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THE ORIGINS OF THE ORGANIC FRACTION IN DIESEL EXHAUST EMISSIONS

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A thesis entitled

THE ORIGINS OF THE ORGANIC
FRACTION IN DIESEL EXHAUST
EMISSIONS.

presented by

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THE ORIGINS OF THE ORGANIC FRACTION IN DIESEL EXHAUST EMISSIONS.

by

Colin James Trier

Diesel exhaust particulates are the subject of increasingly severe legislation controlling mass emissions throughout the world. Other emissions, which are currently unregulated, are also receiving closer scrutiny. In particular, polycyclic aromatic compounds (PAC), some of which are known carcinogens, are being studied.

A total exhaust solvent scrubbing apparatus (TESSA) has been constructed to sample diesel exhaust hydrocarbons, using a solvent mixture to strip organic compounds from exhaust gases. This avoided adsorption of hydrocarbons onto particulates, when fitted close to the exhaust port, and minimised the formation of sampling artifacts. TESSA yielded new information, enabling lighter more volatile organics such as 2- and 3-ringed PAC to be characterised, these could not be collected by a dilution tunnel filter, which trapped particulates effectively but did not sample the hydrocarbons which had remained in the gas-phase. TESSA has proved itself to be uniquely suitable for the sampling of gaseous hydrocarbons with which there is currently an increased interest.

Experiments using TESSA have confirmed that there is a contribution to the exhaust from small amounts of fuel passing through the combustion chamber substantially unchanged, as well as from partially burnt or pyrolysed products of combustion. New techniques have been developed to aid the interpretation of data obtained from high resolution gas chromatography and gas chromatography/mass spectrometry, in order to assess the origin of specific groups of compounds within the highly complex samples obtained from diesel exhaust. Naphthalene and phenanthrene were shown to increase their concentration relative to their alkylated derivatives in an exhaust sample when compared to the relative concentrations found in the fuel. These parent compounds were being formed within the combustion chamber, as well as surviving in unburnt fuel. Nitro-PAC were detected only at considerably lower concentrations than had previously been found on dilution tunnel filter samples.

Two new methods for assessing the contribution of lubricating oil to diesel exhaust emissions have been developed, and involved matching common peaks in a sample and a lubricating oil standard. The results demonstrated that lubricating oil makes a significant contribution to the total particulates. Increased control of lubricating oil leakage to the exhaust would help to reduce particulate emissions to below the new stringent limits.

CHAPTER 1

1.1 Introduction.

Public perception of diesel vehicles in the past has been critical in three principal areas: visible smoke, noise, and smell. These problems have largely been overcome by improvements in engine design, encouraged by relatively minor legislative controls. As a result, the small diesel-powered passenger car is now highly competitive, compared to the equivalent petrol models, in the European market. In Western Europe, diesel engines already power a sizeable part of the total vehicle fleet. As a percentage, this proportion ranges from virtually 100% for heavy goods vehicles to 15% for new passenger cars. The market situation is in stark contrast to that prevailing in the US where less than half of the heavy goods vehicles, and only 1% of new passenger cars, are diesel-powered, (Holman 1987).

European manufacturers are world-leaders in the technology of diesel engines, this means that if the US market developed rapidly in response to a heightened concern for fuel economy, it would be vulnerable to European domination. This market expansion has not occurred because of the very tight emissions legislation in the US, which controls the mass of particulates emitted by diesel vehicles; there is no comparable legislation in force in Europe at the present time. The strict controls on diesel particulate emissions in the US are justified by the regulatory body - the Environmental Protection Agency (EPA) - on the grounds that

they pose a serious environmental concern with respect to their impact on health. Legislation in the US therefore requires the best practical technology available to meet the hazard, and indeed occasionally leads technological innovations in the control of all vehicle emissions including diesel particulates, (Ball 1986).

This process of developing legislation which responds to each new technological innovation with new short-term targets, through regulation, has been severely criticised by Downes (1988). He points out that it has spawned a great deal of costly research and development to find solutions which clean up a problem after its created - essentially by a bolt-on palliative - instead of addressing the fundamental basics of the combustion system and making significant improvements there rather than further down the line.

1.1.1 Diesel Engines and Air Pollution.

Current concern over diesel exhaust emissions focuses on two areas: contribution to air pollution and the hazards to health. Within the context of air quality, gaseous pollutants emitted by motor vehicles, both petrol and diesel, are controlled by legislation. Initially the emissions of CO, HC, and NOx, have been regulated in the EEC by Directive 70/220/EEC. This Directive has been amended several times, most recently in December 1987 as Directives 88/76/EEC (for petrol) and 88/77/EEC (for diesel), which set new tighter gaseous emission limits. These new limits are not as stringent as those currently in force in the US, and accordingly they have attracted considerable debate

concerning their effectiveness in curbing atmospheric pollution in Europe, (Cutting 1987, & Walsh 1987). The gaseous pollutants from motor vehicles make a major contribution to the formation of ozone, a serious pollutant in the lower atmosphere across Europe, (Pearce and Elsworth 1986).

1.1.2 The Health Hazard from Diesel Particulates.

The second area of concern is a specific health hazard relating to the diesel engine and its production of very fine particulate carbon during combustion. These particles are small enough to penetrate deep into the human lung, and carry with them a great variety of organic compounds, products of incomplete combustion of the fuel, adsorbed onto the large surface area of the carbon. An extensive programme of research in the last decade has focused on the assessment of the health risk posed by diesel particulates. It can be divided into four major areas: chemical characterisation, in vitro studies of mutagenicity, whole animal studies, and epidemiological surveys, (McClellan 1986).

A group of compounds known as polycyclic aromatic hydrocarbons (PAH), associated with partial combustion and also present in diesel fuel, is found adsorbed onto diesel particulates; some PAH are known to be human carcinogens. Diesel particulates have been extracted with a suitable solvent to remove the soluble organic fraction (SOF), this extract has been fractionated, and then subjected to a specific test for mutagenicity developed by Ames et al. (1975). The diesel exhaust SOF was found to be mutagenic

and furthermore could be assigned to specific fractions, so that, it was possible to identify specific compounds and groups of compounds that contributed to the mutagenicity. The most prominent representation came from the nitro-arenes, specifically nitropyrene. The interpretation of mutagenicity tests is difficult and the results cannot be extrapolated directly and used to assess the human health risk, (Shore et al.1987).

