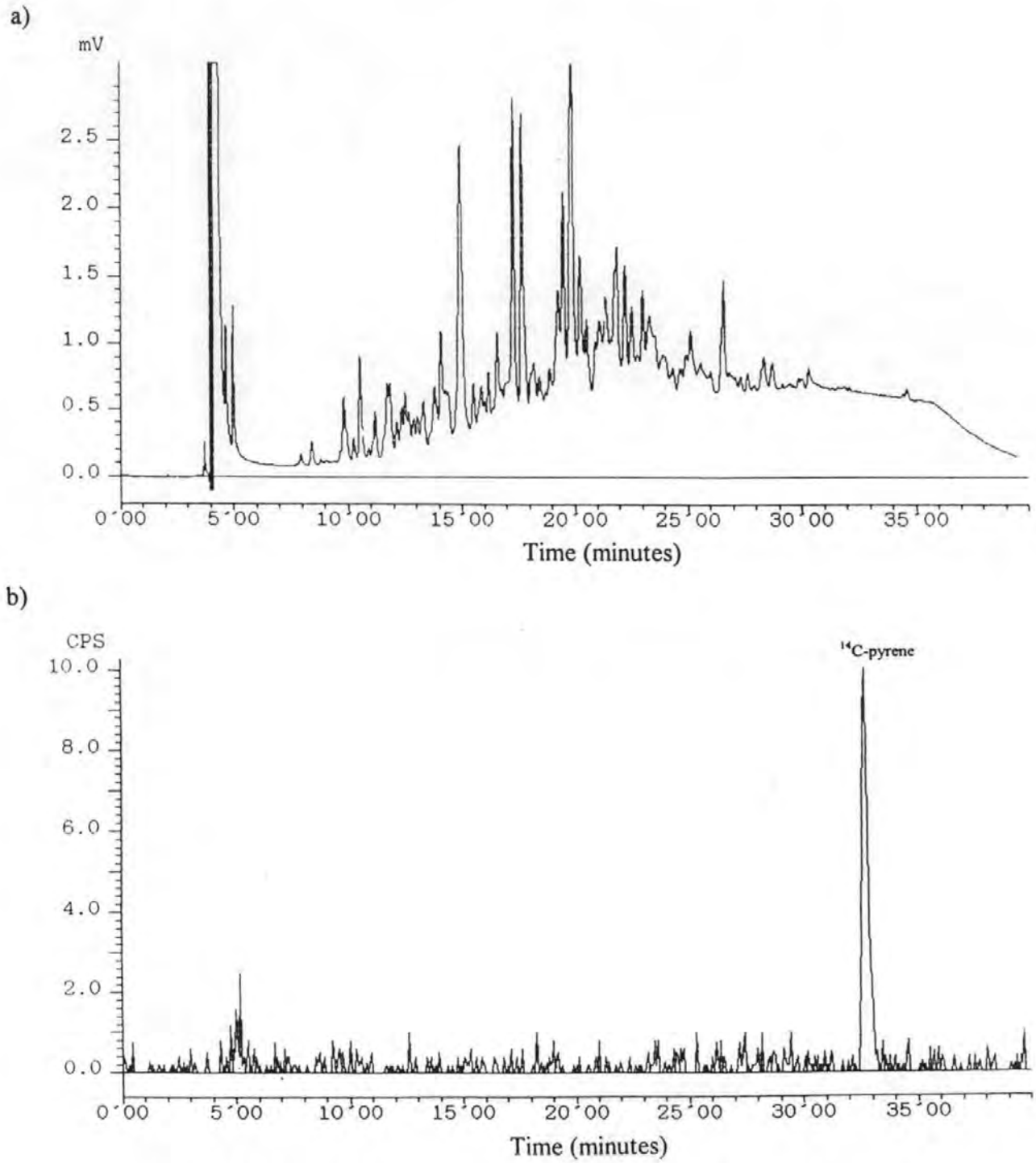


Figure 3.4 Radio-GC analysis of ^{14}C-pyrene exhaust sample showing a) FID response and b) radioactivity chromatogram (for chromatographic conditions see Section 2.12.1)

3.4 Discussion

3.4.1 Control of the PAH composition of diesel exhaust

The distribution of PAH in the Prima emissions reflects the relative contribution of PAH from fuel survival and pyrosynthesis. The contribution from the two sources is, to a large extent, determined by the physical and chemical properties of the PAH themselves, and particularly by their thermodynamic and kinetic stability. The distribution of PAH in the emissions will vary according to whether the reactions that produce and destroy PAH are themselves thermodynamically or kinetically controlled. The following discussion is intended to place the results from the current research in this context and to provide a framework with which to interpret future experimental observations.

3.4.1.1 The influence of thermodynamics on the distribution of PAH in diesel exhaust emissions

In combustion systems, one of the major parameters governing the distribution of species in the emissions, is their stability at high temperatures. The stability of a compound can vary greatly with temperature. For example, acetylene, (C_2H_2) which is highly reactive at room temperature, is one of the most stable hydrocarbons at the high temperatures of diesel combustion. Conversely, alkanes, (C_nH_{2n+2}) which are stable at room temperature, are highly unstable at diesel combustion temperatures. The relative stability of one state compared to another is the realm of chemical thermodynamics and the equilibrium distribution of species at different temperatures may be anticipated in terms of their thermodynamic stability.

Measurement of the thermodynamic stability of a molecule requires the calculation of three main thermochemical values (Stein, 1978; Alberty, 1989 and 1990):

enthalpy of formation at temperature T (ΔH_f^T , $Kjmol^{-1}$)

entropy of formation at temperature T (ΔS_f^T, $J\ mol^{-1}\ K^{-1}$)

heat capacities (C_p, $J\ mol^{-1}\ K^{-1}$)

The enthalpy and entropy terms are combined in the Gibbs Energy to give an absolute measure of the total free energy of formation of a species:

$$\Delta G_f^T = \Delta H_f^T - T.\ \Delta S_f^T$$

The equilibrium distribution of individual components will favour those species with the lowest ΔG_f^T (Lam, 1988).

Recently, Stein *et al.* (1977) and Stein and Fahr (1978) applied an extension of the group additivity (GA) techniques developed by Benson (1969) to the estimation of these thermochemical properties. In this method, individual PAH molecules are broken down into four component groups for which thermochemical values have been determined experimentally from naphthalene and biphenyl. The contributions of these atomic groups, towards a specific thermochemical property, are then summed to obtain the corresponding thermodynamic value for the molecule. For unsubstituted PAH molecules, the groups are $[C_B\text{-}(H)]$, $[C_{BF}\text{-}(C_B)_2(C_{BF})]$, $[C_{BF}\text{-}(C_B)(C_{BF})_2]$ and $[C_{BF}\text{-}(C_{BF})_3]$. where C_B a carbon atom that is a member of only one aromatic ring and C_{BF} is a carbon atom at the junction of two or three fused aromatic rings. These groupings are illustrated in Figure 3.5. Using this data, the authors predicted the most thermodynamically stable PAH in a modelled combustion environment at equilibrium, for a range of temperatures. Reactions were balanced using acetylene (C_2H_2) and H_2, the most stable gaseous products of hydrocarbon combustion at high temperatures (Alberty, 1989). Alberty (1989, 1990) using the group values of Stein and Fahr (1978) determined ΔH_f^T, ΔS_f^T, ΔC_p and ΔG_f^T for the pyrene and coronene series of PAH.

The thermodynamic stability of PAH at high temperatures is primarily a result the delocalised π-electron orbitals providing stable repositories for electrons. PAH with a low H/C ratio also tend to be more thermodynamically favoured. This factor can be visualised in the greater stability of pericondensed PAH (high C/H ratio) compared to catacondensed PAH (lower C/H ratio). For example pyrene, a pericondensed PAH, is less reactive and has a greater thermodynamic stability than chrysene, a catacondensed PAH, even though both have the same number of aromatic rings (Doel and Sanders, 1994).

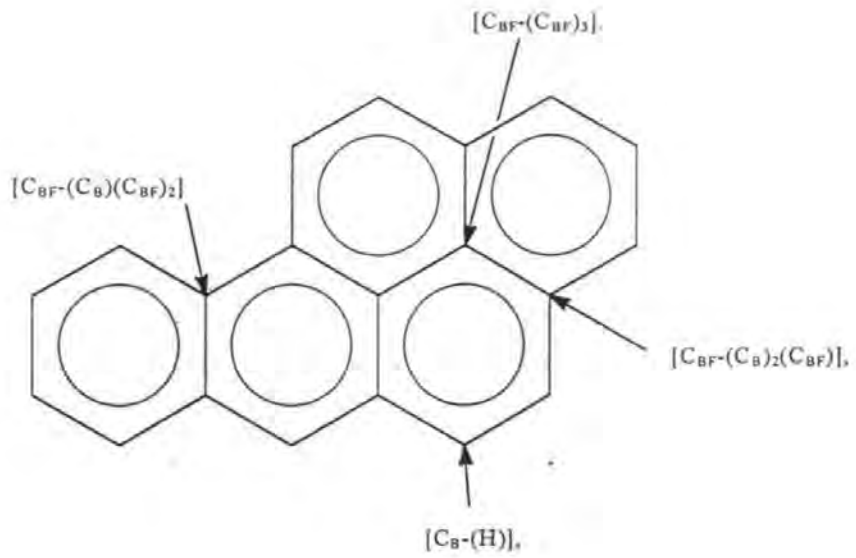


Figure 3.5 B[α]P consists of 12[C_B-(H)], 4[C_{BF}-(C_B)$_2$(C_{BF})], 2[C_{BF}-(C_B)(C_{BF})$_2$] and 2[C_{BF}-(C_{BF})$_3$] groups

PAH in combustion systems may form part of a larger equilibrium existing between the smaller acetylenic molecules which react with PAH to form larger PAH in a mechanism similar to that outlined by Frenklach (1985). These addition reactions are reversible hence an equilibrium may be established between the reactants and products. The equilibrium distribution of products is then related to the Gibbs free energy of the reaction ΔG_f^T by:

$$\Delta G_f^T = RT\ln K_p$$

where K_p is the equilibrium constant and R is the gas constant. The equation applies to reactants and products which behave as ideal gasses, a reasonable assumption in combustion systems (Barnard and Bradley, 1985; Alberty, 1989).

The results of Lam *et al.* (1988), using a jet stirred, plug flow reactor with an ethene/air fuel, suggest that this particular combustion process was tending toward an equilibrium condition. In this work, the authors predicted the thermodynamically favoured distribution of PAH in the exhaust effluent for a range of temperatures, using the thermochemical data for PAH determined by Stein (1978). The authors established that small aromatics (such as benzene and phenylacetylene) reached their

predicted values. Profiles for the aliphatic hydrocarbons declined steeply toward their thermodynamically predicted values.

Doel and Saunders (1994), also using the thermochemical values for PAH determined by Stein and Fahr (1978) investigated the influence of thermodynamics on the PAH distribution from diesel engines. The authors predicted the concentrations of several peri- and cata-condensed PAH found in diesel exhaust, at partial equilibrium with C_2H_2 and H_2 for a variety of temperatures. They then compared these results with experimentally determined exhaust PAH distributions from the literature. The predicted PAH distribution, which demonstrated an increase in larger pericondensed PAH and a decrease in small catacondensed PAH, was not observed experimentally. Interestingly, the model predicted no effect of pressure on the equilibrium concentrations of PAH. The authors concluded that thermodynamics did not influence the PAH distribution in diesel exhaust.

Their result is not surprising since the establishment of a thermodynamic equilibrium during diesel combustion seems unlikely, despite the rapidity of the free radical reactions that dominate the combustion process. Diesel combustion is characterised by short combustion times (<1msec for the engine conditions used in this research), and is highly inhomogenous with regard to the fuel spray distribution, and the temperature regime of combustion. These, and other factors, may preclude the establishment of an equilibrium condition.

3.4.1.2 The influence of kinetics on the distribution of PAH in diesel combustion

Kinetic mechanisms which lead to the formation of PAH are most difficult to investigate owing to the numerous possible reactions that may occur. It is generally accepted that the formation of PAH during combustion proceeds via the kinetics of rapid, reversible free radical pathways similar to that proposed by Frenklach (1985) (detailed in Section 1.9.2.1). In the absence of thermodynamic control, stable intermediate species, or end products of this type of pathway, are expected to increase in their relative abundance regardless of their thermodynamic stability.

Certain combustion experiments where aliphatic fuels have been doped with aromatic compounds have demonstrated that the PAH distribution in the SOF is substantially affected by the composition of the fuel mixture, implying that kinetic

considerations influence the PAH species distribution of the emissions. Ciajolo *et al.* (1992) combusted pure tetradecane and a mixture of tetradecane/α-methylnaphthalene in a diesel engine. They found a substantially increased rate in the emission of PAH for the tetradecane/α-methylnaphthalene fuel. Henderson *et al.* (1984) combusted pure hexadecane in a diesel engine spiked with a variety of PAH. The composition of the emissions in terms of PAH and soot production varied considerably with the composition of the fuel. Certain PAH (*e.g.* naphthalene and B[α]P) were shown to increase the emissions of all PAH and soot, whilst the combustion of hexadecane spiked with other PAH, (*e.g.* pyrene and phenanthrene) increased only the emissions of the same PAH. These observations, suggest that kinetic factors may have an important role to play in determining the emission of PAH.

Hamins *et al.* (1990), in a study of a laminar methane diffusion flame doped with various aromatic species (toluene, styrene, ethylbenzene) observed soot formation to be relatively independent of the composition of the fuel mixture, suggesting that kinetic factors are not important in soot (and therefore PAH) formation. However, experimental observations from simple flame studies may have little practical relevance in terms of the diesel combustion process. These studies employ a continuous combustion source, and under these conditions an equilibrium state may have time to become established. The thermodynamic stability of individual species as opposed to kinetic considerations, would, under these conditions, be expected to control their distribution in the emissions.

3.4.2 The origin of PAH in the Prima emissions.

In this research, the use of radiochemical specific activities has enabled the relative contributions from survival and pyrosynthesis for several PAH to be calculated accurately. Differentiating between these two possible sources is only possible using the radiolabelling technique. It has been demonstrated that for certain PAH (*e.g.* pyrene), pyrosynthesis is the major source of this PAH in diesel exhaust, (see Figure 3.6.). For the other PAH studied (naphthalene, fluorene and B[α]P), survival is the major source of these PAH in the Prima emissions. The significant

variation in the relative contribution of PAH from the two sources suggests that for individual PAH selective formation mechanisms operate during combustion.

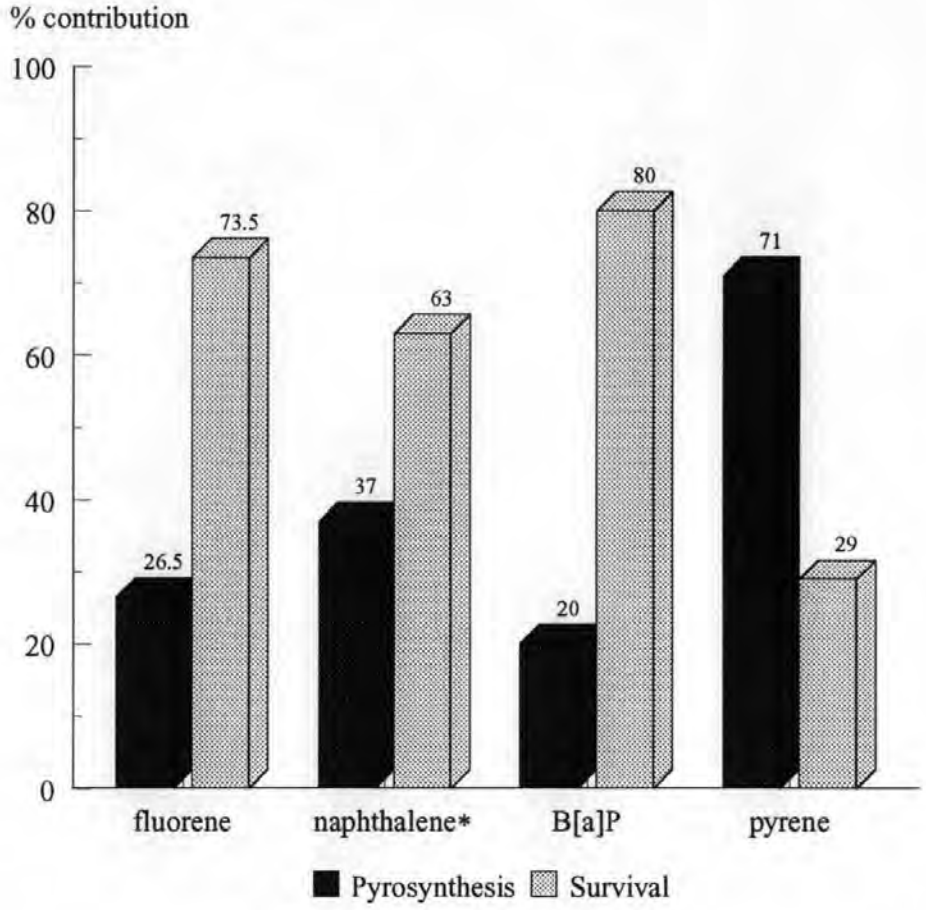


Figure 3.6. Relative contribution of PAH to the Prima emissions from pyrosynthesis and survival.

*Rhead and Pemberton, 1994

3.4.2.1 Pyrosynthesis of PAH during diesel combustion

Two primary routes to the formation of parent PAH exist. The first is through radical addition reactions of aromatic and aliphatic species in the combustion chamber and the second by dealkylation of the alkyl-substituted PAH derivative (Frenklach *et al.*, 1985; Longwell, 1982). The amount of pyrosynthesized PAH would be expected to vary depending on which pathway was dominant. If dealkylation reactions were the major source of pyrosynthesized PAH in the emissions, the pyrosynthetic contribution would be expected to be greatest for PAH

with a large number of alkyl-derivatives in diesel fuel. Where the kinetics of addition reactions was the dominant process in forming PAH, the pyrosynthetic contributions would be greatest for PAH that are intermediates or end products of favoured kinetic routes.

The pyrosynthesis of fluorene is an interesting case to study of the four PAH. Pyrosynthesized fluorene accounts for 26.5% of the total amount of fluorene in the exhaust. Fluorene was not predicted as a thermodynamically stable PAH at high temperatures by Stein (1985) owing to the ring strain that the methylene group bridging the two benzene rings introduces into the structure. A kinetic route to the formation of fluorene via carbene identified from early coal tar pyrolysis studies has been proposed (Wiersum, 1992) and the possibility exists that fluorene may occupy a position in some favoured kinetic pathway during diesel combustion. On the other hand alkylated fluorenes are abundant in diesel fuel and dealkylation reactions may account for the pyrosynthesized fluorene.

The small contribution of B[α]P from pyrosynthetic sources to the emissions is also an interesting result. Unlike fluorene, no alkyl-substituted B[α]P was detected in diesel fuel. The pyrosynthesized B[α]P cannot readily be explained by dealkylation reactions. Kinetic routes to the formation of B[α]P have been identified (Badger and Novotny, 1963) from pyrolysis studies and may also occur during diesel combustion.

For the two remaining PAH, pyrene and naphthalene, the pyrosynthetic contribution for these PAH to the exhaust amounted to 37% and 72% respectively. Both PAH were identified as the most thermodynamically stable isomers of this C/H ratio at high temperature equilibrium by Stein (1985). Both PAH also featured in a thermodynamically favoured pathway to the formation of large PAH through the addition of C_2 and C_4 species, in a mechanism similar to that proposed by Frenklach (1985). It is possible that the stability of these PAH and their presence in kinetic pathways to the formation of larger PAH molecules influence the extent to which they are pyrosynthesized during combustion. However, alkyl-derivatives of these PAH in diesel fuel are relatively abundant (especially alkylnaphthalenes). The loss of the alkyl substituent from these compounds (dealkylation) represents a facile route to the formation of the parent PAH during combustion.

The dealkylation of alkyl-PAH molecules during diesel combustion has been observed by a number of researchers (Trier *et al.*, 1990; Herlan, 1978; Barbella *et al.*, 1989). Recently, research at Plymouth has proved unequivocally, that a dealkylation pathway operates during diesel combustion (Rhead and Pemberton 1994). In this research, the combustion of radiolabelled ^{14}C-1-methylnaphthalene produced ^{14}C-naphthalene as a product.

Alkyl-PAH are present in diesel fuel in much greater concentrations than the parent PAH. A dealkylation pathway may, therefore, have a substantial impact on the emissions of the parent molecule. The relative ease of dealkylation has been linked to the reactivity of the position of the aromatic ring, at the point of substitution (Smith and Savage, 1991). This implies that certain alkyl-PAH isomers may prove more susceptible to dealkylation than others. Limited evidence to support this theory exists (see Chapter 4.). The importance of a dealkylation pathway and its mode of operation, are reviewed more fully in Chapter 4.

Of the PAH investigated in this research, with the exception of B[α]P, a dealkylation pathway during combustion could have accounted for the observed amount of pyrosynthesized naphthalene, fluorene and pyrene. A mass balance approach to the problem gives an indication of the rates of conversion of alkyl-PAH, that are required to account for the amount of pyrosynthesized PAH. The calculation assumes that all mono- and di-substituted PAH may contribute to the formation of the parent molecule by dealkylation. Tri-substituted species, such as the trimethylnaphthalenes have not been included in the mass balance since it is unlikely that the three alkyl side chains will be removed simultaneously to produce the parent PAH.