To overcome the limitations of the Ames test, several extensive whole animal studies have been undertaken recently. One of these studies, funded by the Committee of Common Market Automobile Constructors (CCMC), exposed rats to different concentrations of diluted whole diesel exhaust, filtered diluted diesel exhaust (i.e. without particulates), and diluted petrol exhaust, in parallel experiments, (Brightwell et al.1986). The experiments were carried out continuously for a 2 year period, with an exposure 16 hours/day, 5 days/week. It should be noted, that the concentrations of gaseous and particulate components were at a level of one order of magnitude higher than the highest street values. Nevertheless, towards the end of the observation period, malignant lung tumours were observed in a proportion of the rats which had been exposed to the unfiltered diesel exhaust at the highest concentration, whereas no tumours were observed from exposure to the filtered diesel or petrol exhaust, (Waller 1986).

Epidemiological studies have been inconclusive in their results because it has not been possible to identify suitable groups of people in which occupational exposure to diesel

exhaust has not included additional exposure to other possibly equally significant factors such as cigarette smoking and diet, (Waller 1985, Wynder and Higgins 1986). In spite of these limitations it is now widely accepted that whole diesel exhaust is a probable human carcinogen, but that any risk is very small when compared to other occupational exposures of similar compounds such as from coke ovens or roofing tar, as well as the far more widespread and insidious social exposure to cigarette smoke, (McClellan 1986).

The legislation regulating diesel particulate emissions in Europe remains rudimentary when compared to current controls in the US. Whereas the US regulations limit particulate emissions on a mass basis, in Europe the control is restricted to a subjective smoke opacity test, devised in the UK in 1963 and adopted by the EEC as Directive 72/306/EEC. An EEC proposal for an objective mass-based limit on diesel particulate emissions was circulated in 1986, (COM(86) 261 final), but, as yet, has not been adopted. Even when these new limits are accepted they will still be far more lax than new limits due to be introduced in 1991 in the US. In the prevailing situation, European diesel manufacturers remain vulnerable to a very rapid tightening of Community regulations, in the event of further research evidence on the harmful health effects of diesel particulate emissions. This research, therefore was approached in the context of improving understanding of the fundamental processes involved in the formation of particulate carbon, and, obtaining more precise information on the origins of the organic compounds also found in the exhaust and which rapidly adsorb to the carbon as the exhaust temperature falls.

CHAPTER 2.

Diesel Combustion Research and Exhaust Emissions.

Research into hydrocarbon combustion has been carried out for a number of years, whilst at the same time, a great deal of effort has also been applied to the chemistry of PAH compounds. The current interest in diesel engine combustion, and the associated particulate and gaseous emissions, benefits from the earlier research. There remain specific intransigent problems related to the diesel engine, particularly within the context of the environmental impact of its exhaust emissions, and these still require a concerted research effort.

2.1 Diesel Engine Design and Performance.

The research work described below is restricted to light-duty indirect injection (IDI) passenger car diesel engines based on the Ricardo Comet V swirl chamber system. Other researchers at Leeds University are following broadly parallel work with a direct injection (DI) engine, (Abbass et al.1988). In the IDI system, combustion initially occurs within a small pre-chamber above the main cylinder chamber. Air drawn in at the beginning of the combustion cycle is compressed as the piston rises and about 50% of the air charge is forced through a throat to the swirl chamber creating an intense air motion and efficient air-fuel mixing, (Lily 1984). Fuel is injected at high pressure into the pre-chamber, just before the piston reaches the

top of its stroke, in the form of a fine spray of liquid droplets. After an ignition delay period the high temperature of the compressed gases ignites the sufficiently lean mixture. The IDI diesel engine requires a high compression ratio, ranging from 21:1 to 23.5:1, to compensate for the high heat transfer conditions between the combustion gases and the chamber walls.

There is insufficient air within the swirl chamber to complete the combustion and the high pressure developed by the early part of combustion projects the unburned fuel, together with the early combustion products into the main part of the chamber at very high velocities. This causes very rapid mixing with the air in the space over the piston and results in efficient combustion, (Haddad 1984). In a naturally aspirated diesel engine the volume of air drawn into the cylinder is a function of engine speed whilst the amount of fuel injected depends on both speed and load. Thus, the air/fuel ratio for a diesel engine can vary over a wide range and rarely is stoichiometric. Fuel supply is increased by keeping the injector open over a longer part of the cycle. The timing of the fuel injection is critical both for maximum engine efficiency and minimum hydrocarbon emissions.

2.1.1 Combustion Processes Within an IDI Diesel.

Ricardo (1929) first suggested that the combustion process in a diesel engine can be divided into three stages. The first stage is the ignition delay period, during which fuel

begins to be injected but ignition does not occur. Combustion can take place only in the vapour phase, below the rich flammability limit, when the fuel has sufficiently mixed with air. The physical processes of fuel vapourisation and mixing with air are aided by the high cylinder temperature and pressure along with the intense air swirl induced by the design of the chamber, (Amann and Siegla 1982). Chemical transformations of the fuel will also occur during this period. Thermal fragmentation of fuel molecules by pyrolysis assists vapourisation; oxygen may also be involved as a catalyst or as a reactant, (Dale 1984).

In a swirl chamber diesel the first ignition occurs in a fuel-air mixture that is near to or leaner than stoichiometric. The initiation of combustion marks the beginning of the second stage sometimes described as uncontrolled combustion. Once triggered the combustion proceeds throughout the region of premixed fuel and air very rapidly causing a sharp and characteristic rise in cylinder pressure. Fuel continues to be injected during the second stage and the flame cannot propagate through the entire spray because the core is beyond the rich flammability limit, (Amann and Siegla 1982).