Using these assumptions, a simple calculation establishes that, conversion rates of 3.8% for alkylnaphthalenes and ≈6.0% for alkylfluorenes are required to account for the amount of the pyrosynthesized parent PAH. The required rate of conversion for the alkylpyrenes is >50% and is considerably greater than for either naphthalene or fluorene. This reflects the lower abundance of alkylpyrenes in diesel fuel relative to the parent PAH and the greater pyrosynthesis of pyrene during combustion. It also suggests that the ease with which pyrene undergoes dealkylation is necessarily greater than for naphthalene and fluorene, possibly owing to reduced

alkyl-aryl bond energies in larger aromatic structures, or greater reactivity at the point of alkyl substitution (refer to section 4.3).

The total mass of alkylpyrenes (methylpyrenes and C2-pyrenes) in diesel fuel was ≈400ppm. Quantification was performed by GC/MS integration of the molecular ion peaks of mass 216 and 230 from a fraction of diesel fuel containing four and five ring aromatics (Figure 3.7). Methylpyrenes were identified from by comparison of their mass spectra with a standard reference spectra (National Bureau of Standards, matches were 83% for 1-MePy, 89% for 2-MePy and 93% for 4-MePy) and from GC retention index data (Lee *et al.*, 1979). MePy standards are not commercially available. No methylfluoranthene isomers were detected in the fuel which may have complicated the identification of the methylpyrenes owing to their similar mass spectra. It was assumed that all isomers of molecular mass 230, were isomers of dimethylpyrene and not dimethylfluoranthene isomers.

No alkylated B[α]P have been detected in diesel fuel in this research. It cannot be concluded therefore, whether or not sufficient alkyl-substituted B[α]Ps exists to account for the small degree of pyrosynthesis observed experimentally for this compound. It should be noted however, that an experimental error of +/-10%, may reduce the observed pyrosynthesis of B[α]P to <10% and combustion reactions other than dealkylation may account for this small degree of pyrosynthesis.

3.4.2.2 PAH Survival

Fuel survival in diesel combustion may occur through a variety of physical processes. Primarily, these consist of fuel injected late in the cycle when cylinder temperatures are low, and fuel which experiences oxygen deficient environments in the combustion chamber (Section 1.9.1). In both situations, fuel molecules can by-pass the high temperature flame zone and escape to the exhaust intact. Fuel survival has been regarded as a physical process whereby droplets of fuel in low temperature, oxygen deficient environments escape unscathed to the exhaust. If this were the case, the extent of survival for all PAH would be constant, regardless of the size, stability or chemical reactivity of individual molecules. The current results, however, demonstrate that the extent of survival of specific PAH is not constant. Indeed, there is a 10-fold increase in the rate of survival of fluorene relative to B[α]P.

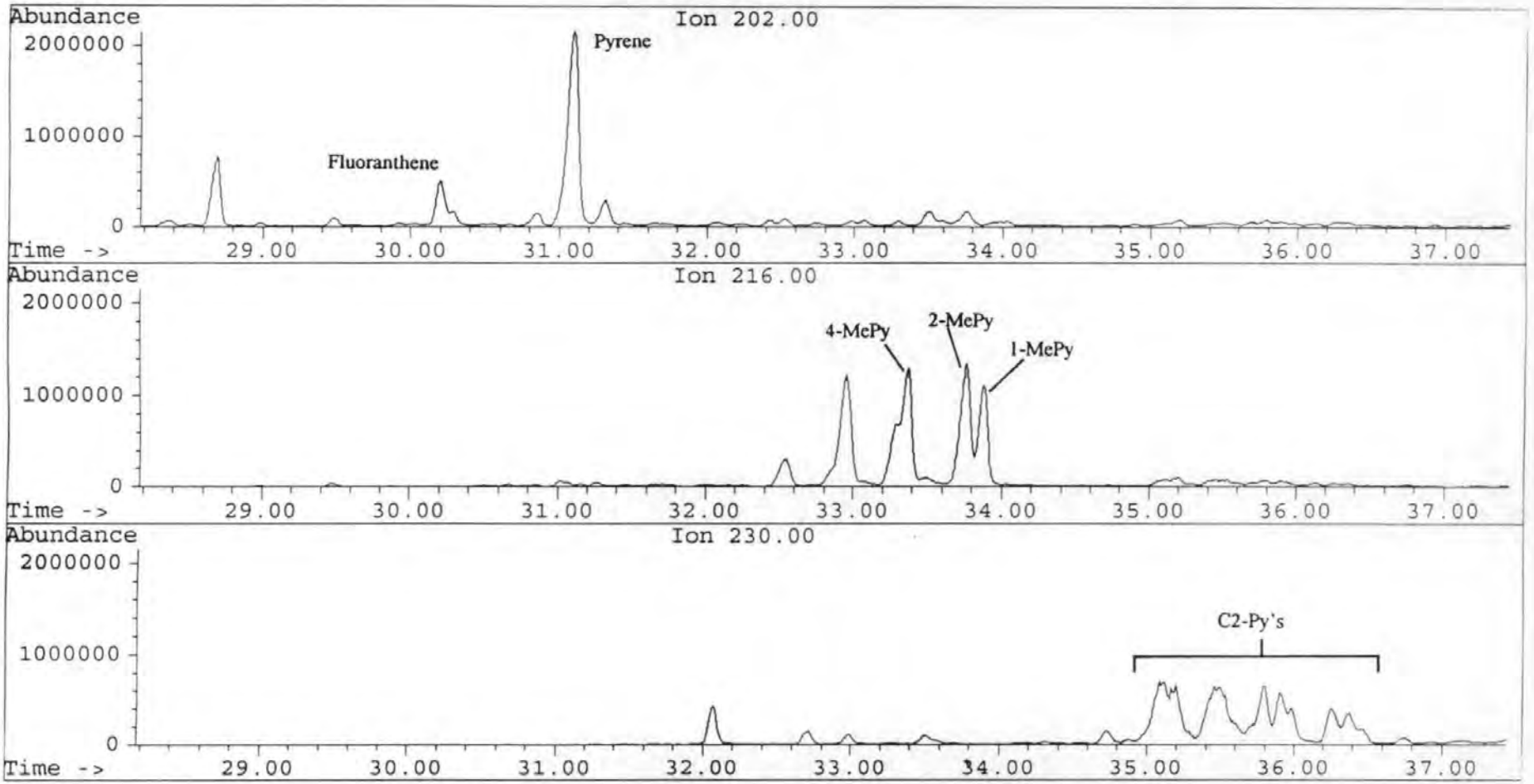


Figure 3.7 GC/MS molecular ions of the methylpyrenes and C2-pyrenes present in diesel fuel

The rates of survival for each of the four PAH are shown in Table 3.4 and represent the extent to which these PAH survive combustion in the Prima engine at these engine conditions.

Table 3.4 Survival of PAH

PAH	Engine Run 1	Engine run 2
	Survival (%)	Survival (%)
[9-^{14}C]fluorene	0.77	0.97
[1,4,5,8-^{14}C]naphthalene	0.47	0.50*
[4,5,9,10-^{14}C]pyrene	0.16	0.18
[9,10-^{14}C]B[α]P		0.04

* Rhead and Pemberton (1994)
Figures are averages of duplicate engine runs with the exception of B[α]P

The large variation in individual PAH survivals, suggests that the physical and chemical properties of individual PAH influence the extent to which they survive combustion. The thermodynamic stability of PAH is an obvious candidate. However, the experimentally determined survivals for the PAH contradict the order of survival predicted by thermodynamics (Stein, 1991). It was concluded therefore, that some additional factor was controlling the extent of survival of PAH during diesel combustion.

PAH that by-pass a high temperature flame zone and hence have the possibility of surviving combustion, remain vulnerable to chemical attack from a wide range of chemically reactive species. Owing to the excess of air in the cylinder the primary attack will involve oxidative species such as molecular oxygen, $OH^{\cdot}$ and $H^{\cdot}$ (Santoro and Glassman, 1979; Prado and Lahaye, 1983; Barnard & Bradly, 1985). These species abstract H atoms to yield aryl radicals, which rapidly undergo further reactions. The ability of a molecule to resist oxidative attack will, in part, determine the extent to which it survives combustion. It follows that PAH which are less reactive toward the initial attacking species will have a greater chance of surviving.

Combustion reactions can be interpreted like any other chemical reaction involving two or more reactant species which combine chemically to produce products. For two species to react and form products, their atomic or molecular orbitals must interact in some way to form new chemical bonds. The greatest

contribution to the stability of the product is made by the reaction of the frontier orbitals of the two reactants (Flemming, 1978). For PAH chemistry, the principal reacting orbitals are those created by the delocalised $C2_{pz}$ π-electrons. The extent to which PAH oxidation proceeds and the rate of reaction, will be determined by the ease of interaction between the electronic orbitals of the reactants. This in turn is dependent on the distribution and relative spacing of the electronic orbitals in the attacking species relative to the PAH π-molecular orbitals. It is reasonable to suppose that the ability of individual PAH molecules to resist oxidation will be influenced by the structure of their π-molecular orbitals.

Various theories have been developed to explain qualitatively and quantitatively the properties of molecules in terms of their molecular orbitals. The most used include, perturbation molecular orbital theory (PMO), self consistent field molecular orbital theory (SCF-MO) and the Huckel molecular orbital theory (Dewar and Dougherty, 1969; Salem, 1974,). Of these, Huckel molecular orbital theory gives good qualitative and quantitative information for conjugated π-electron systems such as those found in PAH molecules, when compared with experimental values (Borden, 1975). Consequently, Huckel MO theory was used in this research to calculate π-MO parameters for each of the four PAH investigated.

Huckel MO parameters were calculated using a MO calculator, computer software package (Trinity Software Ltd). The package allowed computation of the total π-electron energy of the system (the delocalization energy), molecular orbital energy levels, bond orders and bond charges, and π-orbital coefficients. As an illustration, the computed MO energy levels for naphthalene are shown in Figure 3.8 Naphthalene, like all even alternant hydrocarbons, possesses a closed shell of electrons. Energy levels are defined in terms of the Resonance Integral (β) which is the energy associated with the electron density in the region of overlap between two nuclei. The MO energy levels are distributed symmetrically around a zero energy level. This is the energy associated with an isolated electron in the atomic orbital of an isolated atom. In the case of carbon, it corresponds to the energy of an electron in a C_{2p} orbital and is called the coulomb integral (α). Both α and β are constant for all C-C interactions.

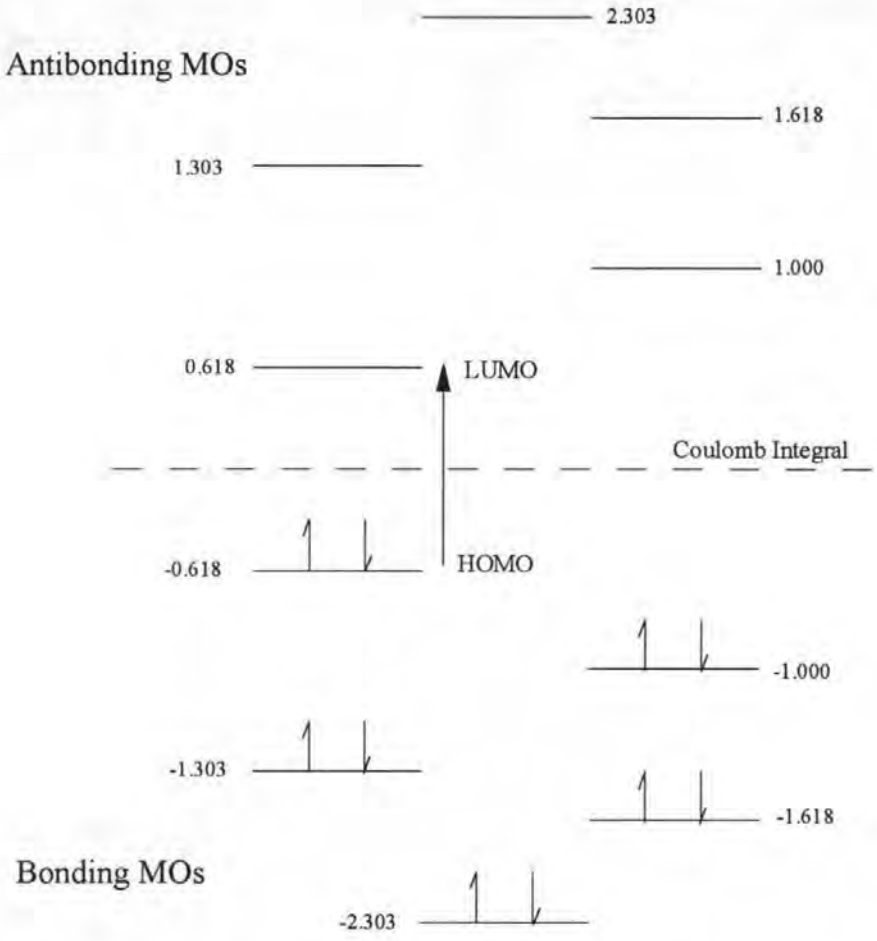


Fig 3.8 Huckel MO energy levels for naphthalene (in units of β)

The two most important orbitals with regard to chemical reactions are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the reacting species (Flemming, 1978). At the high temperatures involved in diesel combustion, radical species are most abundant in the combustion chamber (especially O·, OH· and H·) and hence radical reactions dominate the combustion process. The initial attack on aromatic molecules during combustion are, therefore, likely to be dominated by reactions with radical species. The most important reaction between radicals and aromatic rings involve the LUMO of the aromatic nucleus and the singly occupied molecular orbital (SOMO) of the radical, since the interaction between these two molecular orbitals has the greatest energy lowering potential with regard to the newly formed MOs of the product (Flemming, 1978). The relative energy spacing between these orbitals will determine the rate at

which the reaction proceeds (i.e. the kinetics of the reaction). Reactions will occur most rapidly for small differences in energy between the orbitals.

The HOMO and LUMO energy levels, calculated from Huckel MO theory, for each of three PAH investigated in this research (and for naphthalene) are shown in Table 3.5. The relationship between PAH survival and the energy of the HOMO, the LUMO and the energy gap between the two was investigated and is illustrated graphically in Figures 3.9a to c. Of the three parameters, the best correlation (r^2 = 0.998) was observed with the LUMO (Figure 3.9a). The overall correlation between PAH survival and both the HOMO energy level and the HOMO-LUMO energy gap was poor. However, when the data for fluorene (the only non-alternant PAH investigated) was excluded from the correlation, and only the data for the remaining even-alternant PAH were considered, the correlation with both the HOMO energy level and the energy gap between the HOMO and LUMO is improved considerably (Fig. 3.9b and c, r^2 = 0.995 for both).

Table 3.5 PAH survival and HOMO and LUMO energy

PAH	Survival (%)	HOMO energy level	LUMO energy level	HOMO-LUMO energy gap
Fl	0.87	α - 0.181β	α + 0.812β	0.993β
Np	0.47*	α -0.618β	α + 0.618β	1.236β
Py	0.17	α -0.445β	α + 0.445β	0.890β
B[α]P	0.04	α -0.371β	α + 0.371β	0.742β

* Rhead and Pemberton, (1994)

The high correlation between PAH survival and LUMO energy level suggests that the dominant factor controlling the extent to which PAH survive combustion under these engine conditions is the ease with which an attacking species can react with the LUMO of the PAH. In Huckel theory, the LUMO is a measure of the electron affinity of a molecule. The reaction with the LUMO must therefore include electron donation by the attacking species if the observed correlation is to be more than a coincidence. For PAH with LUMOs of higher energy the ease of this interaction is reduced since for these PAH the reaction pathway has a higher energy

transition state (Flemming, 1978). The reactivity of the PAH is thus reduced and is reflected in the greater tendency for these PAH to survive combustion.

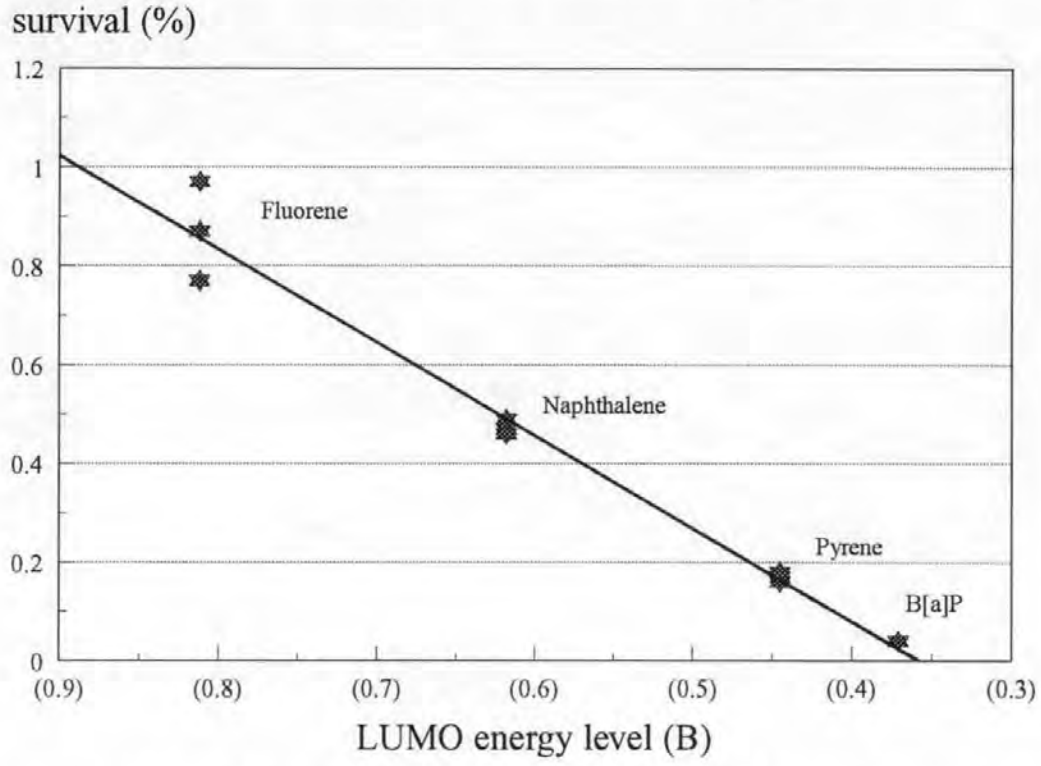


Figure 3.9a Relationship between PAH survival and LUMO energy level

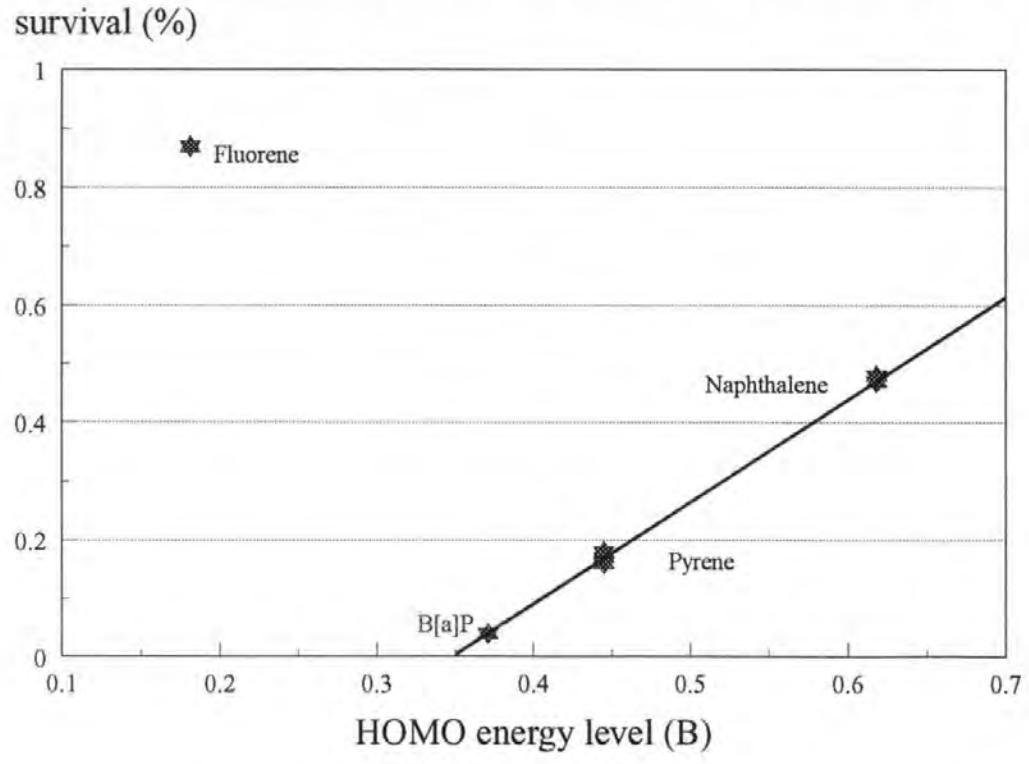


Figure 3.9b Relationship between PAH survival and HOMO energy level

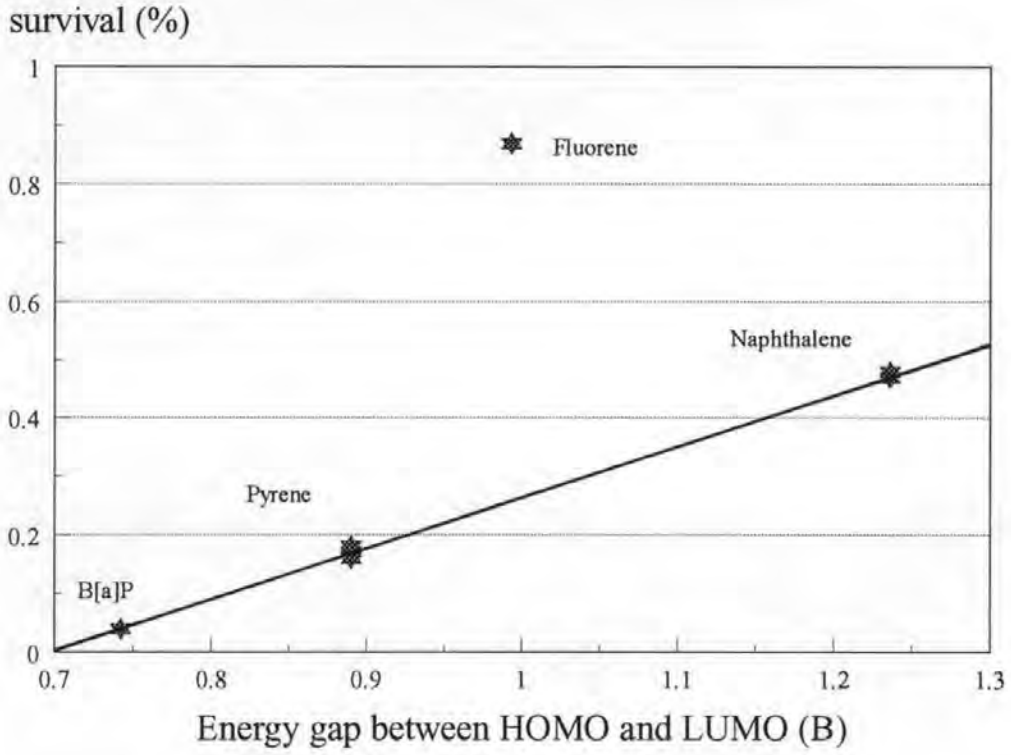


Figure 3.9c Relationship between PAH survival and energy difference between HOMO and LUMO

The results from the current research suggest that it is the kinetic stability of PAH as opposed to their thermodynamic stability that is the controlling factor in determining the extent to which PAH present in diesel fuel survive the diesel combustion process.

It is worth noting that although this research has identified a relationship between PAH survival and molecular orbital structure, they contradict the view of Stein (1991), who pointed out a lack of "any intrinsic relationship between whole molecule properties" such as the HOMO and LUMO energy levels "and the reactivity of specific sites in the molecule."

3.4.2.3 Implications of the current results for PAH emissions from diesel engines

The results from the current study suggest that for the Perkins Prima engine the tendency is for high molecular weight PAH (those with a lower energy LUMO) to be combusted more efficiently than the low molecular weight PAH. This contrasts with the results of Williams *et al.*(1989). In their research using a 4l DI Perkins

diesel engine, it was found that the engine burned lower molecular weight PAH (2 & 3-rings) more efficiently than higher molecular weight PAH (4 & 5 rings).

The trend in PAH survivals, identified in this research has implications for the carcinogenicity of diesel exhaust emissions. The results imply that the more biologically active PAH species will tend to be consumed more efficiently during combustion than other less active PAH, since these are, in general, the larger and more chemically reactive PAH. The contribution of PAH to the carcinogenicity of diesel exhaust may therefore be reduced. However, owing to the greater chemical reactivity of the larger PAH molecules, the contribution to the carcinogenicity of diesel exhaust from their oxidised derivatives (*e.g.* 1-nitropyrene) may be increased. Scintillation assay of the polar exhaust fractions demonstrated that no increase in the radioactivity present in the B[α]P polars relative to the other PAH had occurred (Table 3.6).

Table 3.6 Radioactivity present in the polar fraction of diesel emissions

	Fluorene	Pyrene	B[α]P
Radioactivity (%) in polars	0.006	0.008	0.0046

3.4.3 Diesel combustion of ^{14}C-*n*-Hexadecane (*n*-C_{16})

Straight chain *n*-alkanes are the most abundant class of compound in diesel fuel. The *n*-alkane distribution of diesel fuel ranges from *n*-C_9 to approximately *n*-C_{30}, with the distribution peaking at around *n*-C_{15} (Figure 3.11). The behaviour of aliphatic molecules and especially the *n*-alkanes, is therefore of interest since these species are the most abundant hydrocarbons in diesel emissions.

108μCi and 107μCi of ^{14}C-hexadecane were introduced into the Prima in duplicate engine runs. The exhaust samples were fractionated into aliphatics, aromatics and polars by silica column chromatography. The radioactivity present in each fraction was determined by liquid scintillation assay and is given in Table 3.7.

Table 3.7 Distribution of radioactivity in ^{14}C-*n*-hexadecane exhaust

	Survival (% of original radioactivity)		
	Aliphatics (^{14}C-*n*- hexadecane)	Aromatics	Polars
Duplicate 1	0.3	0.014	0.019
Duplicate 2	0.4	0.018	0.016

Radio-GC analysis demonstrated a single radio-peak in the aliphatic fraction of the exhaust (Figure 3.10). The extent of survival of the ^{14}C-*n*-hexadecane was determined by liquid scintillation assay of the aliphatic fraction of the exhaust and was determined as 0.3% and 0.4% for the two duplicate runs respectively. Small amounts of radioactivity were found in the aromatic and polar fractions of the exhaust sample. These survivals are similar to those quoted by Williams *et al.* (1989), of between 0.1% and 1% for hydrocarbons ranging from *n*-C_{12} to *n*-C_{30}, but again, that research was unable to distinguish between the various sources of hydrocarbons in the emissions.

The specific activity of ^{14}C-*n*-hexadecane in the fuel and in the emissions was used to assess the extent of pyrosynthesis of *n*-hexadecane in diesel combustion. The concentration of *n*-C_{16} in the fuel, was determined as 11,418ppm by GC analysis of unfractionated diesel. The specific activity of the radiochemical was substantially reduced from 250μCi/mg as received, to 2.3μCi/mg and 1.8μCi/mg in the fuel by dilution with nonlabelled *n*-hexadecane in the fuel. This compares with a specific activity of ^{14}C-*n*-hexadecane in the exhaust of 0.75μCi/mg and 0.6μCi/mg respectively. The variation between the specific activities, indicates that a substantial proportion (two thirds) of *n*-hexadecane in the emissions is derived from reactions occurring in the combustion chamber.

There is no obvious explanation for the construction of *n*-alkanes from smaller radical units. A more plausible explanation involves the formation of these species from the cracking of larger aliphatic species present in the fuel. Combustion of aliphatic fuels is reported to start with the thermal cracking of the higher molecular weight hydrocarbons to lower boiling point species.

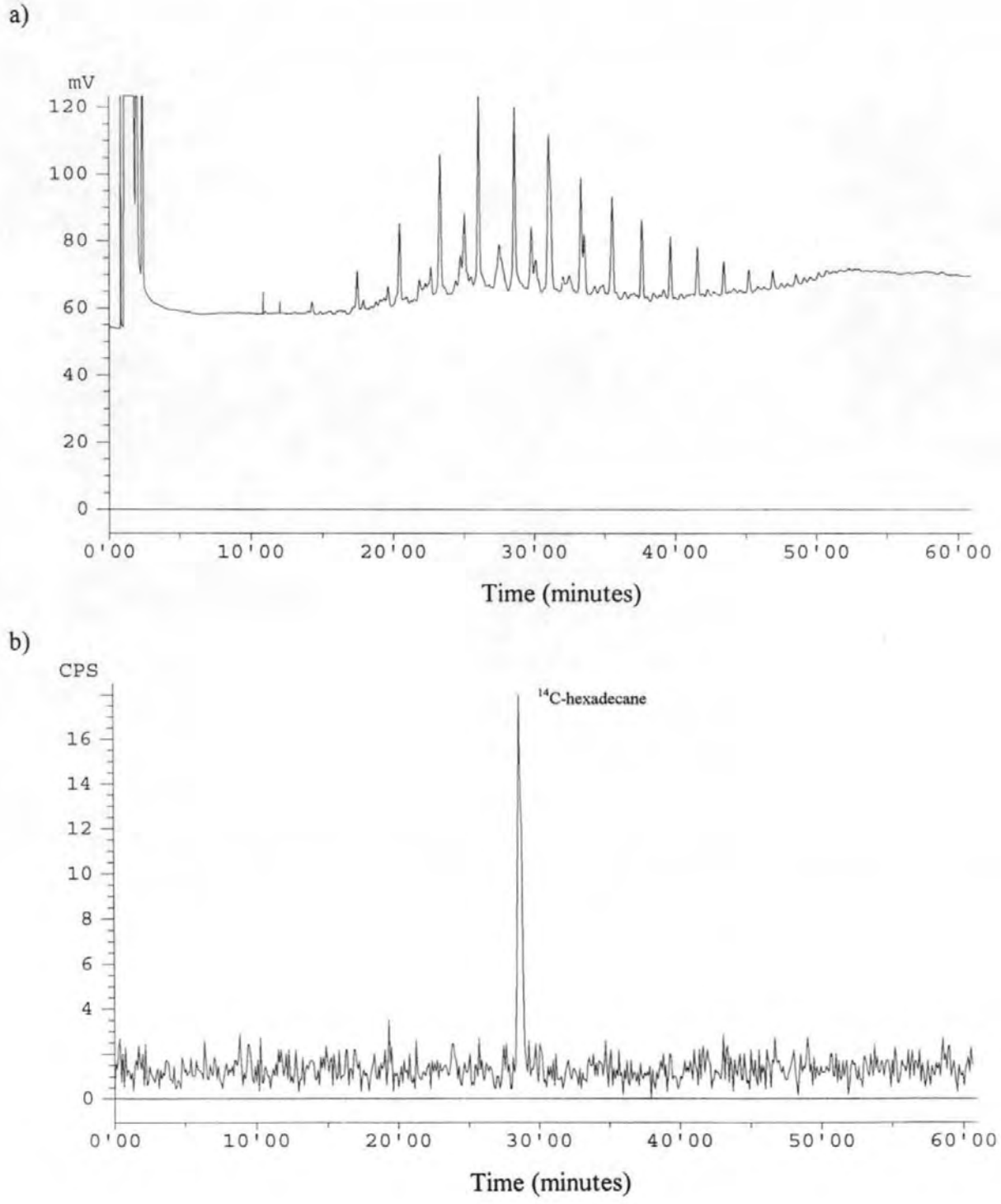


Figure 3.10 Radio-GC analysis of ^{14}C-hexadecane exhaust sample showing a) FID response and b) radioactivity chromatogram

The final products of this process are small (C_2 and C_4) acetylenes and olefins (Crittenden and Long, 1973). Tosaka (1989) pyrolysed a series of *n*-alkanes and small aromatics in an inert nitrogen atmosphere. The authors reported the formation of a range of lighter *n*-alkanes and alkenes from the cracking of *n*-alkanes.

Further evidence for the formation of low molecular weight aliphatics from the thermal cracking of higher molecular weight species present in diesel fuel, is manifest in the distribution of the *n*-alkanes in diesel fuel relative to their distribution in the exhaust. A clear skew in the distribution, from the maximum *n*-alkane in the fuel (*n*-C_{16}) to the maximum n-alkane in the exhaust emissions (*n*-C_{15}) is visible (Figure 3.11).

The relative increase in the abundance of light *n*-alkanes in the emissions suggests that they are created during combustion most probably as a result of the thermal cracking of larger aliphatic compounds in the fuel.. The effect cannot be explained in terms of evaporative losses of the lighter *n*-alkanes during the work-up procedure since this would have the effect of concentrating the heavier *n*-alkanes in the exhaust at the expense of the lighter compounds. Nelson (1989) observed the same effect in research sampling diesel emissions with an XAD-2 trap. The authors came to a similar conclusion that gas-phase cracking reactions were responsible for producing shorter chain material.

The findings of the present research are in direct contrast to those reported by Williams *et al.* (1989). In this research the authors described a 'preferential burn-out of lower molecular weight (aliphatic) compounds." Their research was performed using a 4l DI diesel engine. The exhaust was sampled directly with a probe and was passed through a filter maintained at 52°C which trapped the exhaust particulates. It is well documented in the literature however, that a considerable proportion of exhaust components with a relatively high molecular weight (*e.g.* 200-250 a.m.u), are present in the exhaust gas stream in the vapour phase and not adsorbed to particulate material in the exhaust (Lane, 1989). It seems likely therefore, that the observations described by Williams *et al.*(1989) are at least in part the result of an inefficient sampling system.

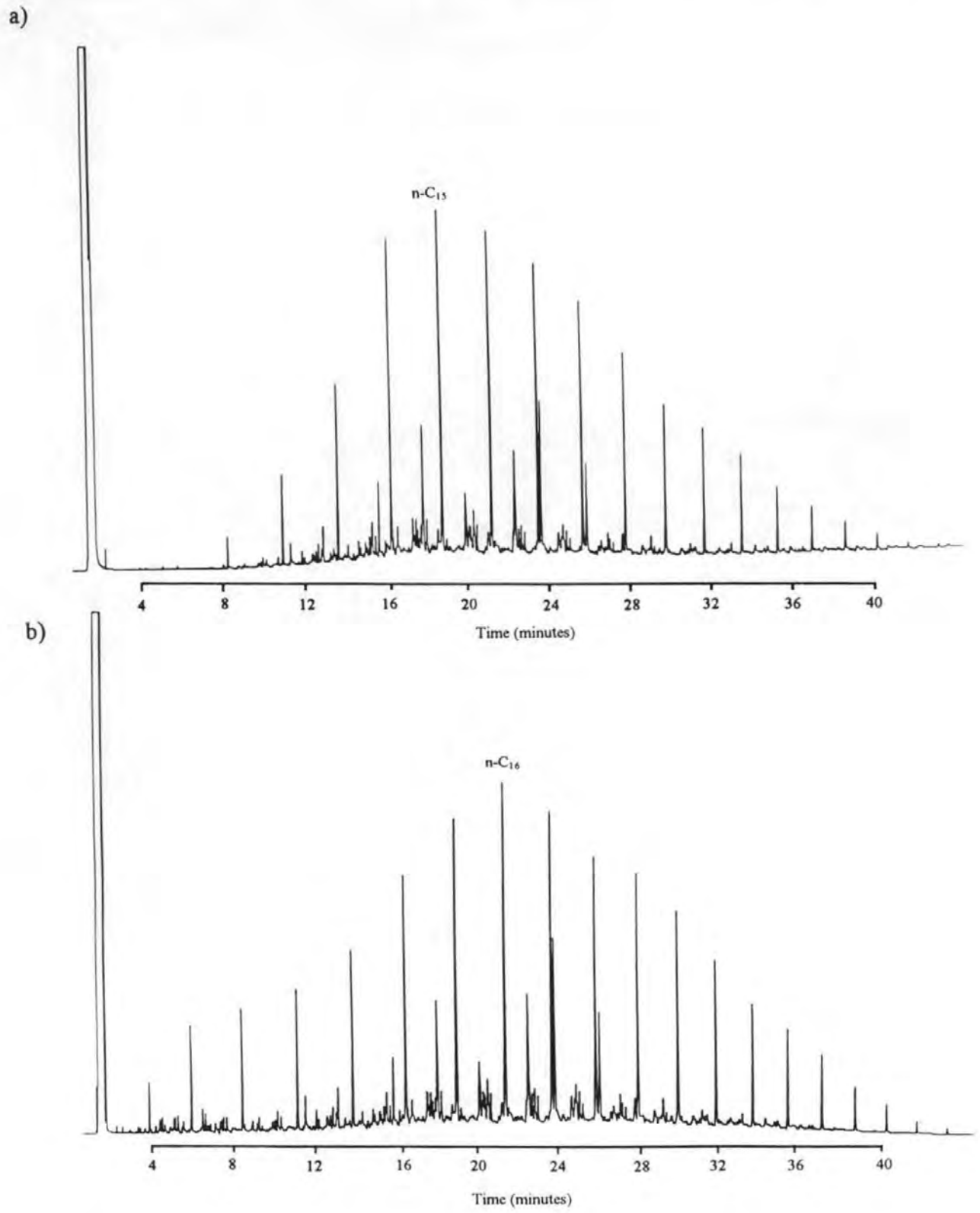


Figure 3.11 Gas chromatograms of the aliphatic fractions of a) diesel fuel and **b) diesel exhaust illustrating a shift in the relative distribution of n-alkanes to lower molecular weight species in the exhaust.**

Chapter 4

DIESEL COMBUSTION of ALKYL-POLYCYCLIC AROMATIC HYDROCARBONS

4.1 Introduction

Alkyl-PAH are major aromatic constituents of diesel fuel. Alkyl-PAH that are most abundant are especially methyl-substituted naphthalenes, phenanthrenes, dibenzothiophenes and fluorenes. PAH substituted with ethyl and propyl groups are also present (Table 4.2). The chemical and biological reactions of alkyl-PAH may differ substantially from their parent PAH. For example, it has been suggested that there is a greater tendency for aromatic molecules with alkyl side chains to form larger condensed aromatic structures during pyrolysis, which, in their turn are considered precursors to the formation of soot (Crittenden and Long, 1973; Bittner and Howard, 1981; Harris *et al.*, 1988; Hamins *et al.*, 1990). In a recent study, Ciajolo *et al.* (1992) investigated the combustion of hexadecane and hexadecane/α-methylnaphthalene and reported an increase in the emission of PAH, higher molecular weight species and soot from combustion of hexadecane spiked with α-methylnaphthalene relative to hexadecane alone. Reactions of alkylated monocyclic aromatic compounds have been studied extensively in simple flame and pyrolysis studies (Badger and Spotswood, 1960; Bittner and Howard, 1981; Hamins *et al.*, 1990; Harris *et al.*, 1988; Smith and Savage, 1991; Freund *et al.*, 1990). Reactions of alkylated polyaromatics however, have received comparatively little attention even though differences in the pyrolysis pathways and kinetics between alkylated monocyclic and alkylated polycyclic aromatic compounds have been reported (Freund *et al.*, 1990; Smith and Savage, 1991).

The carcinogenicity of alkyl-PAH may also differ from that of the parent PAH. Glatt *et al.* (1990) proposed that certain alkylated PAH may be as strong as or even more mutagenic and carcinogenic than the parent molecule. Longwell (1982) demonstrated the carcinogenicity of methylphenanthrenes. In view of their abundance in diesel fuel, the combined carcinogenicity of alkyl-PAH species, may be more significant than that of more highly carcinogenic but less abundant PAH (e.g. benzo(α)pyrene typically <1ppm in diesel fuel). Yu and Hites (1981) concluded that methylphenanthrenes and methylfluorenes are the major mutagens in diesel exhaust rather than B[α]P.

Evidence from pyrolysis studies has shown that pyrolysis of alkyl-aromatics yields the parent aromatics as products and it has been proposed that dealkylation of

fuel aromatics may take place in conditions of partial oxidation and at lower temperatures in combustion systems (Longwell, 1982; Herlan, 1978). With one or two exceptions, the specificity of this dealkylation process, in terms of the size of the alkyl group, the position of substitution on the aromatic nucleus and the size of the aromatic nucleus, has not been investigated. Smith and Savage (1991) pyrolysed a series of alkylated-PAH and found two major reaction pathways which resulted in cleavage of the aryl-alkyl bond, and cleavage of carbon-carbon bonds in the alkyl side chain, respectively. The preferred reaction was not affected by the length of the alkyl side chain but by the position of substitution in the aromatic molecule. This effect was correlated with reactivity indices for the point of substitution on the molecule and allowed predictions to be made regarding the ease of aryl-alkyl bond cleavage for other alkyl-PAH species.

It has been assumed that dealkylation is likely to occur in the extreme conditions of temperature and pressure encountered in a diesel combustion chamber. Various authors have noticed a decrease in the abundance of methyl substituted PAH relative to the parent non-substituted PAH in diesel exhaust (Barbella *et al.*, 1991; Trier *et al.*, 1991). This may implicate a dealkylation pathway during the diesel combustion process. Alternatively, it may be a consequence of the greater combustibility of alkyaromatics relative to the non-substituted aromatics. A dealkylation pathway may impact on the rate of soot formation from fuels if a difference in the sooting tendency between alkyl-aromatics and non-substituted aromatics exists. Similarly, a dealkylation pathway may have an effect on the mutagenicity of diesel exhaust if a significant difference in toxicity between the parent PAH and its alkylated derivatives can be proved.

In the current experiment, a diesel fuel with a low aromatic content (7.0%) spiked with 2 and 3-ethylphenanthrene (2-EtPa, 0.28%; and 3-EtPa, 3.7%), was combusted in a 2L direct injection Perkins Prima diesel engine. The fuel contained less than 0.1% 3-ringed PAH (triaromatics) and was used to enable expected products of combustion, (phenanthrene and/or methylphenanthrene) to be identified more clearly. EtPa has not been detected in the diesel fuel used in this research, although, 1 and 2-ethylnaphthalenes (1 and 2-EtNp) are present in substantial quantities (1460ppm), as are methylethylnaphthalenes (4,423 ppm total).

4.2 Experimental

4.2.1 Modification of fuel supply lines

The fuel lines to the engine were modified to enable the engine to be run on the test fuel. This was achieved by inserting a 5l reservoir, which contained the test fuel, in the main fuel line connected by two three-way valves. The valves were switched manually to form a closed system, isolated from the main fuel supply, in which the test fuel circulated. The reservoir was positioned as close to the engine as possible to minimise the volume of residual fuel left in the fuel lines and the engine. In practise the volume of residual A2 fuel was approximately 800ml, the greatest contribution coming from the fuel filter.

4.2.2 Test fuel specifications

The standard diesel fuel used was an A2 diesel fuel, the specifications of which are presented in Table 2.1. The specifications of the test fuel used are presented in Table 4.1. The test fuel has been used in this research primarily to facilitate the identification of products of combustion. The fuel specifications presented in Table 4.1 however, shows this fuel to be a 'clean diesel fuel" blended to produce a sulphur content of 0.015%/m, an aromatic content of 7%/v, a cetane number of 63.6 and a fuel density of 0.8145Kg/l. The sulphur content meets the 1996 sulphur limit for diesel fuels, whilst the fuel density, aromatics content and cetane number, the main additional factors influencing diesel emissions, are at values suggested by recent research for a 'low emissions" fuel (Betts *et al.*, 1993; Floysand *et al.*, 1993).