In the third stage the burning of the prepared first stage mixture is completed. The pre-chamber now contains combustion products that have burned to completion, rich combustion products that have not yet fully oxidised, and fuel not yet reacted. During the third stage the

remainder of the fuel must be injected and at full load this may represent the majority of the fuel. Combustion during this period is dominated by conditions characteristic of a turbulent diffusion flame, and the rate of combustion is controlled by mixing and diffusion. The injection of liquid fuel droplets at this stage will spray directly into a flame in the absence of surplus oxygen. This causes local regions of very rich mixture to occur and soot tends to form, (Barnard and Bradley 1985).

2.1.2 Combustion Characteristics of Different Fuel

Components.

The different hydrocarbon groups comprising diesel fuel can be divided broadly into straight-chain saturated, branched-chain saturated and aromatic hydrocarbons. The combustibility of each of these three hydrocarbon types depends on their thermodynamic stability, governed by the energy difference between reactants and products, and their kinetic stability, which is determined by the activation energy of the reaction and depends on the shapes of the molecules and the flexibility of their chemical bonds, (Barnard and Bradley 1985).

The point of ignition in diesel engine combustion is preceded by a steady build up of reactive oxidising species. This build up is facilitated by the formation of an intermediate involving five carbon atoms linked in a straight chain, (Cox and Cole 1985). The presence of this structural feature in a fuel molecule such as a

straight-chain saturated hydrocarbon (as long as it comprises at least five carbon atoms) facilitates ignition. Thus straight-chain saturated hydrocarbon molecules are among the most stable thermodynamically but the least stable kinetically.

Aromatic hydrocarbons, on the otherhand, contain rigid hexagonal rings of carbon atoms. Although thermodynamically unstable, the rigidity of the rings which require a concerted and coordinated attack by oxidising species to cause ring-rupture result in aromatic hydrocarbons being kinetically very stable. Therefore the ignition of aromatic hydrocarbons is slow except at high temperatures. Nevertheless, once ignited, they burn with a high flame temperature and in oxygen-rich conditions have a greater tendency to soot formation than other hydrocarbon species. Aromatic hydrocarbons are also less susceptible to pyrolysis than straight-chain saturated hydrocarbons. The hydrogen/carbon ratio for aromatics is 1.0 or less compared to a ratio of slightly more than 2.0 for saturated hydrocarbons, (Hucknall 1985)

The combustion properties of branched-chain saturated hydrocarbons are less easy to predict, but they are generally slightly more stable thermodynamically and considerably more stable kinetically than straight-chain hydrocarbons due to the fact that chain branching reduces the number of molecular sites at which there are five carbon atoms in a straight chain, (Dale 1984). As yet no researcher has developed a model able to predict ignition

delay from fuel structure.

2.1.3 Formation of Soot and PAH.

Soot formation is a phenomenon that has been studied for many years and yet is still not fully understood. The circumstances of soot formation will vary between the different stages of combustion described in section 2.1.1. Furthermore, the formation is matched by a strongly competing oxidation process, so that, what is finally emitted in the exhaust is a result of these two processes. In diffusion flames it is local stoichiometry, fuel rich zones poorly mixed with air, that determine soot formation, since the overall average equivalence ratio in a passenger car diesel never exceeds unity.

Soot formation involves a complex series of chemical and physical processes that occur in a sequential order of nucleation, surface growth and coagulation, followed by agglomeration. Nucleation is the transition from a radical species, generated by pyrolysis or oxidative pyrolysis, to the first appearance of a soot particle, and is probably a gas-phase process, (Horn 1985). It is likely that PAH play a major role in this transition as precursors of soot, (Smith 1981).

The process of soot formation in a flame involves a continual decrease in the H/C ratio of the pyrolysing fuel. Commercial diesel fuel has a H/C ratio of just under 2.0, while the dry diesel soot can have a H/C ratio of 0.21-0.27

reflecting the loss of 85-90% of the hydrogen, (Amann and Siegla 1982).

The majority of combustion-formed PAH are probably by-products formed concurrently with soot, and which subsequently become adsorbed on the surface of these carbon particles. Other PAH with special structural characteristics (such as reactive side chains) may be soot-precursors and act as intermediate species in soot formation, (Cullis 1986). One starting point could be with acetylene which is a common molecule always found in the pyrolysis of hydrocarbons. Work by Badger et al. (1960) had already shown that the high temperature (700°C) pyrolysis of acetylene yielded a number of PAH including benz(a)pyrene - B(a)P - in addition to benzene and its alkyl derivatives. In this case, the progressive addition of acetylene to itself could form polyacetylenes, which in turn, as they grew in length, would be increasingly likely to be attacked in the middle of the chain rather than at the end positions, resulting in branched-chain polyacetylenes. These would be expected to cyclise more readily than linear polyacetylenes, in which case, PAH with side chains would be formed. The one criticism of this proposed route of formation is that it would be relatively slow, (Cullis 1986).

A different explanation developed by Calcote (1983) proposes that ionic mechanisms may be important in the nucleation step of soot formation. Ion molecule reactions are much faster than the free radical reactions proposed in

the polyacetylene pathway. The theory suggests that primary flame ions produced by chemi-ionisation, react by rapid ion molecule reactions with neutral flame species such as acetylene, polyacetylenes, and free radicals to produce larger ions which rapidly rearrange to produce even larger polycyclic aromatic ions. These can go on to form neutral incipient soot particles. Mass spectral studies have shown that gaseous ions rearrange very much more rapidly and easily to form PAH structures than do free radicals, (Calcote 1983).

The presence of aromatic hydrocarbons in a diesel fuel promotes the formation of PAH; alkylated aromatics in particular are easily transformed into polyaromatics by addition of small alkenes e.g. dienes. Badger and Spotwood (1960) demonstrated that the high temperature (700°C) pyrolysis of methyl benzene, and other alkyl derivatives of benzene, yielded higher relative molecular mass PAH. Thus, PAH may be formed by cyclisation mechanisms from the many intermediate species formed from the pyrolysis of the incoming fuel, the mechanism probably involving ions. Alternatively, they can develop from ring building processes involving the pyrolysis of aromatic components of the fuel, (Prado and Lahaye 1983, Longwell 1982, Howard and Longwell 1983).