The low density of the test fuel has been achieved by removing the higher molecular weight species normally present in diesel fuel. The composition of the test fuel in comparison with that of the standard A2 diesel with regard to the distribution of n-alkanes and aromatics reflects this. Thus the *n*-alkane series shows a maximum at *n*-C_{14} compared to a maximum at *n*-C_{16} for the standard fuel, whilst the aromatic content of the test fuel is much reduced and consists mainly of monoaromatics (6.45%). Naphthalenes are the main PAH species in the fuel, three ringed PAH are present only as a small percentage of the overall diesel.

Table 4.1. Test fuel specifications

Diesel fuel reference number: **G091/1030**	
Density at 15°C	0.8145 Kg/l
Sulphur content	0.0510 %m (510 ppm)
Kinematic viscosity at 40°C	2.9 cSt
Kinematic viscosity at 50°C)	2.39 cSt
Flash point (PM closed)	98°C
Cloud point	-15°C
CFPP	-20°C
SFPP	----
Pour point	----
Wax content	----
Melting point of wax	----
Carbon residue (Con) on 10% residue	----
Distillation (IP123)	----
IBP	216°C
5% volume recovered at	235°C
10% volume recovered at	240°C
20% volume recovered at	250°C
30% volume recovered at	256°C
40% volume recovered at	261°C
50% volume recovered at	267°C
60% volume recovered at	272°C
70% volume recovered at	279°C
80% volume recovered at	288°C
90% volume recovered at	303°C
95% volume recovered at	317°C
FBP	327°C
Distillate/ Residue/ Loss	97.5 %Vol/ 1.5 %Vol/ 0 %Vol
Cetane number (D613)	63.6
Hydrogen content	14.0 %mass
Carbon content	86.2 %mass
Calorific value (calculated):	
Net	43.16 MJ/Kg
Gross	46.07 MJ/Kg
Aromatics content (IP391):	
Mono	6.45 %vol
Di	0.46 %vol
Tri	<0.01 %vol

Fuel analysis performed by BP Fuels Ltd, Sunbury

Gas chromatograms of the whole fuel and of the aromatic fraction isolated by normal-phase HPLC using amino bonded silica are shown in Figure 4.1 a and b. The concentration of individual PAH in the fuel are shown in Table 4.2. Their concentration in the test fuel during sampling is also shown and demonstrates the extent to which the test fuel was contaminated with PAH from the standard diesel whilst sampling the exhaust.

4.2.3 Diesel exhaust sampling procedure

The engine was conditioned for 1 hour at full power on the standard A2 diesel before being conditioned for a further 15 minutes at the test conditions of 3000rpm and 10Nm on the test fuel. Previous research had indicated that pyrosynthetic pathways, were most prevalent at conditions of low load and high speed (Collier *et al.*, 1994). These conditions were, therefore, chosen for the initial experiment. To minimise contamination of the test fuel with triaromatics from the standard diesel fuel, the fuel return lines were diverted to waste for several minutes during conditioning on the test fuel until there was no visible trace of the standard diesel (to which red dye had been added) in the return line. This required the system to be purged with approximately 2L of the test fuel. The fuel return line was then diverted back into the auxiliary reservoir. Even with these precautions some dilution of the test fuel with the standard diesel occurred which increased the concentration of PAH in the test fuel during sampling. The increase was most pronounced for PAH which were at the lowest concentration in the test fuel i.e. dibenzothiophenes and phenanthrenes (see Table 4.2).

The sampling procedure consisted of collecting five exhaust samples from the engine operating on the test fuel without the 3-EtPa spike and five exhaust samples collected with the engine operating on the spiked test fuel. The purpose of the first five samples was to establish a baseline for the emissions from the unspiked fuel with which to compare the emissions from the fuel with the EtPa spike.

Table 4.2 Concentration of PAH in diesel fuel G091/1030

PAH	Conc'n in test fuel (ppm)	Conc'n in test fuel during sampling (ppm)
Naphthalene (Np)	144	238
2-MeNp	327	620
1-MeNp	259	460
1 / 2-EtNp	67	155
2,6 / 2,7-diMeNp	187	481
1,3 and 1,6 / 1,7-diMeNp	404	878
1,4 / 2,3 and 1,5-diMeNp	126	284
1,2-diMeNp	40	98
1,3,7-triMeNp	44	152
1,3,6-triMeNp	71	211
1,3,5 / 1,4,6-triMeNp	48	176
2,3,6-triMeNp	48	112
1,2,6 / 1,6,7-triMeNp	64	182
1,2,4-triMeNp	9	19
1,2,5-triMeNp	27	58
Me-Et-Nps*	10	16
Me-Et-Nps*	16	35
Me-Et-Nps*	9	38
Me-Et-Nps*	54	168
Me-Et-Nps*	12	95
Fluorene (Fl)	17	59
9-MeFl	5	29
2-MeFl	11	53
1-MeFl	20	76
diMeFl (total)	35	297
Dibenzothiophene (DBT)		
4-MeDBT	13	43
2 / 3-MeDBT	7	22
1-MeDBT	5	12
diMeDBT (total)	21	97
Phenanthrene (Pa)	21	94
2 / 3-MePa	13	132
9 / 4-MePa	17	117
diMePa (total)	<LOD**	274
3-EtPa spike	---	37,000
2-EtPa spike	---	280

Key: 1 / 2 indicates coeluting isomers not distinguishable.
1 and 2 indicates isomers identified but not quantified individually
* isomer not identified
** below limits of detection

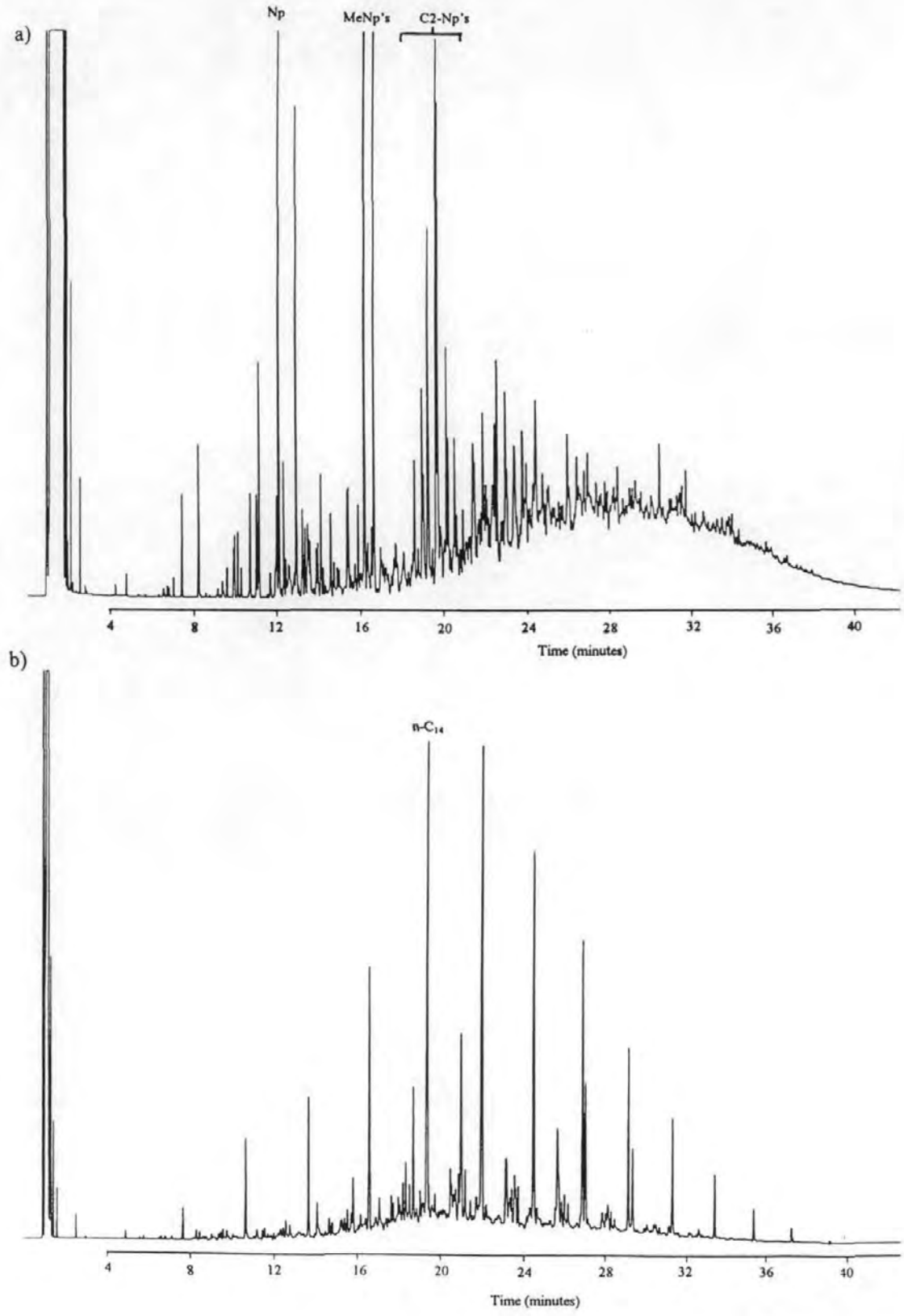


Figure 4.1 Gas chromatograms of a) aromatic fraction of test fuel illustrating the reduced concentration of triaromatics and **b) unfractionated fuel**

Three fuel samples were collected at the beginning, middle and end of the two sets of samples to verify the homogeneity of the fuel in terms of concentration of the spike, which was determined as 3.7% for 3-EtPa and 0.28% for 2-EtPa in each fuel sample by GC analysis. The exhaust sampling time was 1 minute. Fuel consumption during the experiment was determined using a 400ml graduated measuring burette.

4.2.4 Synthesis of 2 and 3-ethylphenanthrene

A commercial source of ethylphenanthrene could not be found. It is possible to obtain either the 2- or 3-EtPa isomers in a pure form following the method of Haworth (1933). The synthetic procedure involves several stages and the final yield is low. Approximately 80g of a mixture of 2 and 3-EtPa was synthesised in a two step procedure. The first stage consisted of a Friedel Crafts acylation of phenanthrene following the method of Mossetig and Van de Kemp (1930). The second stage comprised a Wolf-Kishner reduction (Todd, 1948).

4.2.4.1 Friedel-Crafts acylation of phenanthrene

Phenanthrene (1.124 mols) was dissolved in nitrobenzene (6.7 mols) in a 3-necked reaction vessel equipped with a dropping funnel and mechanical stirrer. Acetylchloride (1.52 mols) was added to the solution whilst constantly stirring. The aluminium chloride catalyst (1.5 mols) was added in 4 aliquot's over a period of 90 minutes. The reaction mixture was kept below 0°C throughout. At the end of this period a capillary tube was inserted into the reaction mixture and the pressure was reduced in the reaction vessel. Copious amounts of HCl gas were produced. After no more gas was evolved excess crushed ice was added to the reaction mixture and the nitrobenzene layer was separated and washed with two aliquots of dilute hydrochloric acid and 5% sodium carbonate solution (100ml) and finally distilled water. The acetylphenanthrene was isolated from the nitrobenzene by reduced pressure distillation. The acetylphenanthrene distilled at 180°C at 1mmHg and was collected in around bottomed flask.

The product was recrystallized in hot ethanol. Fine needle shaped white crystals (m. pt. 133-138°C) were collected by filtration and dried. Infra-red spectroscopy of the crystals indicated that 2-acetylphenanthrene (m. pt. 143°C,

Dictionary of Organic Compounds, p53) was the major isomer present. The remaining solvent was then rotary evaporated and a large amount of white powder (m. pt. 63-65°C) was obtained. It was assumed that this was the more soluble 3-acetylphenanthrene isomer (m. pt. 73°C, Dictionary of Organic Compounds, p53). To further verify the identity of the products a mixture of 2 & 3-acetylphenanthrene (10% and 90% respectively) was purchased from Aldrich. Retention indices and mass spectral data from GC-FID and GC/MS analysis confirmed the identity of the products as 2 and 3-acetylphenanthrene. 2-acetylphenanthrene was obtained in a final purity of >99% whilst 3-acetylphenanthrene was obtained in a yield of 92%, with the remainder being the 2-acetylphenanthrene.

4.2.4.2 Wolff-Kishner reduction of acetylphenanthrene

The acetylphenanthrene from the previous step was reduced to the corresponding ethylphenanthrene via a Wolf-Kishner reduction (Huang-Minlon modification) following the method of Vogel, (5^{th} ed., Ch. IV). 3-acetylphenanthrene (0.17 mols) was dissolved in triethylene glycol (1.35 mols) in round bottomed flask (1L) equipped with a reflux condenser. Potassium hydroxide (0.4 mols) and hydrazine (0.37 mols) were added to the mixture which was refluxed for 3 hours. A small amount of a yellow precipitate formed rapidly and subsequently disappeared after an hour. Presumably, this was the less soluble hydrazone formed from the small amount of the 2-acetylphenanthrene present in the original mixture. The mixture was allowed to cool and was then extracted with ether (3 × 100ml). The ethereal extract was washed with 6M hydrochloric acid (2 × 50ml) and once with distilled water (50ml). The solution was then dried with anhydrous sodium sulphate, filtered and the ether removed by rotary evaporation to yield approximately 30g of fluorescent white leaflets (m. pt. 65-67°C).

The final purity of the 3-EtPa was determined by GC analysis as 93% with the remainder being 2-EtPa (Figure 4.2a). The identity of the product was confirmed by infra-red spectroscopy and mass-spectroscopy. The I.R. spectra of the product is shown in Figure 4.3. The absence of a strong absorbance band at 1680cm^{-1} supports the fact that the carbonyl group has been completely reduced. Strong absorbance bands at 2850cm^{-1} to 2980cm^{-1}, characteristic of aliphatic CH stretching vibrations,

confirms the reduction of the carbonyl (CO) to a methylene (CH_2) group. Similar conclusions can be made from mass spectral data. The molecular ion at m/z 206 is clearly visible whilst fragment ions at m/z 191 and m/z 177 are characteristic of loss of CH_3^+ and $C_2H_5^+$ respectively (Figure 4.2b).

4.3 Results

3-EtPa was spiked in the fuel at a concentration of 3.7% and 2-EtPa at a concentration of 0.28%. The total recoveries after combustion for these PAH amounted to 0.35% and 0.3% respectively. These are similar to the recoveries of other PAH determined at Plymouth (Collier *et al.*, 1994).

Evidence for the dealkylation of EtPa in this research would manifest itself as a relative increase in the emission of phenanthrene resulting from the combustion of a fuel spiked with EtPa, compared to the emission of phenanthrene from the combustion of the non-spiked fuel. The variation in phenanthrene emissions from the spiked and unspiked fuel were determined by ratioing the integrated areas of the phenanthrene molecular ion against that of the molecular ion for the d_{10}-phenanthrene internal standard (d_{10}-Pa I.S.) in each sample. Statistical analysis was performed on the two sets of data to establish any variation in emission rates. No significant variation in the emission of phenanthrene between the two sets of exhaust samples was observed and it was concluded that for 2 and 3-EtPa a dealkylation pathway does not exist or at least is not significant during diesel combustion at these engine conditions.

The same statistical procedure was applied to the emission of methylphenanthrenes (MePa). Fig. 4.4a and b show the integrated molecular ions for the MePa isomers in exhaust samples from spiked and non-spiked fuel. Individual isomers were identified using retention indices which agreed well with literature data (Vasillaros *et al.*, 1982) and from coinjection with standards. The order of elution was identified as 2-MePa, 3-MePa, 9-MePa and 4-MePa coeluted, and finally 1-MePa.

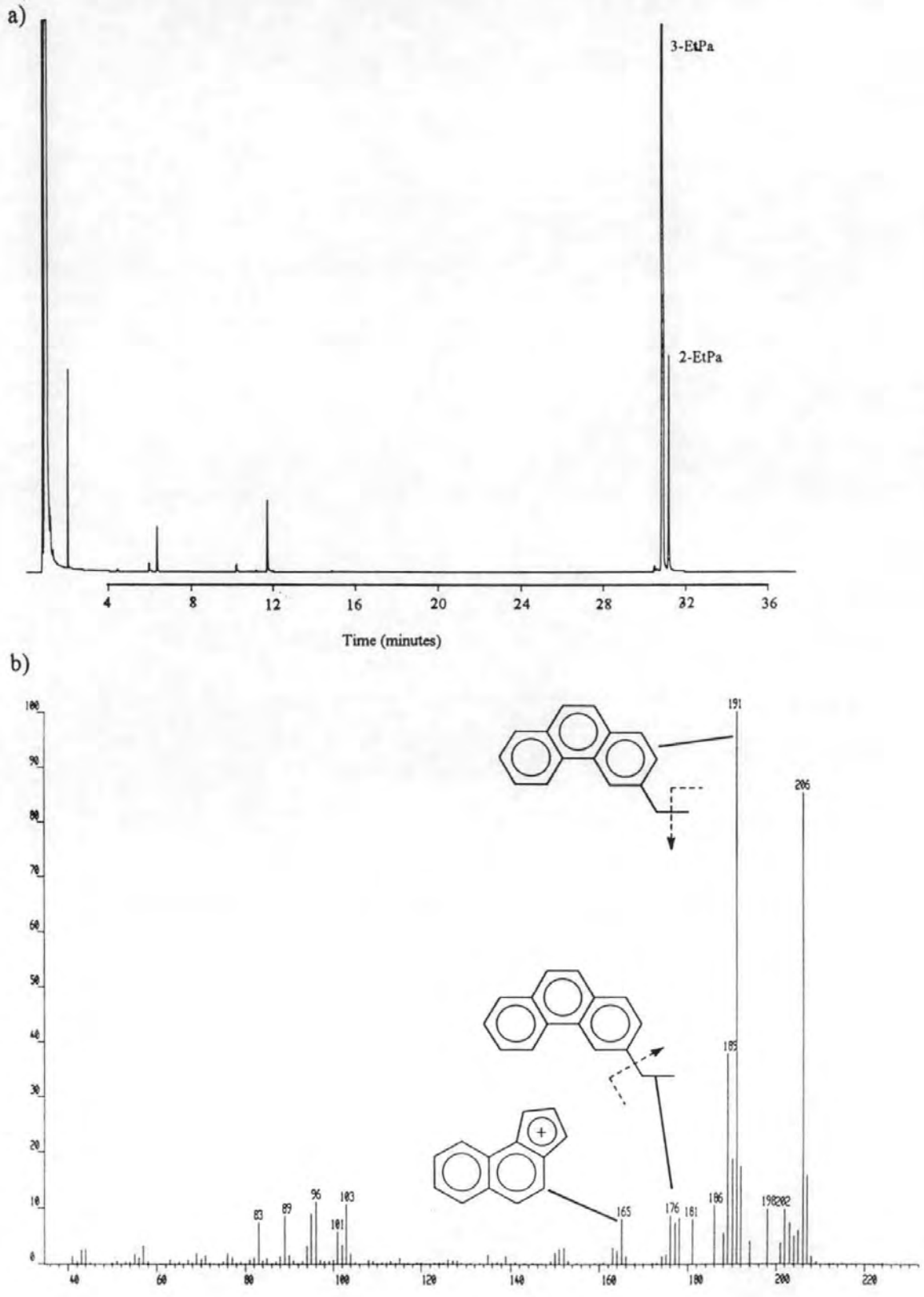


Figure 4.2 a) Gas chromatogram of 2- and 3-EtPa showing purity and **b) mass spectrum of 3-EtPa**

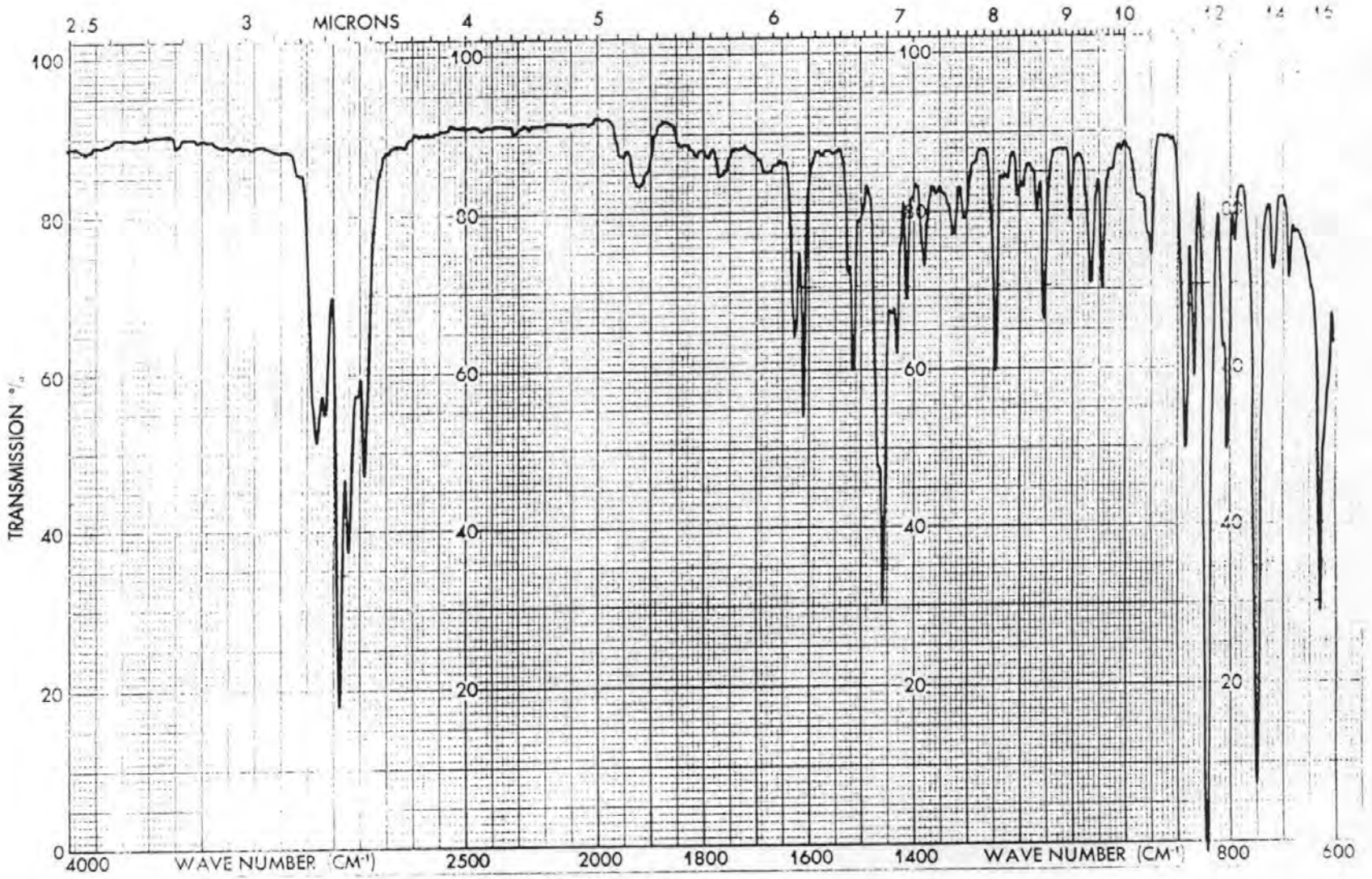


Figure 4.3 Infra-red absorbance spectrum of the mixture of 2- & 3-ethylphenanthrene

A visual inspection of Figure 4.4 suggests that there has been an increase in 3-MePa relative to the 2-MePa in the spiked exhaust relative to the baseline exhaust. This was confirmed by ratioing the integrated peak areas of the molecular ions for the two isomers in the two sets of exhaust samples. Analysis of variance assigned the difference between the two sets of data a significance of 0.0009 at 95% C.I. No significant difference in the ratio between the 9 and 4-MePa and the 1-MePa in the spiked and non-spiked exhaust samples was detected. This was taken as a further indication that the increase in 3-MePa was a product of the combustion of 3-EtPa and was not a chance result. The increase in the emission of 3-MePa is equivalent to a conversion rate of less than 0.0004% of the 3-EtPa spike.

Gas chromatograms of two exhaust samples collected from the spiked and unspiked fuel are shown in Figure 4.5a and b. 2 and 3-EtPa surviving combustion are clearly visible at around 37 minutes. The two exhaust samples were compared in order to identify additional products of combustion of alkylated-PAH. A peak eluting at around 38 minutes was identified in the spiked exhaust sample that was not present in the baseline sample. Components eluting this late in the chromatogram are not usually encountered at this concentration in diesel exhaust samples collected from the Prima engine in this laboratory. This peak, representing a compound, formed presumably from the combustion of EtPa, was identified as vinylphenanthrene (ViPa) by GC/MS mass spectral data and was present in a yield of 0.01% of the 3-EtPa.. A vinylphenanthrene standard was not available with which to compare the mass spectrum of the compound. However, comparison of the mass spectra for the ViPa peak with a vinylnaphthalene (ViNp) standard confirmed the peak identification as ViPa. The mass spectra for ViNp and ViPa are shown in Figure 4.6.

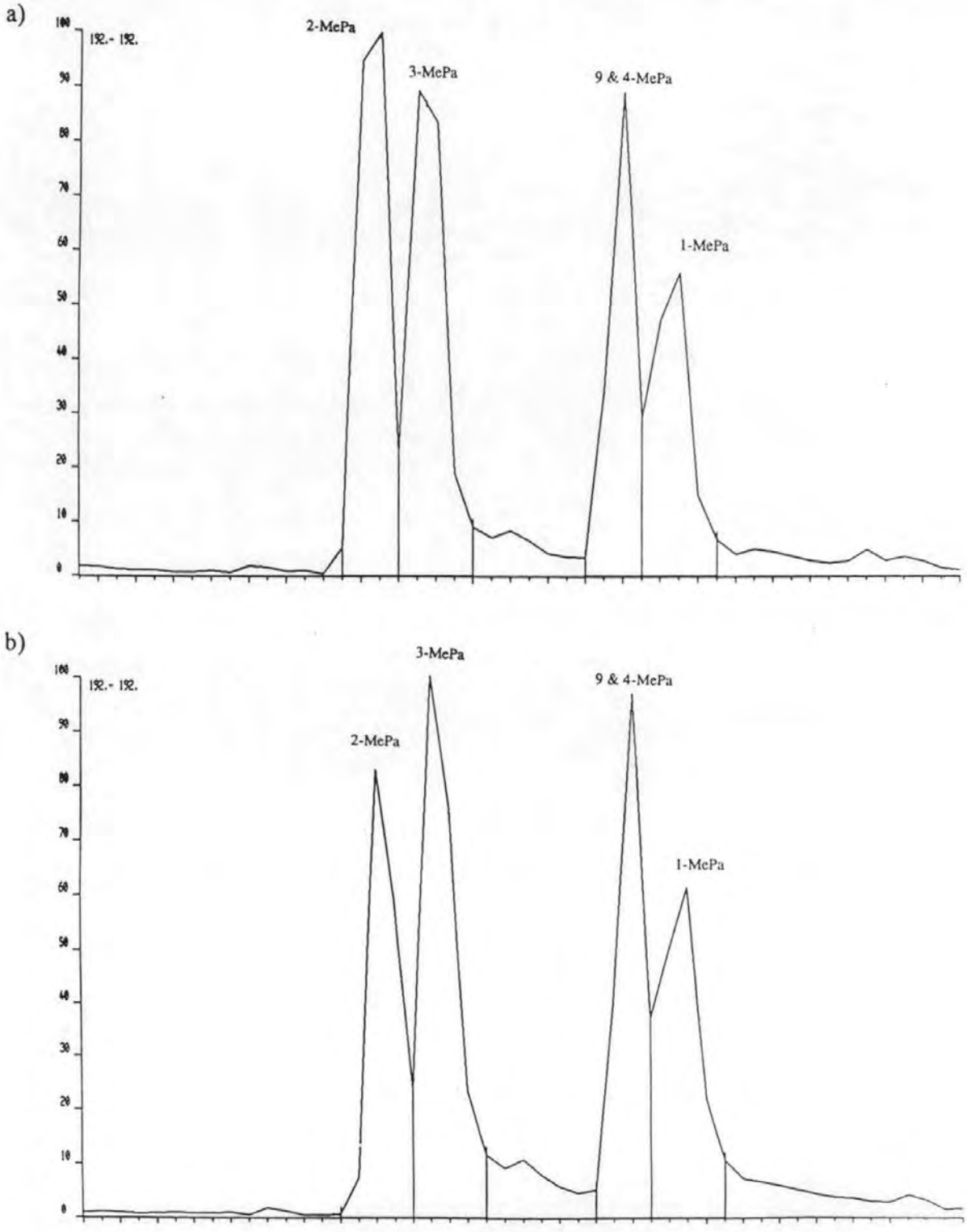


Figure 4.4 GC/MS molecular ion integration of MePa's from a) exhaust sampled from unspiked fuel and **b) exhaust sampled from fuel spiked with 2- and 3-EtPa**

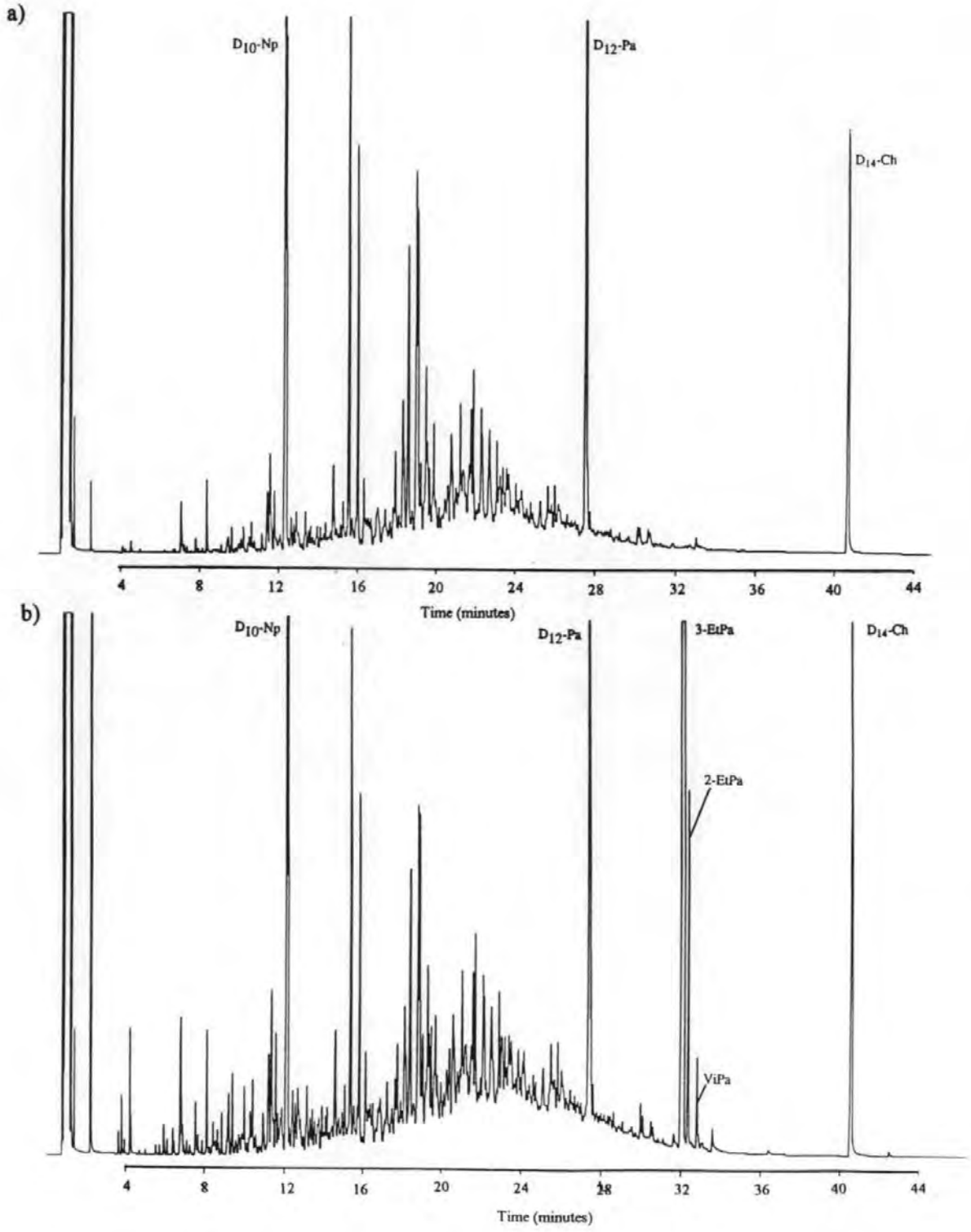
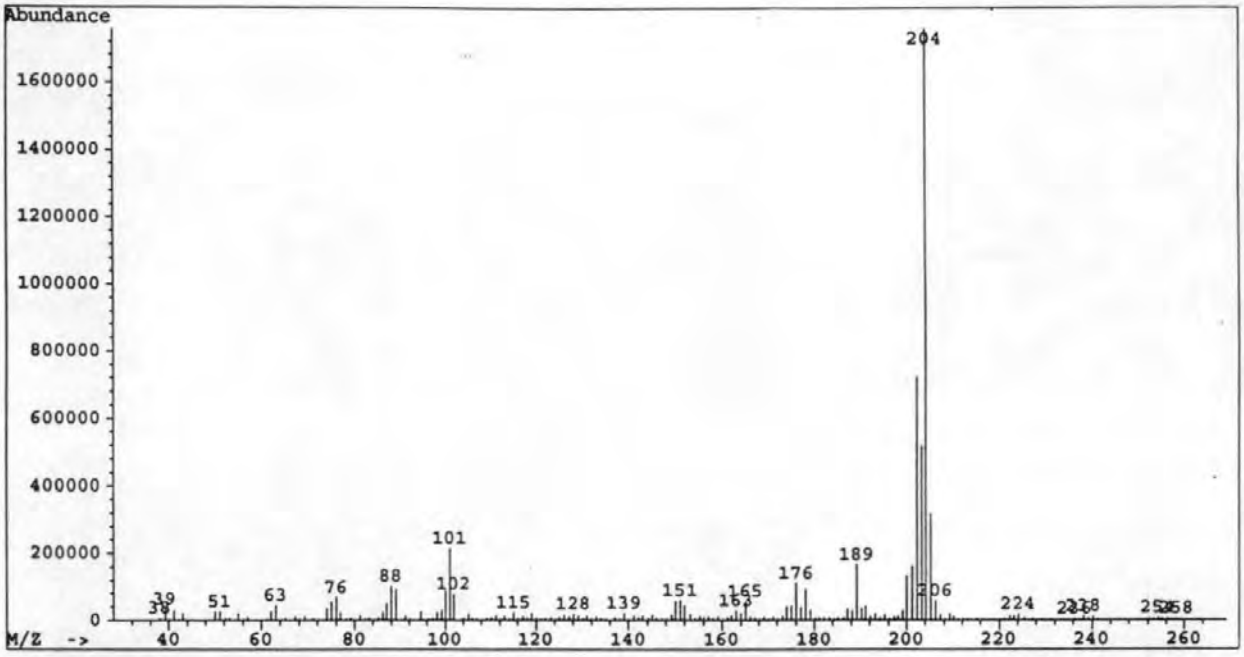


Figure 4.5 Gas chromatograms of a) "baseline" exhaust sample collected from unspiked fuel and **b) spiked exhaust sample, showing 2 & 3-EtPa surviving combustion and the ViPa product at retention times of ca. 32 minutes**

a)



b)

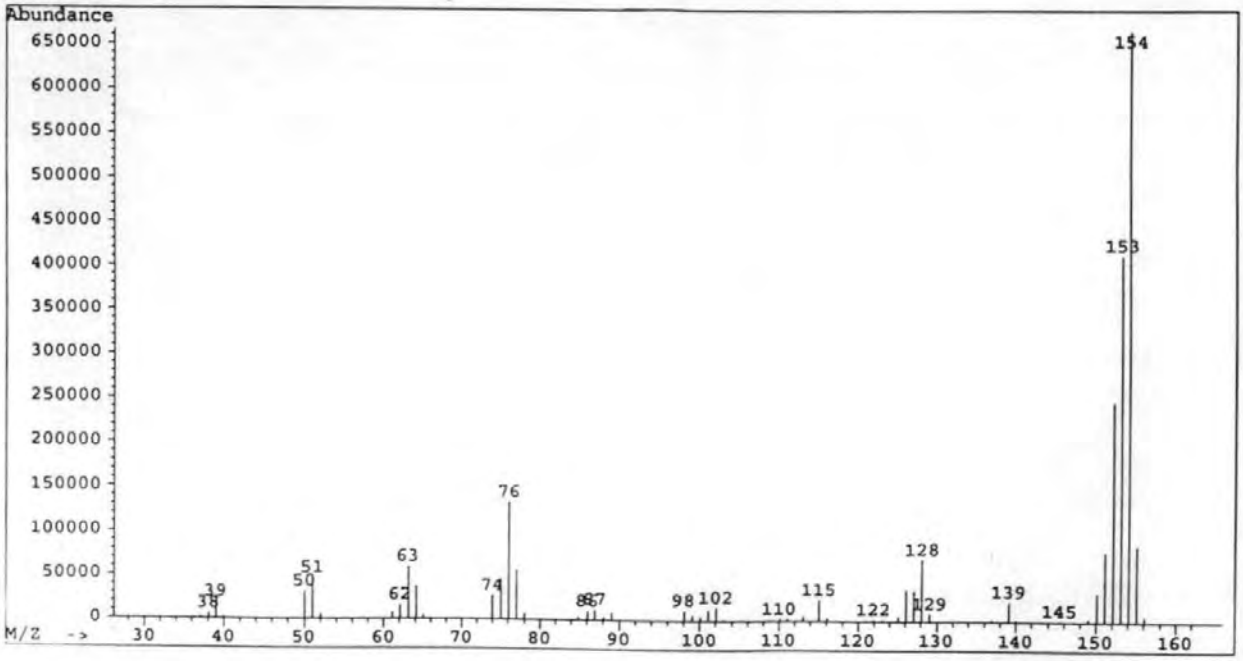


Figure 4.6 Mass spectra of a) vinylphenanthrene and **b) vinylnaphthalene**

4.4 Discussion

The behaviour of alkyl-PAH during diesel combustion is of interest owing to their abundance in the fuel, and their importance in influencing the composition of the emissions. Comparatively little research has been performed in this area. In Chapter 3 (section 3.3.2.1), a mass balance approach to the formation of the parent PAH during combustion has shown that comparatively small rates of dealkylation of individual alkyl-substituted homologues of the parent PAH (especially naphthalene and fluorene), are required to account for the amount of the parent PAH pyrosynthesized during combustion from the various daughter dealkylations. Evidence suggests, that the ease with which individual isomers are dealkylated may vary according to the position of substitution of the alkyl substituent on the aromatic nucleus, and with engine operating conditions. Evidence for the latter assumption may be found in the slight changes in the ratio between alkyl-PAH in the exhaust samples collected from the Prima at different engine conditions (Trier *et al.*, 1990; Tancell, 1991). The thermodynamic stability of alkyl-PAH may influence their distribution in the emissions according to the temperature regime at that engine condition. Budzinski *et al.* (1991) used successfully the thermodynamic stability of di-, tri- and tetramethylnaphthalene isomers, estimated from the group additivity values of Stein *et al.* (1985), to predict their relative distribution in oils obtained from mature and immature sediments.

The combustion of two alkyl-PAH isomers, 2 and 3-EtPa, is here described. This was achieved by combusting a low aromatic diesel fuel spiked with 2 and 3-EtPa and comparing these emissions with those collected from unspiked fuel. This technique allows the behaviour of individual diesel fuel molecules to be studied in detail and is complementary to the radiolabelling techniques developed at Plymouth (Petch *et al.*, 1988; Rhead *et al.*, 1990; Trier *et al.*, 1991; Tancell *et al.*, 1994).

Several researchers have noticed the tendency for the PAH emissions from diesel engines to be strongly dealkylated (Herlan, 1978; Barbella *et al.*, 1989 Trier. *et al.*, 1990). Pyrolysis experiments have also demonstrated the tendency for alkyl-aromatics to be dealkylated (Smith and Savage, 1991; Badger and Spotswood, 1960; Hamins *et al.* 1990; Smith *et al.*, 1979). Freund et al., (1991) studied the pyrolysis of 1,20-di(1-pyrenyl)eicosane. These authors proposed that the dealkylation of PAH

may be regarded as a substitution reaction in which the alkyl side chain is replaced by hydrogen (Figure 4.7). The critical step in the substitution reaction is the formation of the intermediate species. Several mechanisms leading to the formation of the intermediate have been proposed including, a) *ipso* hydrogen atom addition, b) radical hydrogen transfer c) internal hydrogen transfer. The importance of the individual reactions and their mechanistic details of the reaction pathways have not yet been resolved.

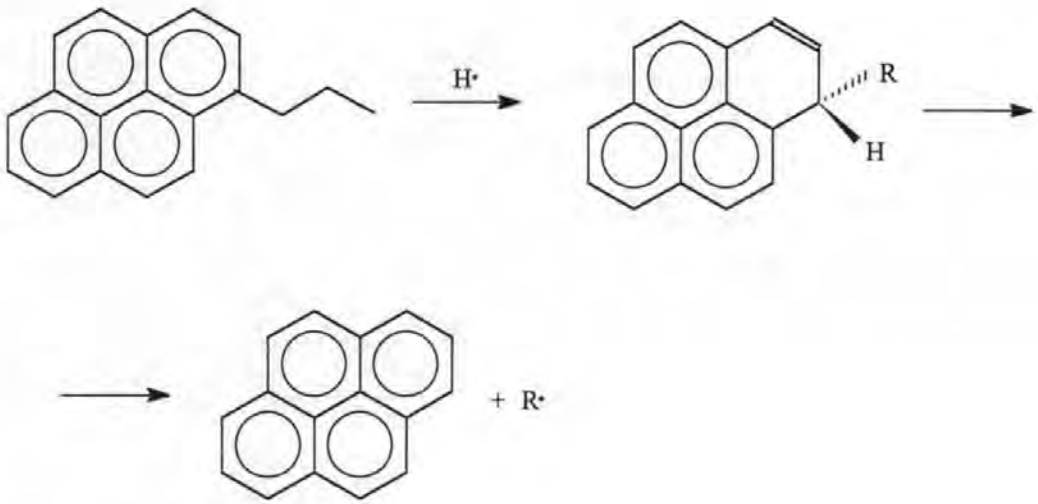


Figure 4.7 Proposed mechanism for the dealkylation of PAH during pyrolysis (Freund *et al.*, 1990)

Smith and Savage (1991) investigated the pyrolysis chemistry of a series of alkylated naphthalenes, phenanthrenes, anthracenes, pyrenes and chrysenes and, from detailed GC-MS analysis of the products, proposed a reaction scheme for the pyrolysis of alkyl-PAH, which proceeds through two main parallel pathways. The first pathway operated mainly through scission of C-C bonds in the alkyl side chain and produced three product groups:

1) methylated-PAH and the corresponding $C_{n-1}H_{2n-2}$ alkene,
2) styrene and the corresponding $C_{n-2}H_{2n-2}$ alkene,
3) a series of minor products consisting of alkenes of varying chain lengths and the corresponding alkyl-PAH.