2.1.4 The Contribution that Polycyclic Aromatic Compounds (PAC) in the Fuel Makes to Diesel Exhaust Emissions.

Diesel fuel can contain a significant aromatic hydrocarbon

fraction which will lower the cetane value of the fuel. The aromatic content cannot, at present, exceed 30% because this would lower the cetane number below the minimum level of 50, for an A1 fuel, specified in BS2689, (Tims 1983).

Aromatic hydrocarbons in the fuel include PAC's at varying concentrations; usually the PAC's make up just over 1% of a typical diesel fuel, (Mills 1983). These PAC are predominantly represented by the PAH's naphthalene, fluorene, phenanthrene, and their alkylated derivatives, along with the heterocyclic compounds of nitrogen and sulphur, carbazole and dibenzothiophene, at lower concentrations, (Williams et al.1986).

Considerable research has been devoted in the past to investigating the influence of aromaticity in a diesel fuel on exhaust particulate emissions. Mills (1983) tested PAH emission levels that resulted from the combustion of six specially blended fuels, each with an increasing aromatic content. He reported that the total PAH emissions increased with increasing fuel aromaticity. He relates this result to a decrease in combustion efficiency due to the lowering of the cetane number. His results were confirmed by Barbella et al. (1987) who used four fuels with different aromatic content, they found that aromaticity was a dominant factor for soot emissions, they did not measure any PAC concentrations.

Total aromatic content, in itself, can only be poorly

correlated with exhaust emissions of PAC, and is insufficient to be used as a general predictor. The type of aromatics present is critical; Candeli et al. (1983) found that aromatic compounds containing nine or more carbon atoms increased PAC exhaust emissions much more than did benzene and its methyl derivatives. Other workers, (Andrews et al. 1983, Williams et al. 1986, Williams et al. 1987a), set out to determine the relationship more specifically by individually identifying and quantifying the PAC within the fuel and the corresponding PAC in the extracted exhaust. They concluded that the bulk of the PAC within the exhaust originated from unburnt fuel. Between 0.01 and 1.8 % of PAC in the fuel survived the combustion process unchanged and the survival was found to be dependent on engine design and the test conditions of load and speed. They also postulated that a small part of the PAC in the exhaust, notably the higher relative molecular mass 5-ringed PAH, were combustion-formed in the cylinder, probably by the pyrolysis of lower relative molecular mass PAH from the fuel.

Early work by Badger et al. (1958) had indicated that PAH could be formed from the cyclisation or cracking and subsequent cyclisation of C10 and other longer chain aliphatic hydrocarbons. Yergey et al. (1982) used a two component aliphatic hydrocarbon fuel which did not contain PAC for an engine test. The major group of compounds identified in the extracted exhaust particulates were PAH. The results indicated that the PAH found on the particulates were inherent products of the diffusion

controlled combustion processes and that, therefore, PAC found in the exhaust were not exclusively derived from the fuel. This result was confirmed by Henderson et al. (1984); using hexadecane as a fuel they noted the formation of certain PAH including phenanthrene and fluorene. Petch (1988) used a predominantly aliphatic fuel (ca.99%) and identified naphthalene and its methyl-derivatives in the extracted exhaust; this offered further evidence that aliphatic compounds in the fuel can produce aromatic compounds during the combustion reactions within the cylinder.

Several experiments have been undertaken involving the addition of a specific PAH to the diesel fuel. Henderson et al. (1984) made up separate fuel mixtures with 1% additions of pyrene, phenanthrene, and benz(a)pyrene. For each mixture they detected an increase in the concentration of the specific PAH in the corresponding extracted exhaust. The effect was not linear; a 100-fold increase in pyrene concentration in the fuel resulted in only a 10-fold increase in the pyrene associated with particulates in the exhaust. However similar 1% additions of methyl naphthalenes or acenaphthene did not result in enhanced levels of these compounds in the exhaust, and, therefore, must have been fully burnt in the combustion process. These researchers further noted that specific PAH, 1-methyl naphthalene, acenaphthene, and benz(a)pyrene promoted soot formation whilst other PAH, including pyrene and phenanthrene, appeared not to do so.

Petch et al.(1988) used radiolabelled molecules of PAH added to diesel fuel to determine unequivocally the origin of the PAH found in the extracted exhaust samples. The results, using anthracene, 9-methyl anthracene, and benz(a)pyrene in separate experiments, confirmed that some of the PAH present in diesel fuel does survive the combustion process unchanged. The percent survival for the three different PAH were as follows:

Anthracene	0.006%
9-methyl anthracene	0.024%
Benz(a)pyrene	0.015%

One result of these experiments was to show that a substantial amount of the radiolabelled PAH, spiked in the fuel, was transformed by the combustion process to form partially burnt or pyrolysed products, thus, both PAC from unburnt fuel and combustion-formed PAC contribute to the PAC in the diesel exhaust.

2.2 Sampling Techniques for Diesel Exhaust.

The PAC in the exhaust products which are forced out of a diesel engine at the end of each combustion stroke may undergo subsequent chemical modification because of heterogeneous chemical reactions on particle surfaces. Organic vapour emissions of PAC adsorb and condense onto highly active surfaces of particulate carbon in the cooler parts of the exhaust system, below 200°C, (Cuthbertson et al.1979). Sampling systems currently in use are designed

primarily to quench exhaust reactions and trap out the particulates, any remaining vapour phase organics are separately trapped if there is interest in them.