The second major pathway involved scission of the aryl-alkyl bond to yield the aromatic nucleus and an alkane. The importance of the two reaction pathways was found to be dependent not on the length of the alkyl side chain but on the point of substitution in the aromatic molecule. A relationship between alkyl-aryl bond cleavage and the localisation energy at the point of substitution, as measured by Dewar reactivity numbers, was determined.

Smith and Savage (1991), like Freund *et al.* (1990), also considered the cleavage of the aryl-alkyl C-C bond to constitute a substitution reaction in which the alkyl side chain is replaced by a hydrogen atom (Smith and Savage, 1991). In anionic, cationic or radical substitution of even alternant PAH the intermediate is an odd alternant hydrocarbon and has the structure proposed by Wheland (Wheland, 1942, cited by Dewar, 1952). The change in the π-energy of the system (ΔE_π) between the aromatic molecule and the intermediate should be the same for a given type of substitution by reagents of all three types since these differ only in the number of electrons present in their non-bonding molecular orbitals (Dewar and Dougherty, 1975). ΔE_π of the substitution reaction is related to the reactivity number for the position of the aromatic nucleus where the substitution occurs by the equation:

$$\Delta E_\pi = 2\beta(a_{or} + a_{os}) \quad \text{(Dewar, 1952)}$$

where:

β is the resonance integral,

a_{or} and a_{os} are the coefficients for the non-bonding molecular orbitals at the positions adjacent to the point of substitution.

the Dewar reactivity number is given by the term $2(a_{or} + a_{os})$

Dewar reactivity numbers for the 5 substitution positions in phenanthrene have been calculated and are shown in Figure 4.8.

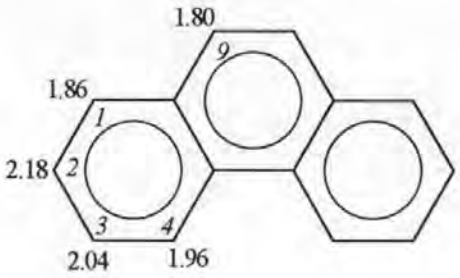


Figure 4.8 Dewar reactivity numbers of phenanthrene

Using Dewar reactivity numbers, Smith and Savage (1991) were able to predict that alkyl-aryl bond cleavage would occur only where the alkyl substituent occupied a carbon centre with Dewar reactivity number less than 1.33. For alkyl-PAH with the substituent at a centre with a Dewar reactivity number greater than 1.81, cleavage of the C-C bond at the β position in the alkyl side chain was the dominant reaction pathway. For those PAH substituted at positions with intermediate Dewar reactivity numbers, a mixture of the two main product groups would be expected.

The results from this research suggest that dealkylation reactions make a negligible contribution to emissions in the Prima engine under these engine conditions and for the 2 & 3-EtPa isomer. Instead, cleavage of the alkyl C-C bond is favoured over cleavage of the alkyl-aryl C-C bond. This may be explained in terms of bond energies. The alkyl-aryl C-C bond is the strongest in the alkyl chain and its bond dissociation energy is about 423KJmol^{-1} (McMillen and Golden, 1982), whereas the bond energy of the alkyl C-C bond in ethylbenzene has been estimated as 264KJmol^{-1} (Szwarc, 1949). Szwarc (1949) suggested a mechanism for the formation of methylbenzene from the pyrolysis of ethylbenzene. The initial stage is a unimolecular splitting of the alkyl C-C bond generating methyl and benzyl radicals. Subsequent capture of hydrogen by the benzyl radical would generate ethylbenzene. The same reaction mechanism applied to the formation of MePa from EtPa is shown in Figure 4.9.

Formation of methylated-PAH during diesel combustion has also been observed by Rhead and Pemberton (1994). These authors in a study of the combustion of ^{14}C-1-methylnaphthalene (1-MeNp), demonstrated that approximately

one third of the 1-MeNp collected in the exhaust was formed during combustion. It seems likely that the 1-MeNp was formed by a similar reaction mechanism to that identified for EtPa, i.e. loss of a methyl group from an ethyl substituted naphthalene.

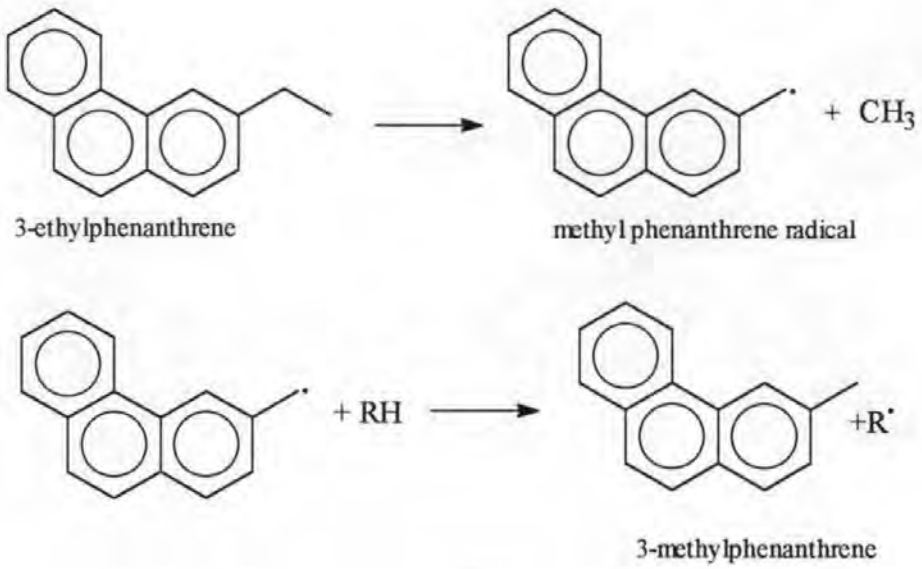


Figure 4.9 Proposed mechanism for the formation of MePa from EtPa during diesel combustion

The results of the current work are in agreement with those of the pyrolysis experiments performed by Smith and Savage (1991). The mean localisation energy for the 3 position in phenanthrene is 2.04. On the basis of the model proposed by Smith and Savage alkyl-aryl bond cleavage would not be expected to occur. Instead cleavage of the C-C bond in the ethyl side chain would be preferred. The lack of any measurable increase in the emission of phenanthrene in the exhaust collected from the spiked fuel in the current experiment, supports this hypothesis. The radiolabelling experiments of Rhead and Pemberton (1994) however, are not in agreement with the proposed model. In their research radiolabelled 2-MeNp produced a small amount of radiolabelled naphthalene equivalent to a 5% conversion of the original 2-MeNp. The localisation energy for the 2-position in naphthalene is 2.12 and according to the model, dealkylation at this position would not be expected to occur. This suggests that the model proposed by Smith and Savage (1991) may not be applied literally to the dealkylation processes occurring during diesel combustion. Under the more

extreme conditions of diesel combustion the probability is that even the more stable alkyl-substituted PAH isomers may be dealkylated. However, the use of reactivity numbers, whilst not being able to specify whether or not a particular isomer will undergo dealkylation, may give an indication of the relative ease with which individual alkyl-substituted PAH are dealkylated.

Aromatic substitution reactions result in a perturbation of the MOs at the point of substitution on the aromatic nucleus and a loss of aromaticity of the carbon atom at which the substitution is occuring. Dewar reactivity numbers are a measure of the degree to which the orbitals are perturbed. This explains their success in being able to predict the relative ease with which substitution will occur at a particular position in the aromatic nucleus. If on the other hand dealkylation reactions during diesel combustion involved predominantly homolytic fission of the alkyl-aryl C-C as opposed to substitution, then reactivity numbers should not be able to predict the relative ease with which substitution will occur at the various carbon centres on the aromatic nucleus since this process does not disrupt the aromaticity or perturb the Mos of the aromatic nucleus. In this research, no measurable dealkylation of the 2- & 3-EtPa was observed. As shown, both the predictions of Smith and Savage (1991), based on reactivity numbers, and alkyl/aryl C-C bond energies are successful in predicting this result. This may suggest that the two factors, i.e the energy required to split the C-C bond, and the reactivity number of the alkyl-substituted carbon, are related, in that the localisation energy of the substituted carbon atom in the aromatic ring will influence the alkyl-aryl bond energy.

The major identifiable product in this research was ViPa. Formation of vinyl-aromatics from alkyl-aromatic precursors has been noted in research by a number of workers (Szwarc, 1949; Badger and Spotswood, 1960; Harris *et al.*, 1988; Hamins *et al.*, 1990; Smith and Savage, 1991). Vinylaromatics and in particular styrene, are thermodynamically stable at high temperatures owing to the stability introduced through conjugation of the π-electrons of the aromatic nucleus with the vinyl moiety (Stein, 1985).

The initial stage in the formation of the vinyl group has been reported to be the loss of a hydrogen atom from the α-carbon through either abstraction with $O^{\cdot}$, $OH^{\cdot}$ and $H^{\cdot}$ radicals or simple bond homolysis (Hamins, 1990). The resulting aryl

radical regains aromaticity by subsequent loss of hydrogen to produce styrene. The proposed mechanism is illustrated in Figure 4.10. PAH with alkyl side chains longer than ethyl will, according to this reaction, decompose to form vinylaromatics and unsaturated alkenes (Badger and Spotswood, 1960).

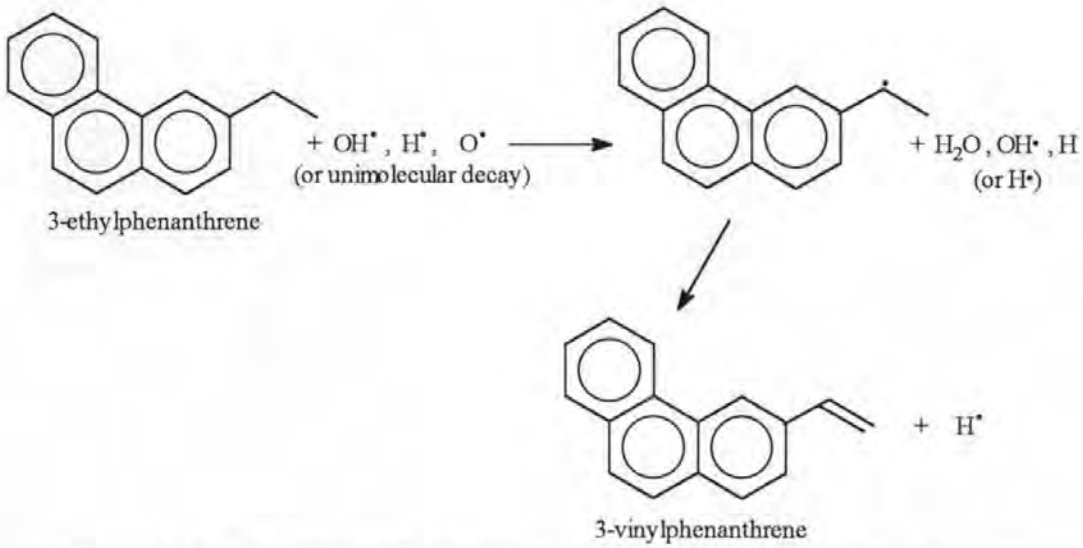


Figure 4.10. Formation of vinylphenanthrene from ethylphenanthrene

These results suggest that the formation of vinyl-aromatics from alkyl-aromatic precursors may be a common reaction pathway in diesel combustion. Further evidence in support of this has come from the identification of ViNp in diesel exhaust emissions. The absence of ViNp in diesel fuel suggests that it is a product of combustion, formed, presumably from alkylnaphthalenes (*e.g.* EtNp) present in diesel fuel by a similar reaction pathway. Styrene and similar structures have been identified as key intermediates in the formation of larger aromatic structures through combination with unsaturated aliphatics and acetylenic species (Crittenden and Long, 1976; Bittner and Howard, 1981). It has also been suggested that similar diaromatic intermediates such as naphthyl and vinylnaphthalene may promote the formation of larger aromatic species and eventually soot (Glassman, 1988). The formation of these compounds may represent an important intermediate step in the formation of soot in diesel fuel combustion.

Chapter 5

CONCLUSIONS and SUGGESTIONS for FUTURE WORK

5.1 Conclusions

This research has demonstrated that the use of radiotracers in the field of diesel emissions research can yield information with regard to the origin of PAH in diesel emissions, that is unavailable by any other technique. There are, however, significant analytical difficulties associated with the technique. In the first instance, the levels of radioactivity in the emissions are very close to the analytical limits of detection. Secondly, the radioactive species present in the emissions sample are diluted by many hundreds of other exhaust components. In the current research, multi-dimensional, radio-chromatographic techniques designed to isolate and quantify radioactive species in diesel emissions, have been successfully developed and applied to a study of the combustion of several ^{14}C-labelled PAH.

PAH present in the exhaust emissions of the Perkins Prima Engine, originate primarily from the sources of fuel survival and pyrosynthesis. The contribution of PAH to the emissions with lubricating oil was negligible. Radiotracer experiments have demonstrated that the relative contribution from survival and pyrosynthesis varies considerably for individual PAH. For certain PAH (e.g. B[α]P) the contribution is greatest from fuel survival (80%). For other PAH (e.g. pyrene) the contribution to the emissions is greatest from pyrosynthesis (70%).

It has not been possible in the current research to determine unequivocally those factors that are responsible for determining the relative contribution of PAH from the two sources. A mass balance calculation has determined that the amount of pyrosynthesized PAH in the exhaust may be accounted for in terms of a comparatively low conversion rate of alkyl-substituted PAH to their parent PAH (5% for alkyl-naphthalenes, 50% for alkyl-pyrenes), by dealkylation reactions. The dealkylation of alkyl-aromatics during diesel combustion has been investigated. Preliminary results suggest that the dealkylation process may be selective. The susceptibility of individual alkyl-PAH isomers to dealkylation may be related to the localisation energy of the aromatic nucleus at the point of substitution.

The extent of PAH survival has been shown to be related to the molecular orbital distribution of the molecule and especially the energy level of the LUMO. It was concluded that the initial reaction responsible for the destruction of PAH during diesel combustion must involve the LUMO of the PAH and electron donation by an

unknown reacting species. The extent to which PAH survive combustion is dependent on their kinetic stability and hence chemical reactivity as opposed to their overall thermodynamic stability.

The combustion of ^{14}C-radiolabelled hexadecane, a major *n*-alkane present in diesel fuel has also been investigated. The extent to which this fuel component survived combustion (0.35%) was demonstrated to be similar to that for PAH molecules. It was also demonstrated that a significant proportion of *n*-hexadecane in diesel emissions is derived from other pyrosynthetic sources during combustion. The most likely source is from the thermal cracking of higher molecular weight alkanes, present in the fuel, during combustion. An increase of lower molecular weight *n*-alkanes in the emissions relative to their concentration in the fuel was observed and supports this conclusion.

5.2 Suggestions for Future Work

The focus of this research has been the use of radiotracers to investigate the diesel combustion of PAH. It has been demonstrated from a limited number of experiments, that the sources of PAH in the emissions varies considerably for individual species. Future research will involve a comprehensive programme designed to investigate the combustion of all major PAH present in diesel fuel at a variety of speeds and loads. The contribution from pyrosynthesis and survival will be accurately determined for each PAH. The eventual aim of the research programme is to generate a database of results which will then be used to generate mathematical models to help predict the composition of PAH in the emissions from a knowledge of their composition in the fuel. These results will be used to test the validity of thermodynamic models which have been used to predict the PAH emissions composition from combustion systems.

Few ^{14}C-radiolabelled hydrocarbons are commercially available. Synthesis of a wide range of hydrocarbons, especially alkyl-PAH and *n*-alkanes of varying chain length is required in order to perform a comprehensive investigation into the fate of diesel fuel in diesel combustion. Synthesis of wide range of alkyl-PAH standards is also necessary for identification work, especially methyl, ethyl and isopropyl-substituted PAH of three and four ringed PAH.

The correlation between PAH survivals and their molecular orbital distribution, identified in this research, may be used as an empirical model to predict the extent of survival of individual PAH in specific diesel fuels. Further research is required to test the relationship between PAH survivals and molecular orbital distribution, especially at varying engine conditions. The model will be applied to the prediction of rates of survival for other PAH. Specifically, the combustion of phenanthrene and fluoranthene will be investigated. These PAH are present in diesel fuel and are available commercially as ^{14}C-radiolabelled species. On the basis of the present results the model predicts survivals for phenanthrene and fluoranthene, of 0.53% and 0.35% respectively at the specified engine conditions. Of the two PAH, the combustion of fluoranthene may prove of particular significance. Fluoranthene is a non-alternant PAH and its molecular orbitals of are not distributed symmetrically around the coulomb integral (α). It is likely therefore that, as has been observed with fluorene, the extent of survival of fluoranthene should correlate more precisely with the energy level of either the HOMO or the LUMO or the energy difference between the two. This will help to confirm which of the three molecular orbital measurements is the main parameter in determining the extent of PAH survival and hence should yield more information on the mechanistic processes responsible. In addition, the concentration of alkyl-fluoranthenes in diesel fuel is low. If dealkylation reactions are responsible for the observed pyrosynthesis of PAH, it might be predicted that the amount of pyrosynthesized fluoranthene in the emissions, determined from specific activities, would be small.

In view of the abundance of alkylaromatic species in diesel fuel, and their importance in determining the PAH distribution in the emissions, a programme to investigate their behaviour during diesel combustion is proposed using both ^{14}C-radiolabelled and non-labelled alkyl-PAH. Mass balance calculations have indicated that dealkylation may account for the extent of pyrosynthesis of the parent PAH determined from radiotracer experiments. The combustion of 2-EtPa and 3-EtPa described in Chapter 4 demonstrated that the importance of dealkylation reactions varies for individual alkyl-PAH isomers. The future research programme will, therefore, involve a methodical investigation into the combustion of all the major alkyl-PAH species in diesel fuel with a particular emphasis on the tendency for

specific alkyl-PAH isomers to undergo dealkylation. The ease with which methyl- and dimethyl-substituted pyrenes are dealkylated is of especial interest owing to the high level of pyrosynthesized pyrene that has been observed in the present research. Hence , initial experiments will involve the synthesis of alkyl-PAH isomers of 3 and 4-ring PAH to investigate the ease with which these species undergo dealkylation. These experiments will use a low aromatic fuel as outlined in Chapter 4 to facilitate the identification and quantification of specific products of combustion. Arrangements for its aquisition from fuel companies have been made.

In Chapter 3, the combustion of ^{14}C-*n*-hexadecane was described. Aliphatic species are the major constituents of diesel fuel. It has been proposed that the extent to which aliphatic species survive combustion is a function of their size. This research has suggested that the formation of short chain n-alkanes from higher molecular weight *n*-alkanes occurs during combustion. Further research is needed to investigate the relationship between the size of aliphatics and their origin in the emissions as a function of survival and pyrosynthesis. Investigations into the combustion of aliphatic species have been limited since the subsequent analytical procedure requires a radio-GC which has not been readily available during this research. The future availability of a radio-GC will now facilitate the proposed investigations feasible.

LITERATURE CITED

Literature cited

Abbass M. K., Andrews G. E., Williams P. T. *et al.*, 1988, Diesel particulate emissions: Pyrosythesis of PAH from hexadecane., *Society of Automotive Engineers*, paper no. 880345

Abbass M. K., Andrews G. E. and Williams P. T., 1991, Comparison of methods for the determination of the SOF of diesel particulates and development of a rapid TGA method for the estimation of the unburnt fuel and lubricating oil fractions., Experimental methods in engine R & D, *Institute of Mechanical Engineers Seminar*

Alberty R. A., Chung M. B. and Reif A. K., 1989, Standard chemical thermodynamic properties of polycyclic aromatic hydrocarbons and their isomer groups. II. Pyrene series, naphthopyrene series, and coronene series., *Journal of Physical and Chemical Reference Data*, 18 (1), 77-109

Alexander R., Kagi R. I. and Sheppard P. N., 1983, Relative abundance of dimethylnaphthalene isomers in crude oils, *Journal of Chromatography*, 267, 367-372

Andrews G. E., 1992, Diesel particulates: An introduction to factors that influence their production and composition., *Notes presented at a short course on diesel particulates*. University of Leeds

Andrews G. E. *et al.*, 1983, Unburnt hydrocarbon and polynuclear aromatic hydrocarbon emissions and their relationship to diesel fuel composition., *Institute of Mechanical Engineers*. paper no. C73/83

Atkins P. W., 1986, Physical Chemistry. 3rd ed. Oxford University Press, p394

Badger G. M. and Spotswood T. M., 1960, The formation of aromatic hydrocarbons at high temperatures. Part IX. The pyrolysis of toluene, ethylbenzene, propylbenzene and butylbenzene., *Australian Journal of Chemistry*, 4420-4427.

Badger G. M. and Novotny J., 1963, Mode of formation of 3,4-benzpyrene at high temperature, *Nature*, 198, 1086

Baranescu R. A., 1988, Influence of fuel sulphur on diesel particulate emisions., *Society of Automotive Engineers*, paper no. 881174

Barbella R., Ciajolo A. and D'anna A., 1989, Effect of fuel aromaticity on diesel emissions., *Combustion and Flame*, 77, 267-277.

Barbella R., Bertoli C., Ciajolo A and D'Anna A., 1990, Behaviour of a fuel oil during the combustion cycle of a direct injection diesel engine., *Combustion and Flame*, 82, 191-198

Barnard J. A. and Bradley J. N., 1985, Flame and Combustion (2nd ed.), Chapter 6. Chapman and Hall, London

Batts B. D. and Zuhdan Fathoni A., 1991, A literature review on fuel stability studies with particular emphasis on diesel oil., *Energy and Fuels*, 5, 2-21.