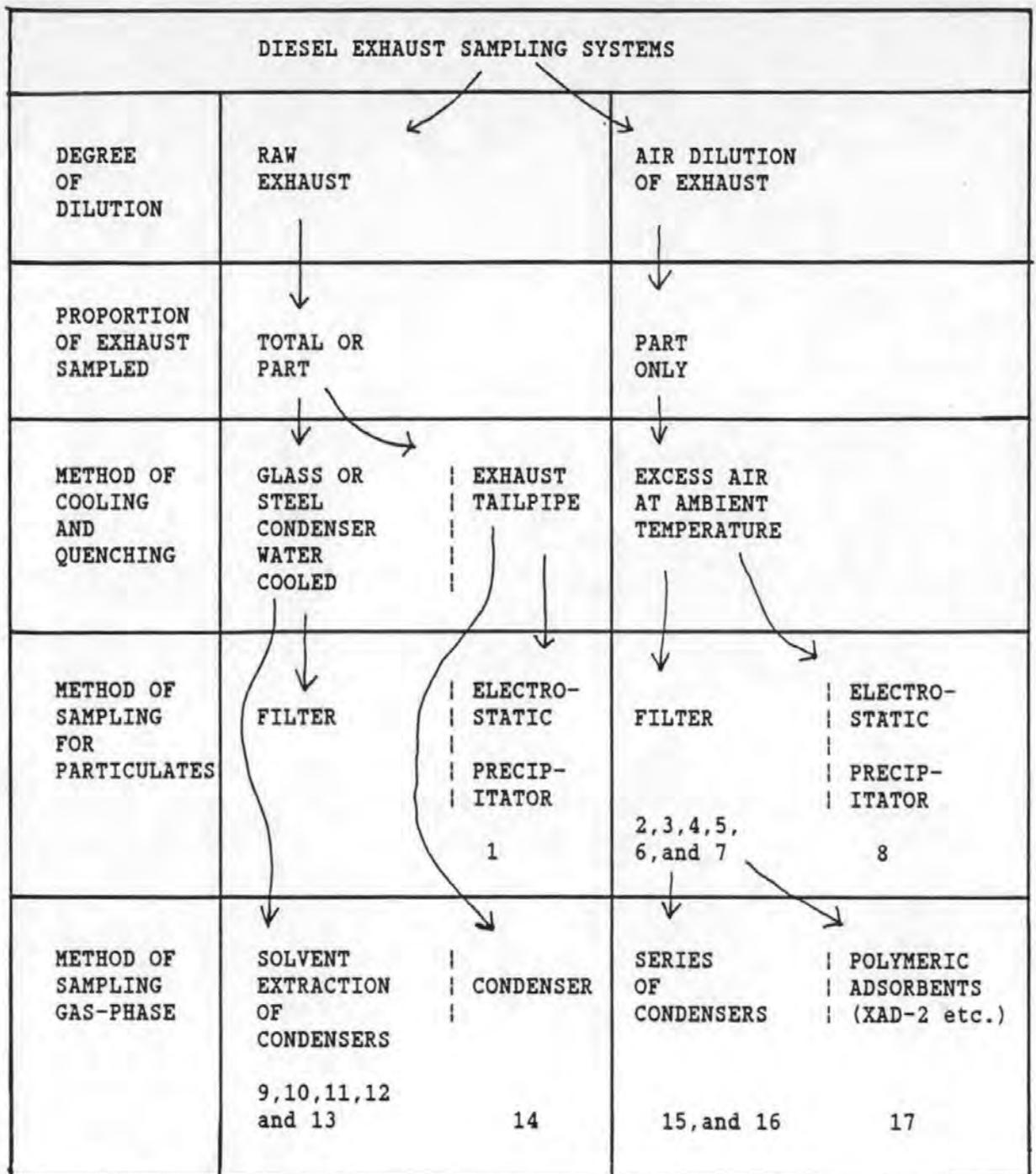
2.2.1 Review of Existing Sampling Systems.

Two principal methods have been developed to sample vehicle exhaust. The first involves the dilution of exhaust gases by air, prior to sampling a part of the exhaust, usually by filter. The second method involves cooling the raw exhaust in a condenser prior to filter sampling. Both systems involve the rapid cooling of the exhaust, and the subsequent trapping of particulate material on a filter. Several detailed reviews have been made of these methods (Schuetzle 1983, Stenberg et al.1983, Bradow 1982, Mills 1983, Lee and Schuetzle 1983). The most widely used methods are summarised in Table 2.1.

2.2.2 The Dilution Tunnel.

The air dilution tunnel has become the most widely used diesel exhaust sampling system. In the US, the EPA has laid down specifications for the sampling of diesel exhaust particulate emissions. The dilution tunnel system has been designed to meet these regulations and is intended to simulate the processes which diesel exhaust undergoes during the first few minutes after being expelled from the exhaust tailpipe into the atmosphere (Schuetzle 1983).

In operation, exhaust gases pass down a short length of



Key to References:

- | | |
|-----------------------------|-------------------------|
| 1/ Chan et al.1981 | 2/ Macdonald et al.1984 |
| 3/ Alkidas et al.1984 | 4/ Tritthart 1984 |
| 5/ Williams et al.1985 | 6/ Yamaki et al.1986 |
| 7/ Lies et al.1986 | 8/ Gaddo et al.1984 |
| 9/ Begeman and Colucci 1962 | 10/ Grimmer et al.1973 |
| 11/ Kraft and Lies 1981 | 12/ Andrews et al.1983 |
| 13/ Yamaki et al.1986 | 14/ Grimmer et al.1979 |
| 15/ Pedersen et al.1980 | 16/ Stenberg et al.1983 |
| 17/ Lee et al.1979a | |

Table 2.1 Summary of Most Widely Used Techniques for Sampling Diesel Exhaust .

exhaust pipe before being mixed with a known and reproducible quantity of ambient filtered air, (typically in a ratio of 10:1 v/v), in a large volume stainless steel tube. The diluent air may be both temperature- and humidity- controlled. The rapid cooling by the air dilution has two effects. First, it causes the condensation of PAC and its adsorption onto the surface of carbon particulates present in the exhaust. Second, the large dilution and lowering of temperature act to quench further chemical reactions between organic species present within the exhaust, in particular, the rapid termination of radical reactions, (Schuetzle 1983). These chemical reactions are very rapid in the initial stages of the exhaust manifold and tailpipe, after the engine, where reactants are concentrated and at high temperature, (Williams et al.1985).

For particulate measurements, a portion of the diluted exhaust is isokinetically drawn off by a probe and passed through a filter. The EPA regulations require that the temperature within the dilution tunnel at the point of sampling does not exceed 52°C. Indeed, the EPA make a rather specific definition of diesel particulate as all that material which is trapped by a filter operated at or below this threshold temperature of 52°C in the manner described above. High relative molecular mass organic compounds present in the exhaust, such as those originating from the lubricating oil, will condense at this temperature and be trapped by the filter regardless of whether they were first adsorbed to particulate material; they will

therefore be included in the EPA definition of diesel particulates.

A significant proportion of 3 and 4-ringed PAH, along with other low relative molecular mass organic species, will remain in the gas phase and pass through the filter without being trapped. In circumstances that require the total hydrocarbons to be sampled it has been necessary for further devices to be placed downstream of the filter to collect the gas-phase PAC. Stenberg et al.(1983) used a cryogradient technique with three condensers in series arranged so that the temperature was lowered in successive condensers. The first condenser was cooled by ice/water, the second by dry ice/ethanol, and the third by liquid nitrogen. Others, notably Lee et al.(1979a), used polymeric adsorbents such as XAD-2 to trap gas phase hydrocarbons. It is difficult to avoid contamination using these polymeric adsorbents and furthermore they are thermally unstable.

A significant problem with diesel exhaust sampling has been to define at what point in the exhaust system continuing chemical reactions within the exhaust gases are considered to be artifacts of the sampling regime. Post combustion reactions are especially significant at elevated temperatures. As far as the dilution tunnel method is concerned, the intention has been that these reactions are fully quenched by the dilution process. Diesel particulates trapped on a filter medium are vulnerable to the formation of sampling artifacts.

2.2.3 The Problem of Sampling Artifacts

It is possible for PAH to be nitrated in the presence of minute traces of nitric acid acting as a catalyst. Nitric acid is a trace constituent associated with the presence of nitrogen dioxide, (Pitts et al.1978). For this reason there remains uncertainty whether minute traces of nitrated PAH detected in diesel exhaust particulate extracts, which show a strong direct acting mutagenicity in the Ames test, are in part or wholly artifacts of the filter sampling technique.

Stenberg et al.(1983) added nitrogen dioxide to dilute exhaust before filtering, and found that they could increase the direct acting mutagenic nitro-PAH in this way. Ross et al. (1987) report results which show that it is in fact $\text{NO}_2/\text{N}_2\text{O}_4$ and not HNO_3 which causes the nitration of pyrene. Nevertheless, Harris et al.(1987) used a tunable diode laser absorption spectrometer to make real-time measurements of NO_2 and HNO_3 in diesel engine exhaust. They found that levels of HNO_3 in diluted diesel exhaust were sufficiently high to promote some nitration of PAH, on filter materials, during sampling. Any sampling system which traps PAH, but then allows continued exposure of them to the exhaust stream, for the duration of a prolonged sampling time, is likely to cause chemical transformation of some PAH compounds.

A theoretical kinetic study by Risby and Lestz (1983) used

bimolecular collision theory to assess the rate of formation of nitropyrene in the combustion chamber, exhaust system, or on the filter. They found that the probability of nitropyrene forming on the filter was much higher than at other points in the system. Further work on rates of reaction, by Schuetzle (1983), estimated that chemical conversion during dilution tunnel sampling accounted for 10-20% of the 1-nitropyrene found on diesel particulate extracts.

More recent work has emphasised that thermal decomposition and chemical reactions of PAH occur very rapidly in raw exhaust at elevated temperature above 200°C, (Williams et al.1985). Chemical transformation of PAH species in diesel exhaust is a function of temperature, reactant concentration and contact time. Consequently the half-lives of many PAH at the hot end of the exhaust, as they exit the engine, will be of the order of fractions of a second. The residence time in any pre-sampling transfer line must be kept to a minimum to limit these reactions. The nitration of PAC during or after sampling is the most likely artifact-forming reaction.

2.2.4 Sampling Raw Exhaust with a Condenser.

Sampling of raw exhaust has mostly been achieved utilising a system consisting of a preliminary cooling stage with a condenser which condenses out combustion-generated water and gas-phase organics on a large internal cooling surface, followed by filtration to trap out particulates. Begeman

and Colucci (1962) used a steel condenser tower with approximate dimensions of 15 cms width by 180 cms in length. A similar method of condensation/filtration has extensively been used by Grimmer et al. (1973), based on a vertical glass condenser with a cooling area of 0.25 m², sufficient to sample the total exhaust from small engines. The exit temperature was below 70°C and the particulates were trapped on a paraffin impregnated filter.

Grimmer's design was improved by Kraft and Lies (1981) who enlarged the heat exchange capacity of the condenser to 3.0 m² to maximise its heat exchange capacity. They made comparisons between PAC emissions from petrol and diesel engines using this sampling technique. All the various systems yielded three fractions for analysis: a condensed aqueous phase collected below the condenser, an acetone wash with which the condenser system was rinsed after sampling, and the particulates collected on the filter.

The methodology has been extensively used, especially in Europe. It has the same shortcomings as the dilution tunnel in so far as the collected material remains continuously exposed to the exhaust gas stream throughout the period of sampling with the consequent possibility of artifact-forming reactions.

2.2.5 Other Sampling Techniques.

Chan et al. (1981) successfully used an electrostatic precipitator to trap out particulates from the end of a

short exhaust pipe. The main drawback appears to be the formation of highly reactive ozone as a result of the corona discharge, both of which might be expected to encourage chemical transformation of the organic species adsorbed to the particulate.

An interesting technique reported by Laity et al. (1973), in which real-time measurements of PAC in exhaust were made continuously using fluorescence detection, appears not to have been taken further. Presumably, any PAC which were adsorbed to particulates would not have been detected.