Bayona J. M., Markides K. E. and Lee M. L., 1988, Characterisation of polar polycyclic aromatic compounds in a heavy-duty diesel exhaust particulate by capilliary column GC and high-resolution mass spectrometry., *Environmental Science and Technology*, 22, 1440-1447

Bechtold W. E., Dutcher A. S., Brooks A. L. and Henderson T. R., 1985, Fractionation of diesel exhaust particle extracts by sephadex LH-20 and thin-layer chromatography., *Journal of Applied Toxicology*, 5 (5), 295-300

Beckman C., Israel G. and Mollenhauer K., 1989, Artifact formation of nitrated polycyclic aromatic hydrocarbons during diesel soot sampling on teflon coated glass fibre filters., *Journal of Aerosol Science*, 20 (8), 1385-1388.

Begeman C. R. and Colluci J. M., 1970, Polynuclear aromatic hydrocarbon emissions from automotive engines., *Society of Automotive Engineers*, paper no. 700469

Bemgard A., Colmsjo A. and Lundmark B., 1993, Gas chromatographic analysis of high molecular mass polycyclic aromatic hydrocarbons. II. PAH with relative molecular masses exceeding 328., *Journal of Chromatography*, 630, 287-295

Benson S. W. Cruickshank F. R., Golden D. M., *et al.*, 1969, Additivity rules for the estimation of thermochemical properties, *Chemical Reviews*, 69, 279

Betts W. E., Floysand S. A. and Kvinge F., 1992, The influence of diesel fuel properties on particulate emissions in European cars., *Society of Automotive engineers*, paper number 922190.

Bittner. J. D and Howard J. B., 1981, 18th International Symposium on Combustion/ The Combustion Institute, 1105.

Blanco C. G., Canga. J. S., Dominguez .A., Iglesias M. J. and Guillen M. D., 1992, Flame ionisation relative response factors of some polycyclic aromatic compounds. Determination of the main components of the coal tar pitch volatile fraction., *Journal of Chromatography*, 607, 295-302.

Borden W. E., Modern Molecular Orbital Theory for Organic Chemists. Prentice-Hall, New Jersy, 1975

Brear F., Fredholm S. C. G. and Andersson E. S., 1992, The role of the trough flow oxidation catalyst in the development of a low emissions specification HD diesel engine., *Society of Automotive Engineers*, paper no. 920367

Brindle I. D. and Li X., 1989, Investigation into the factors affecting performance in the determination of polycyclic aromatic hydrocarbons using capillary GC-MS with splitless injection., *Journal of Chromatography*, 11-21

British Standard 2869: Part 1., (1988), Specification for Automotive Diesel Fuel, British Standards Institution

Budzinski H., Garrigues Ph., Radke M. *et al.*, 1993, Use of molecular modelling as a tool to evaluate thermodynamic stability of alkylated polycyclic aromatic hydrocarbons., *Energy and Fuels*, 7, 505-511

Bundt J., Herbel W., Steinhart H., Franke S. and Francke W., Structure type separation of diesel fuels by solid-phase extraction and identification of the two- and three-ring aromatics by capilliary GC-mass spectrometry., *Journal of High Resolution Chromatography*, 14, 91-98

Cartellieri W. and Tritthart P., 1984, Particulate analysis of light duty diesel engines with particular reference to the lube oil particulate fraction., *Society of Automotive Engineers*, paper no. 840418

Chan T. L., Lee P. S. and Siak J., 1981, Diesel particulate collection for biological testing. Comparison of electrostatic precipitation and filtration., *Environmental Science and Technology*, 15 (1), 89-93

Chmielowiec J. and George A. E., 1980, Polar bonded-phase sorbents for high performance liquid chromatographic separations of polycyclic aromatic hydrocarbons., *Analytical Chemistry*, 52, 1154-1157

Ciajolo A. D'Anna A., Barbella R. and Bertoli C., 1992, Combustion of tetradecane and tetradecane/α-methylnaphthalene in a diesel engine with regard to soot and PAH formation., *Combustion Science and Technology*, 87, 127-137

Claessens H. A. and Lammerts van Beuren L. G. D., 1987, An off-line two-dimensional analytical procedure for the determination of polycyclic aromatic hydrocarbons in smoke aerosol., *Journal of High Resolution Chromatography and Chromatography Communications*, 10, 342-347

Clarke A. G., 1991, Sulphate formation and analysis., *Notes presented at A Short Course on Diesel Particulates*, Leeds University, Department of Fuel and Energy

Cole J. A., Bittner J. D., Longwell J. P. and Howard J. B., 1984, Formation mechanisms of aromatic compounds in aliphatic flames., *Combustion and Flame*, 56, 51-70.

Collier A., Trier C. J., Rhead M. M., Bell M. and Fussey D. E., 1994, Polycyclic aromatic compound profiles for a light-duty direct-injection diesel engine., *Fuel*, In the Press

Collier A., unpublished

Cooke V. B., 1990, Lubrication of low emission diesel engines., *Society of Automotive Engineers*, paper no. 900814

Cookson D. J., Rix C. J., Shaw I. M. and Smith B. E., 1984, High performance liquid chromatographic procedure for the direct determination of the compound class composition of diesel and kerosine fuels using refractive index detection., *Journal of Chromatography*, 312, 237-246

Corcione F. E., Prati M. V., Vaglieco B. M. and Valentino .G., 1991, Improvement of combustion systems of a small D.I. diesel engine for low exhaust emissions., *Society of Automotive Engineers*, paper no. 910481

Crittenden B. D. and Long R., 1973, Formation of polycyclic aromatics in rich premixed acetylene and ethylene flames., *Combustion and Flame*, 20, 359-368.

Crittenden B. D. and Long R., 1976, The mechanisms of formation of polynuclear aromatic compounds in combustion systems., Polynuclear Aromatic Hydrocarbons: Chemistry, Metabolism and Carcinogenesis, R. I. Freudenthal & P. W. Jones (Eds.), Raven Press, New York

Cullis C. F., 1986, Possible chemical pathways to combustion generated polycyclic aromatic compounds., *Notes presented at a short course on diesel particulates.* The University of Leeds.

Cuthbertson R. D., Shore P. .R., Sundstrom L. and Heden P. O., 1987, Direct analysis of diesel particulate-bound hydrocarbons by gas chromatography with solid sample injection., *Society of Automotive Engineers*, paper no. 870626

Davies I., L., Raynor M. W., Williams P. T., Andrews G. E. and Bartle K. D., 1987, Application of automated on-line microbore high-performance liquid chromatography/capilliary gas chromatography to diesel exhaust particulates., *Analytical Chemistry*, 59, 2579-2583

Davies M. J., Blaikley D. C. W. Jorgensen N., 1993, Catalytic control of diesel particulates., *Proceedings of the Institute of Mechanical Engineers*, London, May

Deuring H., 1981, Valve stem seals handle oil metering and wear., *Society of Automotive Engineers*, paper no. 810292

Dewar M. J. S and Dougherty R. C., 1969, The Perturbation Molecular Orbital Theory of Organic Chemistry., McGraw Hill, New York.

Dewar M. J. S., 1952, A molecular orbital theory of organic chemistry. VI Aromatic substitution and addition., *Journal of the American Chemical Society*, July, 3357

Dictionary of Organic Compounds 5th edition, Volume II, Chapman and Hall, London

Doel R. C. and Saunders A. C., 1994, Thermodynamics shown not to dictate polyaromatic hydrocarbon species distribution in a diesel engine. *Shell Research, Thornton Research Centre, Personal Communication.*

Dunne J. M., 1993, European emission standards to the year 2000., *Proceedings of the Institute of Mechanical Engineers*, London, May

Durnholz M., Eifler G. and Endres E., 1992, Exhaust-gas recirculation. A measure to reduce exhaust emissions of DI diesel engines., *Society of Automotive Engineers*, paper no. 920725

Emmelin A., Nystrom L. and Wall S., 1993, Diesel exhaust exposure and smoking: A case reference study of lung cancer among Sweedish dock workers., *Epidemiology*, 4 (3), 237-244

Engler B. H., Leyrer J., Lox E. S. and Ostgathe K., 1993, Catalytic reduction of NO_x with hydrocarbons under lean diesel exhaust gas conditions., *Society of Automotive* Engineers, paper no. 930735

Essig G., Kamp H. and Wacker E., 1990, Diesel engine emissions reduction - The benefits of low oil consumption design., *Society of Automotive Engineers*, paper no. 900591

European Community (1991) EC Directive 91/441/EEC, Official Journal of the European Communities

Farrar-Khan J. R., Andrews G. E., Ishaq R., Williams P. T. and Bartle K. D., 1991, Quantitative GC/MS for diesel particulate analysis., *Institute of Mechanical Engineers Seminar, December., Experimental Methods in Engine Research and Development.*

Fernandez P., Port C., Barcelo D., Bayona J. M. and Albaiges J., 1988, Selective enrichment procedures for the determination of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in environmental samples by gel-permeation chromatography. *Journal of Chromatography*, 456, 155-162

Fetzer J. C., Biggs W. R. and Jinno. K., 1986, HPLC analysis of the large polycyclic aromatic hydrocarbons in a diesel particulate., *Chromatographia*, 21 (8), 439-442

Fetzer J. C., Gas and Liquid Chromatographic Techniques. In: Chemical Analysis of Polycyclic Aromatic Compounds., (Vo-Dinh. T., Ed.), 1989, Wiley, New York

Flemming I., 1978, Frontier Orbitals and Organic Reactions, Wiley, New York
Floysand S. A., Kvinge F. and Betts W. E., 1993, The influence of diesel fuel properties on particulate emissions in a catalyst equipped European car., *Society of Automotive engineers*, paper no.SAE 932683.

Frenklach M., Clary D. W., Gardener W. C. Jr. and Stein S. E., 1985, Twentieth Symposium (International) on Combustion., p889, The Combustion Institute

Freund H., Matturro M. G., Olmsted W. R. *et al.*, 1990, Anomalous side chain cleavage in alkylaromatic pyrolysis., *American Chemical Society, Division of Fuel and Chemistry*, 35, 496-504

Furniss B. S., Hannaford A. J. *et al.*, Chapter IV. Aromatic Compounds, Textbook of Practical Organic Chemistry, Vogel, 5th Edition, Longman Scientific & Practical Publishers, London

Garrigues Ph. and Bellocq J., 1989, Rapid clean-up of natural organic extracts for the recovery of polycyclic aromatic hydrocarbons by solid phase extraction., *Journal of High Resolution Chromatography*, 12, 400-403

Gerde P., Medinsky M .A. and Bond J. A., 1991, Contemporary Issues in Toxicology. Particle-associated polycyclic aromatic hydrocarbons-A reappraisal of their possible role in pulmonary carcinogenisis., *Toxicology and Applied Pharmacology*, 108, 1-13

Glassman I., 1988, Soot formation in combustion processes., *22nd International Symposium on Combustion/ The Combustion Institute*, 295-311.

Glatt H., Henschler R., Phillips D. H. *et al.*, 1990, Sulfotransferase-mediated chlorination of 1-hydroxymethylpyrene to a mutagen capable of penetrating indicator cells., *Environmental Health Perspectives*, 88, 43-48

Gotze H. J., Schneider J. and Herzog H. G., 1991, Determination of polycyclic aromatic hydrocarbons in diesel soot by high-performance liquid chromatography., *Fresenius Journal of Analytical Chemistry*, 340, 27-30

Gough M. A. and Rowland S. J., 1990, Characterisation of unresolved complex mixtures of hydrocarbons in petroleum., *Nature*, 344 (6267), 648-650

Grimmer G., Hildebrant A. and Bohnke H., 1973, Investigations of the carcinogenic burden by air pollution in man. III. Sampling and analysis of polycyclic aromatic hydrocarbons in automobile exhaust., *Zbl. Bakt. Hyg. I. Abt. Orig. B.*, 158, 35-49

Grimsrud E. P. and Valkenburg C. A., 1984, New schemes for the electron-capture sensitization of aromatic hydrocarbons., *Journal of Chromatography*, 302, 243-256

Grizzle P.L. and Thompson J. S., 1982, Liquid chromatographic separation of aromatic hydrocarbons with chemically bonded (2,4-dinitroanilinopropyl)silica., *Analytical Chemistry*, 54, 1071-1078

Grizzle P. L. and Sablotny D. M., 1986, Automated liquid chromatographic compound class group-type separation of crude oils and bitumens using chemically bonded aminosilane., *Analytical Chemistry*, 58, 2389-2396

Grob Jr. K., 1982, Band broadening in space and the retention gap in capillary gas chromatography., *Journal of Chromatography*, 237, 15-23

Grob Jr. K. and Grob K., 1983, Determination of the depth of retention gaps in capillary gas chromatography., *Journal of Chromatography*, 270, 17-27

Guillemin M. P., Herrera H., Huynh C. K., Droz P. and Druc T. V., 1992, Occupational exposure of truck drivers to dust and polynuclear aromatic hydrocarbons: a pilot study in Geneva, Switzerland., *International Archives of Occupational and Environmental Health*, 63, 439-447

Halsall R., McMillen M. L. and Schwartz B. J., 1987, An improved method for determining the hydrocarbon fraction of diesel particulates by vacuum oven sublimation., *Society of Automotive Engineers*, paper no. 872163

Hamins A., Anderson D. T. and Miller J. H., 1990, Mechanistic studies of toluene destruction in flames., *Combustion Science and Technology*, 71, 175-195

Hansen A. M., Olsen I. L. B., Holst E. and Poulsen O. M., 1991, Validation of HPLC/flourescence detection method for the simultaneous quantification of fifteen polycyclic aromatic hydrocarbons., *Annals of Occupational Hygeine*, 35 (6), 603-611

Handbook of Chemistry and Physics, 1992/3, D. R. Lide (Ed. in Chief), CRC Press, Chapter 9, p132

Hansen A. M., Olsen I. L. B., Holst E. and Poulsen O. T., 1991, Validation of HPLC fluorescence detection method for the simletaneous quantification of fifteen polycyclic aromatic hydrocarbons., *Annals of Occupational Hygiene*, 35 (6), 603-611

Hansen. E. S., 1993, A follow-up study on the mortality of truck drivers, *American Journal of Industrial Medicine*, 23, 811-821

Harris S. J., Weiner A. M. and Blint R. J., 1988, Formation of small aromatic molecules in a sooting acetylene flame., *Combustion and Flame*, 72, 91-109

Haworth R. D. *et al.*, 1933, *Journal of the Chemical Society*, p1012

Haynes B. S. and Wagner H. G., 1981, Soot formation., *Prog. Energy. Combust. Sci.*, 7, 229-273.

Heinrich U., Dungworth D. L., Pott F., *et al.*, 1993, Carbon particulates and irritant gasses as modifiers of the carcinogenic potency of polycyclic aromatic hydrocarbons. In: Polycyclic Aromatic Hydrocarbons

Henderson T. R., Sun J. D., Albert P. L., *et al.*, 1984, GC/MS and MS/MS studies of diesel exhaust mutagenicity and emissions from chemically defined fuels., *Environmental Science and Technology*, 18, 428-434

Herla A., 1978, On the formation of polycyclic aromatics: Investigation of fuel oil and emissions by high-resolution mass spectrometry., *Combustion and Flame*, 31, 297-307

Hilden. D. L. and Mayer W. J., 1984, The contribution of engine oil to particulate exhaust emissions from light duty diesel powered vehicles., *Society of Automotive Engineers*, paper no. 841395

Holman C., Wade J. and Fergusson M., 1993, Future emissions from cars 1990 to 2025: The importance of the cold start emissions penalty., *WWF*, UK.

Horrocks R W., 1993, Light-duty diesels. An update on the emissions challenge., *Proceedings of the Institute of Mechanical Engineers*, London, 6-7 April

Husingh. J. L., Waters M. D., Nesnow S., *et al.*, 1978, Application of short-term bioassays in the fractionation and analysis of complex environmental mixtures, US EPA, report EPA-600/9-78-027, September

Hunter C. E., Cikanek H. A. and Gardener T. P., 1989, Evaluation of some factors controlling DI diesel combustion and exhaust emissions., *Journal of Engineering for Gas Turbines and Power*, 111, 379-386.

Hutcheson R. C. and Van Paassen C. W. C., 1990, Diesel fuel quality into the next century., *Institute of Petroleum Conference*, London, April

International Agency for Research on Cancer (IARC), 1989, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans., Vol.46, Diesel exhaust and gasoline engine exhausts and some nitroarenes., IARC, Lyon

Ishinishi N., Kuwabara N., Nagase S., *et al.*, 1986, Long-term inhalation studies on effects of exhaust from heavy and light duty diesel engines on F334 rats., In: Carcinogenic and Mutagenic Effects of Diesel Exhaust., N. Ishinishi, R.O. McClellan. and W. Stober (eds.), Elsevier Science Publications., Amsterdam, pp329-348

Jinno K., Yamamoto K., Nagashima H., *et al.*, 1990, Silicas chemically bonded with multidentate phenyl groups as stationary phases in reverse-phase liquid chromatography used for non-planarity recognition of polycyclic aromatic hydrocarbons., *Journal of Chromatography*, 517, 193-207

Josefsson B., Mass Spectrometric Analysis of Polycyclic Aromatic Hydrocarbons., In: Handbook of Polycyclic Aromatic Hydrocarbons (Bjorseth. A. ed), 1983, Marcel Dekker, New York., Chapter 7

Karlesky D., Shelly D. C. and Warner I., 1981, Reactivation of an amino-bonded phase liquid chromatographic column., *Analytical Chemistry*, 53, 2146-2147

Kato T., Tsujimura T., Shintani M. and Minami T., 1989, Spray characteristics and combustion improvement of DI diesel engine with high pressure fuel injection., *Society of Automotive Engineers*, paper no. 80265

Kelly G. W., Bartle K. D., Clifford A. A. and Robinson R. E., 1992, Application of coupled LC-GC to the analysis of the polar fraction of diesel particulate matter., *Journal of High Resolution Chromatograhy*, 15, 527-531

Kelly G. W., Bartle K. D., Clifford A. A. and Scammells D., 1993, Identification and quantification of polycyclic aromatic compounds in diesel exhaust particulate extracts by LC-GC., *Journal of Chromatographic Science*, 31, 73-76

Kibbey C. E. and Meyerhoff M. E., 1993, Shape selective separation of polycyclic aromatic hydrocarbons by reverse-phase liquid chromatography on tetraphenylporphyrin based stationary phases., *Journal of Chromatography*, 641, 49-55

Kittelson D. B., Pipho M. J., Ambs J. L. and Siegla D. C., 1986, Particle concentrations in a diesel cylinder: Comparison of theory and experiment., *Society of Automotive Engineers*, paper no. 861569

Kobayashi S., Takayuki S., Nakahira T., Komori M. and Tsujimura K., 1992, Measurement of flame temperature distribution in a DI diesel engine with high pressure fuel injection., *Society of Automotive Engineers*, paper no. 920692

Konno M., Chikahisa T. and Murayama T., 1992, Reduction of smoke and NO_x by strong turbulence generated during the combustion process in a D.I. diesel engine., *Society of Automotive Engineers*, paper no. 920467

Konno M., Chikahisa T., Murayama T. and Iwamoto M., 1992, Catalytic reduction of NO_x in actual diesel engine exhaust., *Society of Automotive Engineers*, paper no. 920091

Kotin P., Falk H. L. and Thomas T. M., 1955, Aromatic hydrocarbons II. Presence in the particulate phase of diesel-engine exhaust and the carcinogenicity of exhaust extracts., *Archives of Industrial Hygiene and Occupational Medicine*, 9, 164-177

Kraft J. and Lies K. H., 1981, Polynuclear aromatic hydrocarbons in the exhaust of gasoline and diesel vehicles., *Society of Automotive Engineers*, SAE paper no. 810082

Kruzel E. L., Lafleur A., Braun A. G., *et al.*, 1991, A high yeild sampler for toxicologicol characterization of complex mixtures in combustion effluents., *Environmental Health Perspectives*, 90, 305-314

Lafleure A. L., Monchamp P. A., Plummer E. F. and Wornat M. J., (1987) Universal calibration method for the determination of polycyclic aromatic hydrocarbons by high performance liquid chromatography with broadband diode-array detection. *Analytical Letters*, 20 (8), 1171-1179

Lam F. W., Howard J. B and Longwell J. P., 1988, The behaviour of polycyclic aromatic hydrocarbons during the early stages of soot formation., *22nd International Symposium on Combustion/ The Combustion Institute*, 323-332.

Lane D. A., The Fate of Polycyclic Aromatic Hydrocarbons in the Atmosphere and During Sampling., In: Chemical Analysis of Polycyclic Aromatic Hydrocarbons., Chapter 2. (Vo-Dinh T., Ed), Wiley, New York

Later D. W., Wilson B. W. and Lee M. L., 1985, Standardization of alumina and silica adsorbents used for chemical class separations of polycyclic aromatic compounds., *Analytical Chemistry*, 57, 2979-2984.

Lee M. L., Vassilaros D. L., White C. M. and Novotny M., 1979, Retention indices for programmed-temperature capillary-column gas chromatography of polycyclic aromatic hydrocarbons., *Analytical Chemistry*, 51 (6), 768-773

Lida N. and Sato G. T., 1988, Temperature and mixing effects on NO_x and particulate., *Society of Automotive Engineeers*, paper no. 880424

Lindsay R., Marriot J. M., Booth M. and Van Passen C., 1992, Automotive diesel fuel: The balance between cost-effectiveness and environmental acceptibilty., *The Institute of Petroleum, Petroleum Review*, July.

Liston T. V., 1992, Engine lubricant additives, what they are and how they function., *Journal of the Society of Tribologists and Lubrication Engineers*, May, 389-397

Longwell J. P., 1982, The formation of polycyclic aromatic hydrocarbons by combustion., *19th International Symposium on Combustion/ The Combustion Institute*, 1339-1350.