In-cylinder sampling techniques have been reported in the literature, (Hayano et al. 1985, Yates 1986). A considerable difference between in-cylinder PAC levels compared to those in the exhaust was noted.

Work currently being done by Fiat, as a member of the CCMC, is assessing a technique incorporating a glass tower through which diluted exhaust is passed. The tower is flushed with a buffered alkaline aqueous solution which removes particulates (Johnson 1986). The particulates are collected at the end of sampling by centrifuge. As yet no results from this programme have been published.

2.3 The Role of Lubricating Oil in Diesel Exhaust Particulates.

Lubricating oil with its high relative molecular mass is trapped on dilution tunnel filters, even when it is not

adsorbed on carbon particulates. Accurate assessment of the lubricating oil contribution to diesel exhaust emissions is useful not only in the control of particulates for legislation, but also as a more fundamental indicator of how well a particular engine design functions.

2.3.1 Diesel lubricating oil.

The crankcase lubricating oils used in diesel engines are made up from highly refined base oils. The refining process applied to a crude oil in the preparation of these base oils includes atmospheric followed by vacuum distillation, solvent extraction to remove the aromatic compounds, catalytic hydrogenation to saturate the olefins, and solvent or catalytic dewaxing to remove the high relative molecular mass paraffins, (IARC 1981). The resulting base oils are further performance-enhanced by additives which include viscosity index improvers, pour-point depressants, antioxidants and detergent dispersants, (Haddad 1984). Typically these additives may make up 12 - 20% of a modern automobile lubricating oil (Clark et al.1984).

The function of the engine oil is to separate and cool all moving parts of the engine in order that they operate with the minimum of frictional resistance (Wood 1969). The oil also acts as a scavenger for combustion products within the cylinder. The thin coating of lubricating oil on the cylinder wall prevents engine deposits building up around the pistons. The soot particles associated with diesel

engines have a tendency to form varnishes if they are not prevented from doing so; these and other particles along with dissolved material are scraped back into the engine sump in the oil avoiding harm to the engine. The lubricating oil while being subjected to high temperature is at the same time exposed to oxidation by sulphuric acid formed in the cylinder, from sulphur in the fuel, which must be neutralised. Soot resulting from the incomplete combustion of fuel must be kept dispersed to avoid engine wear, and pyrolysis products from both fuel and oil, which tend to form varnishes on engine surfaces must also be removed from the cylinder. The engine sump oil therefore becomes the sink for a wide range of materials passing through or forming within the engine, (Lily 1984). These inputs into the engine sump are summarised in Table 2.2

-
- a) Unburnt fuel
 - b) Pyrolysed fuel and lubricating oil
 - c) PAC, from unburnt fuel and formed in-cylinder
 - d) Soot
 - e) Partially oxidised products of combustion :
e.g. organic acids such as acetic and benzoic acid
 - f) Metal fragments
-

Table 2.2 Products from the engine combustion chamber that end-up in the oil sump.

2.3.2 Build Up of PAC in Engine Oil.

For petrol engines it is well established that there is a considerable build up of PAC in the engine oil which increases linearly with the length of use of the lubricating oil, (Lee et al.1975, Cotton et al.1977, Peake and Parker 1979, Handa et al.1979, Grimmer et al.1981,

Colmsjo et al.1984). However diesel engines are much less susceptible to the accumulation of PAC in the lubricating oil. A paper by Handa and co-workers (1979) reports the accumulation of PAC in the lubricating oil, from a petrol engine, with increased mileage. By extrapolation from measurements of PAC levels in the fuel and in the exhaust gas they conclude that the origins of the PAC in the engine oil at low speed almost entirely originates from the fuel, whilst at high speed a significant additional contribution is made by the pyrolysis of lubricating oil as a result of the higher temperature around the pistons. They conducted an experiment which showed that leaked oil could reach a pyrolysis temperature of 500 - 800°C which would be sufficient to form PAH.

Grimmer et al.(1981) confirm the build up of PAC in used lubricating oil from petrol engines, these can be 100 to 1000 times higher concentrations than in the fresh oil, and also show that the major source is from PAC in the fuel. However extensive work by Grimmer summarised in the IARC monograph on mineral oils (IARC 1981) shows that PAC do not accumulate in diesel engine oil in the way that they do in a petrol engine. Petrol engine accumulate on average 10 times the levels of PAC than do small diesel engines, so that the typical levels of B(a)P in the lubricating oil from a petrol engine after 1000 km use was 5-10 mg/litre, whereas it was found to be 0.1-1.0 mg/litre for a range of small passenger car diesels. Furthermore oil samples taken from larger truck and bus diesel engines showed little significant increase in PAC at all when compared to

the fresh lubricating oil (Grimmer et al.1981).

The higher temperature and pressure experienced in the cylinder of the diesel engine explains why PAC are less likely to accumulate in the engine oil; they are either combusted or remain in the vapour phase and are vented to the exhaust.

2.3.3 Oil Consumption.

Average oil consumption in a diesel engine is variously reported as being 0.4%, 0.35%, and 0.25% of the fuel burnt (Mayer et al.1980, Williams et al.1987b, Cuthbertson et al.1987). Ricardo report 75 - 85% of lubricating oil consumed will be fully combusted during the combustion stroke within the cylinder (Cuthbertson et al.1987), AVL quote slightly higher burn-up rates of 86 - 94% of oil consumed being fully oxidised (Cartellieri and Tritthart 1984). There will also invariably be a small amount of lubricating oil which is pyrolysed or partially burnt in the cylinder (Wood 1969, Handa et al.1979, Mayer et al.1980), particularly at high speed.

The hydrocarbon content of diesel exhaust particulates contain a significant contribution from unchanged lubricating oil which is broadly identical to the engine oil in the sump (Mayer et al.1980, Cartellieri and Tritthart 1984, Trier et al.1987). It seems likely that this unchanged lubricating oil, found in the exhaust particulates, has not been subjected to the excessive

conditions of combustion within the cylinder, but rather represents a minor leakage of oil, through routes to the exhaust which do not involve a significant exposure to combustion processes. The two sources of oil leakage are the valve stem seals and the piston rings (Furuhama 1979). Of the two, the latter source is normally the more significant, and it follows that engine design can play a major role in lubricating oil consumption and contribution to total particulates.