Lowenthal D. H., Zielinska B., Chow J. C. *et al.*, 1994, Characterisation of heavy-duty diesel vehicle emissions., *Atmospheric Environment*, 28 (4), 731-743

Marcomini A., Pavoni B., Donazzolo R. and Orio A. A., 1986, Combined preparative and analytical use of normal-phase and reverse-phase high performance liquid chromatography for the determination of aliphatic and polycyclic aromatic hydrocarbons in sediments of the Adriatic Sea., *Marine Chemistry*, 18, 71-84

Matsuzawa S., Garrigues P., Setokuchi O., *et al.*, 1990, Separation and identification of monomethylated polycyclic aromatic hydrocarbons in heavy oil., *Journal of Chromatography*, 498, 25-33

May W. E. and Wise S. A., 1984, Liquid chromatographic determination of polycyclic aromatic hydrocarbons in air particulate extracts., *Analytical Chemistry*, 56, 225-232

Mauderly J. L., Jones R. K., McClellan R. O. *et al.*, 1986, Carcinogenicity of diesel exhaust inhaled chronically by rats. In: Carcinogenic and Mutagenic Effects of Diesel Exhaust., N. Ishinishi, R. O. McClellan and W. Stober (eds.), Elsevier Science Publications., Amsterdam, 397-409

McMillen D. F. and Golden D. M., 1982, Hydrocarbon bond dissociation energies., *Annual Review of Physical Chemistry*, 33, 493-532

Milazzo A. N. and Bidini G., 1991, Lubrictaing oil consumption in reciprocating internal combustion engines., *Notes presented at A Short Course on Diesel Particulates*, Leeds University, Department of Fuel and Energy

Mosettig E. and Van de Kemp J., 1930, Synthesis in the phenanthrene series. I. Acetylphenanthrenes., *Journal of the American Chemical Society*, 52, 3704

Naber D., Lange W. W., Reglitzky A. A., Schafer A., Gairing M. and Le'Jeune A., The influence of fuel properties on diesel exhaust emissions., *Society of Automotive engineers*, paper no. 932685, 1993.

Natusch D. F. S. and Tomkins B. A., 1978, Isolation of polycyclic organic compounds by solvent extraction with dimethyl sulfoxide., *Analytical Chemistry*, 50 (11), 1429-1434

Nelson P. F., 1989, Combustion generated polycyclic aromatic hydrocarbons in diesel exhaust emissions., *Fuel*, 68, 283-286

Newby P. T., Mansfield T. A. and Hamilton R. S., 1991, The sources and ecomonic implications of building soiling in urban areas., *The Science of the Total Environment*, 100, 347-361

Nielson T., 1979, Determination of polycyclic aromatic hydrocarbons in automobile exhaust by means of HPLC with fluorescence detection., *Journal of Chromatography*, 170, 147-156

Nikula K. J., Snipes N. B., Griffith W. C., *et al.*, 1993, Influence of soot associated organic compounds on pulmonary carcinogenicity of diesel exhaust in rats. Toxic and carcinogenic effects of solid particles in the respiratory tract., *4th International Inhalation Symposium*, Hanover

Novotny M. N., Hirose A. and Wiesler D., 1984, Separation and characterisation of large neutral polycyclic molecules in fossil fuels by microcolumn liquid chromatography and mass-spectrometry., *Analytical Chemistry*, 56, 1243-1248

Obuchi A., Aoyama H., Ohi A. and Ohuchi H., 1984, Determination of polycyclic aromatic hydrocarbons in diesel exhaust particulate matter and diesel fuel oil., *Journal of Chromatography*, 312, 247-259

Oehme M., 1985, Negative ion chemical ionisation mass spectrometry- A useful technique for the selective detection of polar substituted PAH with mutagenic properties., *Chemosphere*, 14 (9), 1285-1297

Olsen D. B. and Pickens J C., 1984, The effects of molecular structure on soot formation, I. Soot thresholds in premixed flames., *Combustion and Flame*, 57, 199-208

Ostman C. E. and Colmsjo A. L., 1989, Separation of polycyclic aromatic compounds from complex oil samples using bonded phase backflush HPLC and GC/MS techniques., *Fuel*, 68, 1248-1250

Ostman C., Bemgard A. and Colmsjo A., 1992, On-line liquid chromatography-gas chromatography for automated clean-up and analysis of polycyclic aromatic hydrocarbons., *Journal of High Resolution Chromatography*, 15, 437-443

Palmentier J. P. F., Britten A. J., Charbonneau G. M. and Karasek F. W., 1989, Determination of polycyclic aromatic hydrocarbons in lubricating oil basestocks using HPLC and GC-MS., *Journal of Chromatography*, 469, 241-251

Petch G. S., Trier C. J., Rhead M. M., Fussey D. E. and Milward G. E., 1987, The development of a novel exhaust gas sampling technique with particular relevance to polycyclic aromatic hydrocarbons., *Institute of Mechanical Engineers*, paper number C340/87

Petch G. S., Rhead M. M. and Fussey D. E., 1988, The use of radiolabelled polycyclic aromatic hydrocarbon fuel components to investigate diesel engine emissions., *Institute of Mechanical Engineers*, paper number C65/88

Peterson B. A., Chuang C. C., Hayes L. H. and Trayser D. A., 1983, Analysis of PAH in diesel exhaust particulate by gas chromatography/mass spectrometry., *Society of Automotive Engineers*, SAE paper number 820774

Pitts J. N., van Cauwenberghe K. A., Grosjean D. and Schmid J. P., 1978, Atmospheric reactions of polycyclic aromatic hydrocarbons: Facile formation of mutagenic nitro derivatives., *Science*, 202, 515-519

Pope C. A., Schwartz J. and Ransom M. R., 1992, Daily mortality and PM_{10} pollution in Utah Valley., *Archives of Environmental Health*, 47 (3), 211-217

Pourkashani M., 1991, Fundamentals of NO formation in turbulent flames., *Notes presented at A Short Course on Diesel Particulates*, Leeds University, Department of Fuel and Energy

Prado G. and Lahaye J., 1983, Mechanisms of PAH formation and destruction in flames. Relation to organic particulate emissions., Mobile Source Emissions Including Polycyclic Organic Species., D Rondia et al. (eds.) 259-275.

Pullen D. L. and Scammells D. V., 1988, A chromatographic procedure for the comprehensive separation and estimation of polycyclic aromatic hydrocarbons in petroleum products., *Fuel*, 67, 251-255

QUARG 1993 (January), First Report, Urban Air Quality in the United Kingdom, QUARG, London

QUARG, 1993 (December), Second Report, Diesel Vehicle Emissions and Urban Air Quality, QUARG, London

Rao K.K., Winterborne D. E. and Clough E., 1993, *Society of Automotive Engineers*, paper no. 930987

Reis M. and Silva Jeronimo M., 1988, Waste lubricating oil rerefining by extraction-flocculation. 1. A scientific basis to design efficient solvents., *Industrial and Engineering Chemical Resources*, 27, 1222-1228

Reis M. and Silva Jeronimo M., 1990, Waste lubricating oil rerefining by extraction-flocculation. 2. A method to design efficient composite solvents., *Industrial and Engineering Chemical Resources*, 29, 432-436

Rhead M. M., Fussey D. E., Trier C. J., Petch G. S. and Wood D., Investigation of the fate of specific hydrocarbon fuel components in diesel combustion., *The Science of the Total Environment*, 93, 207-214

Rhead M. M., Pemberton R., unpublished

Rivers K. J., Paassen C. W. C., Booth M. and Marriot J. M., 1993, Future diesel fuel quality- balancing requirements., *Proceedings of the Institute of Mechanical Engineers*, London, May

Rogge W. F., Hiderman L. M., Mazurek M. A., Cass G. R. and Simonelt B. R. T., 1993, Sources of fine organic aerosol. 2. No catalyst and catalyst-equipped automobiles and heavy-duty diesel trucks., *Environmental Science and Technology*, 27, 636-651

Rossi D. T., Desilets. D. J. and Pardue H. L., 1984, Quantitation and identification of PAH by liquid chromatography with multi-wavelength absorption spectroscopy., *Analytica Chemica Acta*, 161, 191-199

Rowland S. J., Alexander R. and Kagi R. I., 1984, Analysis of trimethylnaphthalenes in petroleum by capillary gas chromatography., *Journal of Chromatography*, 294, 407-412

Ruckmick S. C. and Hurtubise R. J., 1985, Class separation of polycyclic aromatic hydrocarbons nitrogen heterocycles and hydroxyl aromatics by liquid chromatography., *Journal of Chromatography*, 331, 55

Salem L., 1974, Molecular Orbital Theory of Conjugated Systems. W. A. Benjamin Publishers, London

Sander L. C. and Wise S. A., 1987, Effect of phase length on column selectivity for the separation of polycyclic aromatic hydrocarbons by reverse-phase liquid chromatography., *Analytical Chemistry*, 59, 2309-2313

Sander L. C. and Wise S. A., 1990, Evaluation of shape selectivity in liquid chromatography., *LC-GC international*, 3 (6), 24-34

Santoro R. J. and Glassman I., 1979, A review of oxidation of aromatic compounds., *Combustion Science and Technology*, 19, 161-164

Scheepers P. T. J and Bos R. P., 1992, Combustion of diesel fuel from a toxicological perspective. II. Toxicity, *International Archives of Occupational and Environmental Health*, 64, 163-177

Schuetzle D., 1983, Sampling of vehicle emissions for chemical analysis and biological testing., *Environmental Health Perspectives*, 47, 65-80

Shundoh S., Komori T. M., Tsujimura K. and Kobayashi S., 1992, NO_x reduction from diesel combustion using pilot injection with high pressure fuel injection, *Society of Automotive Engineers*, paper no. 920461

Singh R. P., Brindle I. D., Jones I. R. B., Miller J. M. and Chiba M., 1993, Determination of polycyclic aromatic hydrocarbons by HPLC particle-beam mass spectrometry., *Journal of the American Chemical Society for Mass Spectrometry*, 4 (11), 898-905

Smith C. M. and Savage P. E., 1991, Reactions of polycyclic alkylaromatics: Structure and Reactivity, *Archives of Industrial and Chemical Engineering Journal*, 37 (11)

Smith R. D., 1979, A direct mass spectrometric study of the mechanism of toluene pyrolysis at high temperatures., *Journal of Physical Chemistry*, 83, 1553

SMMT, 1993, Society of Motor Manufacturers and Traders, Statistical Department, Motor Industry of Great Britain, World Automotive Statistics, London, Table 39, p104,

Snyder L. R. and Schunk T. C., 1982, Retention mechanism and the role of the mobile phase in normal-phase separation on amino-bonded phase columns., *Analytical Chemistry*, 54, 1764-1772

Sonnefeld W. J., Zoller W. H., May W. E. and Wise S. A., On-line multidimensional liquid chromatographic determination of polynuclear aromatic hydrocarbons in complex samples., *Analytical Chemistry*, 54, 723-727

Stein S. E., Golden D. M. and Benson S. W., 1977, Predictive scheme for thermochemical properties of polycyclic aromatic hydrocarbons., *The Journal of Physical Chemistry*, 81 (4), 314-317

Stein S. E. and Fahr E., 1978, On the high temperature chemical equilibria of polycyclic aromatic hydrocarbons., *The Journal of Physical Chemistry*, 82 (5), 566-571

Stein S. E., High temperature stabilities of hydrocarbons., 1985, *The Journal of Physical Chemistry*, 89 (17), 3714-3725.

Stein S. E., 1991, Thermal reactions and properties of polycyclic aromatic hydrocarbons., *Accounts of Chemical Research*, 24, 350-356.

Stenburg U. R., 1985, Handbook of Polycyclic Aromatic Hydrocarbons. Volume II (Bjorseth. A. and Ramdahl. T. eds), Marcel Dekker, New York., Chapter 4

Stenburg U. R., Alsberg T. and Westerholm R., 1983, Applicability of a cryogradient technique for the enrichment of PAH from automobile exhausts: Demonstration of methodology and validation experiments., *Environmental Health Perspectives*, 47, 43-51

Stober W., 1992, Health aspects of combustion gasses and diesel exhaust., *Journal of Aerosol Science*, 5 (2), 81-102

Stradling R. J., Cowley L. T., Lange W. W. and Maillard C., 1993, The influence of fuel properties and test cycle procedures on the exhaust particulate emissions from light-duty diesel vehicles., *Institute of Mechanical Engineers International Seminar, Fuels for Automotive and Industrial Diesel Engines*, 6-7th April

Streitwieser A., Molecular Orbital Theory for Organic Chemists, Wiley, New York, 1961, p239

Swarz M., 1949, The C-C bond energy in ethylbenzene.,*The Journal of Chemical Physics*, 17 (5), 431-435

Tan Y. L., 1988, Analysis of polynuclear aromatic hydrocarbons in shale oil and diesel particulates., *Analytical Letters*, 21 (4), 553-562

Tancell P. J., Rhead M. M., Trier C. J., Bell M. A. and Fussey D. E., 1994, The sources of benzo[α]pyrene in diesel exhaust emissions., *Science of the Total Environment*, In The Press

Tancell P. J., 1991, The Origin of Polycyclic Aromatic Hydrocarbons in Diesel Exhaust Emissions., Bsc (Hons) Environmental Sciences Degree, Final year project.

Theobald N., 1985, Rapid preliminary separation of petroleum hydrocarbons by solid-phase extraction cartridges., *Analytica Chemica Acta*, 204, 135-144

Todd D., 1948, Volume IIII, Chapter 8. The Wolf-Kishner Reduction., Organic Reactions, R. Adams (Editor in Chief), Chapman and Hall, London

Tong H. Y., Sweetman J. A., Karasek F. W., Jellum E. and Thorsrud A. K., 1984a, Quantitative analysis of polycyclic aromatic compounds in diesel exhaust particulate extracts by combined chromatographic techniques., *Journal of Chromatography*, 312, 183-202

Tong H. Y. and Karasek F. W., 1984b, Quantitation of polycyclic aromatic hydrocarbons in diesel exhaust particulate matter by high performance liquid chromatography fractionation and high resolution GC., *Analytical Chemistry*, 56, 2129-2134

Tosaka S., Yasuhiro F. and Murayama T., 1989, The effect of fuel property on diesel engine exhaust particulate formation., *Society of Automotive Engineers*, paper no. 890421

Stenburg U. R., Alsberg T. and Westerholm R., 1983, Applicability of a cryogradient technique for the enrichment of PAH from automobile exhausts: Demonstration of methodology and validation experiments., *Environmental Health Perspectives*, 47, 43-51

Stober W., 1992, Health aspects of combustion gases and diesel exhaust., *Journal of Aerosol Science*, 5 (2), 81-102

Stradling R. J., Cowley L. T., Lange W. W. and Maillard C., 1993, The influence of fuel properties and test cycle procedures on the exhaust particulate emissions from light-duty diesel vehicles., *Institute of Mechanical Engineers International Seminar, Fuels for Automotive and Industrial Diesel Engines*, 6-7th April

Streitwieser A., Molecular Orbital Theory for Organic Chemists, Wiley, New York, 1961, p239

Swarzc M., 1949, The C-C bond energy in ethylbenzene.,*The Journal of Chemical Physics*, 17 (5), 431-435

Tan Y. L., 1988, Analysis of polynuclear aromatic hydrocarbons in shale oil and diesel particulates., *Analytical Letters*, 21 (4), 553-562

Tancell P. J., Rhead M. M., Trier C. J., Bell M. A. and Fussey D. E., 1994, The sources of benzo[α]pyrene in diesel exhaust emissions., *Science of the Total Environment*, In The Press

Tancell P. J., 1991, The Origin of Polycyclic Aromatic Hydrocarbons in Diesel Exhaust Emissions., Bsc (Hons) Environmental Sciences Degree, Final year project.

Theobald N., 1985, Rapid preliminary separation of petroleum hydrocarbons by solid-phase extraction cartridges., *Analytica Chemica Acta*, 204, 135-144

Todd D., 1948, Volume IIII, Chapter 8. The Wolf-Kishner Reduction., Organic Reactions, R. Adams (Editor in Chief), Chapman and Hall, London

Tong H. Y., Sweetman J. A., Karasek F. W., Jellum E. and Thorsrud A. K., 1984a, Quantitative analysis of polycyclic aromatic compounds in diesel exhaust particulate extracts by combined chromatographic techniques., *Journal of Chromatography*, 312, 183-202

Tong H. Y. and Karasek F. W., 1984b, Quantitation of polycyclic aromatic hydrocarbons in diesel exhaust particulate matter by high performance liquid chromatography fractionation and high resolution GC., *Analytical Chemistry*, 56, 2129-2134

Tosaka S., Yasuhiro F. and Murayama T., 1989, The effect of fuel property on diesel engine exhaust particulate formation., *Society of Automotive Engineers*, paper no. 890421

Trevelin W.R., Vidal L. H., Landgraf M. D. *et al.*, 1992, Optimization of parameters for the gas chromatographic determination of polycyclic aromatic hydrocarbons., *Analytica Chemica Acta*, 268, 67-71

Trier C. J., Fussey D. E., Petch G. S. and Rhead M. M., 1988, A comparison of diesel engine exhaust emissions collected by an environmental protection agency recommended dilution tunnel/filter with the sample collected from a new solvent scrubbing system., *Institute of Mechanical Engineers*, C64/88

Trier C. J., Rhead M. M. and Fussey D. E., 1990, Evidence for the pyrosynthesis of parent polycyclic aromatic compounds in the combustion chamber of a diesel engine., *Institute of Mechanical Engineers*, C394/003

Trier C. J., Fussey D. E., Ryder D. E. and Graham M. A., 1991, Development of radiotracer techniques for diesel fuel and exhaust emission research., *Institute of Mechanical Engineers*, C433/010

Tritthart P., Cichocki R. and Cartellieri W., 1993, Fuel effects on emissions in various test cycles in advanced passenger car diesel vehicles., *Society of Automotive engineers*, paper no.SAE 932684.

UNECE, 1970, ECE Regulation No. 15, Addendum 14, 30 January 1970

Van Gerpen J. H., Huang C.and Borman G. L., 1985, The effects of swirl and injection parameters on diesel combustion and heat transfer., *Society of Automotive Engineers*, paper no. 850265

Vassilaros D. L., Kong R. C., Later D. W. and Lee M. L., 1982, Linear retention index system for polycyclic aromatic compounds. Critical Evaluation and additional indices., *Journal of Chromatography*, 252, 1-20

Vogel A. I., Textbook of Practical Organic Chemistry, 4th Edition, (Furniss B. S., Hannaford A. J., Rogers V., Smith P. W. G. and Tatchell A. R. eds.) Longman Scientific and Technical, Chapter IV

Wade J. Holman C. and Fergusson M., 1993, Current and projected global warming potential of passenger cars in the UK., A report for the WWF.

Wang P., Yen. V. O., Tsai H. T. and Cheng J. C., 1988, Determination of polycyclic aromatic hydrocarbons in airborne particulate by high performance liquid chromatography., *Journal of Chinese Chemical Society*, 35, 13-21

Wels C. M., 1977, High sensitivity method of radio-gas chromatography for ^{3}H and ^{14}C labelled compounds., *Journal of Chromatography*, 142, 459-467

Westerholm R. N., Alsberg T. E., Frommelin A. B., *et al.*, 1988, Effect of fuel polycyclic aromatic hydrocarbon content on the emissions of polycyclic aromatic hydrocarbons and other mutagenic substances from a gasoline-fueled automobile., *Environmental Science and Technology*, 22, 925-930

Wiersum U. E., 1992, On the mechanisms that govern the thermal build-up of polycyclic aromatic hydrocarbons and soot., *Janssen Chemica Acta*, 10 (3), 3-13

Williams P. T., Bartle D. B. and Andrews G. E., 1986, The relation between polycyclic aromatic comounds in diesel fuels and exhaust particulates., *Fuel*, 65, 1150-1157

Williams P. T., Andrews G. E .and Bartle K. D., 1987, Diesel particulate emissions: The role of unburnt fuel in the organic fraction composition., *Society of Automotive Engineers*, SAE paper no. 870554.

Williams P. T., Abass M. K., Andrews G. E. and Bartle K. D., 1989, The influence of PAH contamination of lubricating oil on diesel particulate PAH emissions., *Society of Automotive Engineers*, paper no. 890825

Williams R. L., Perez J. M. and Griffing M. E., 1985, A review of sampling condition effects on polynuclear aromatic hydrocarbons (PNA) from heavy-duty diesel engines., *Society of Automotive Engineers*, SAE paper no. 852081

Wise S. A., Chester S. N., Hertz H. S., Hilpert L. R. and May W. E., 1977, Chemically bonded aminosilane stationary phase for the high performance liquid chromatographic separation of polynuclear aromatic compounds., *Analytical Chemistry*, 49 (14), 2306-2310

Wise S. A. and Sander L. C., 1985, Factors affecting the reverse phase liquid chromatographic separation of polycyclic aromatic hydrocarbon isomers., *Journal of High Resolution Chromatography and Chromatography Communications*, 8, 248-255

Wise S. A. and Sander L. C., 1993, Determination of polycyclic aromatic hydrocarbons by liquid chromatography., *Journal of Chromatography*, 642, 329-349

Wong V. W. and Hoult D. P., 1991, Experimental survey of lubricant-film characteristics and oil consumption in a small diesel engine., *Society of Automotive Engineers*, paper no. 910741

Yu M. L. and Hites R. A., 1981, Identification of organic compounds on diesel engine soot., *Analytical Chemistry*, 53, 951-954

Zelenka P., Herzog P. L., 1993, Exhaust gas aftertreatment systems for diesel engines with respect to future emission legislation., *Proceedings of the Institute of Mechanical Engineers*, London, May

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