Measurement of oil consumption for a diesel engine can be made using several different techniques. The main problem is in ensuring that, whatever parameter of the lubricating oil is used for the measurement, it is truly representative of the oil as a whole.

Radio-labelled compounds have been effectively used by several researchers to measure engine oil consumption very accurately. Radio-labelled tritium has been successfully used in this manner as a tracer element by Cartellieri and others (Warrick and Dykehouse 1970, Cartellieri and Tritthart 1984). Mayer et al. (1980) used radio-labelled bromine in 1,2-dibromo-82-octadecane. In the latter technique a measured portion of the exhaust gas was drawn through a solution of 1 molar sodium hydroxide, thereby efficiently removing the radioactive bromine for measurement. Other non-radio techniques have involved measuring levels in the exhaust gas of either calcium (Hilden and Mayer 1984), cobalt (Furuhama 1979), or chlorine (Ise et al. 1985), and comparing these levels to

the presence of the particular element in the lubricating oil.

2.3.4 Lubricating Oil Contribution to Exhaust Particulates.

Radio-labelled compounds also provide the best technique for accurately assessing the engine oil contribution to the total particulates in diesel exhaust. Mayer et al. (1980) used a radio-labelled carbon -14 isotope located in the main carbon skeleton of n-octacosane to this end. The results of this experiment showed that the high relative molecular mass material found to be associated with the particulates, was almost completely extractable in the SOF fraction. Furthermore it showed such a high degree of similarity with the original lubricating oil that they concluded that the bulk of lubricating oil contributing to the exhaust particulates is passing through the engine unchanged by pyrolysis or partial combustion. The unchanged lubricating oil therefore must contribute to the particulate matter after most of the chemical reactions forming the non-extractable portion of the particulate matter has been completed.

In other words, the formation of soot occurs, under specific conditions, through pyrolysis or partial combustion within the cylinder at high temperature; both fuel and/or lubricating oil may contribute. Lubricating oil reaching the exhaust, for the main part, represents a leakage of oil outside of the period of combustion within the cylinder, and it adsorbs to the soot particles after

entering the exhaust or even after the carbon particulates have been trapped on a filter during sampling.

These radio-labelled tracer experiments provide fundamental information, but require sophisticated equipment and stringent control. They do not therefore offer a routine methodology, and several techniques have been published which are more available if less unequivocal. Cuthbertson et al. (1979) used thermogravimetric analysis coupled with heated flame ionisation detection, TGA/HFID, to give a crude separation of hydrocarbons in an diesel exhaust particulate sample, a typical result is shown in Fig 2.1. They tentatively identified part of the hydrocarbon thermal desorption curve, between 300 and 500°C, as material originating from the lubricating oil. Black and High (1979) used packed column GC to determine the relative molecular mass distribution of gaseous and particulate bound hydrocarbons from diesel engine exhaust. This distribution could be compared to the relative molecular mass distribution from the fuel and lubricating oil

More recently, Cartellieri and Tritthart (1984) developed an elegant method, based on packed column gas chromatography, which separated the SOF fraction into fuel and lubricating oil components. The method involves generating the simulated distillation curve (SIMDIS) for a series of calibration blends of fuel and oil at different comparative concentrations. The SIMDIS curve is based on the boiling point range of a sample. The 50% boiling point on the SIMDIS curve for each calibration blend is

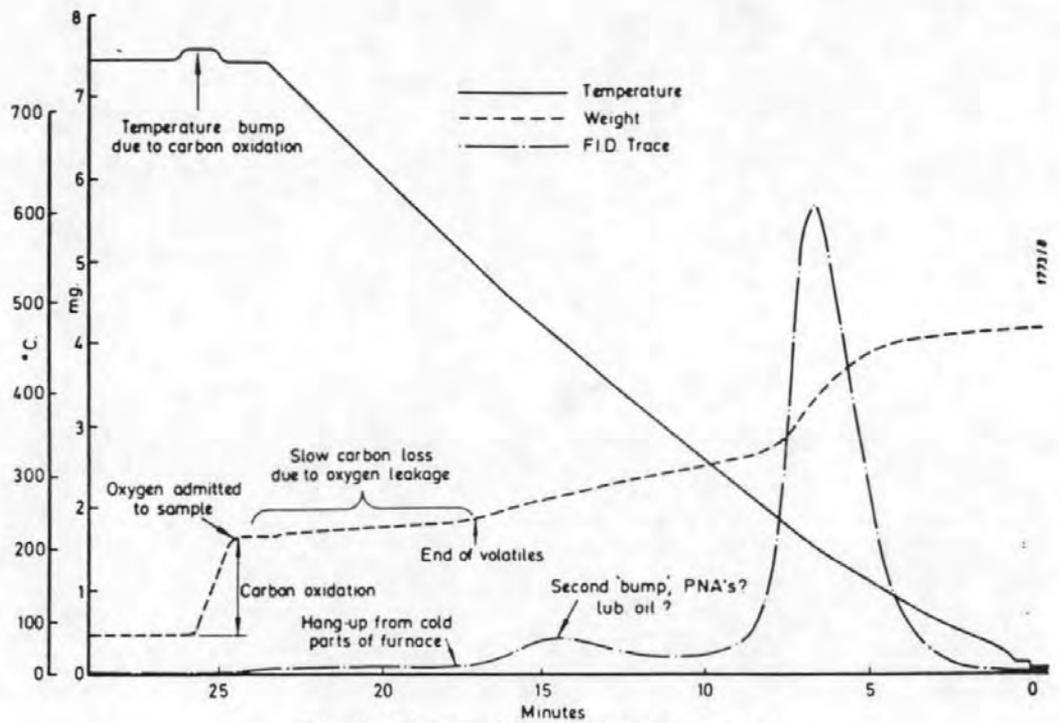


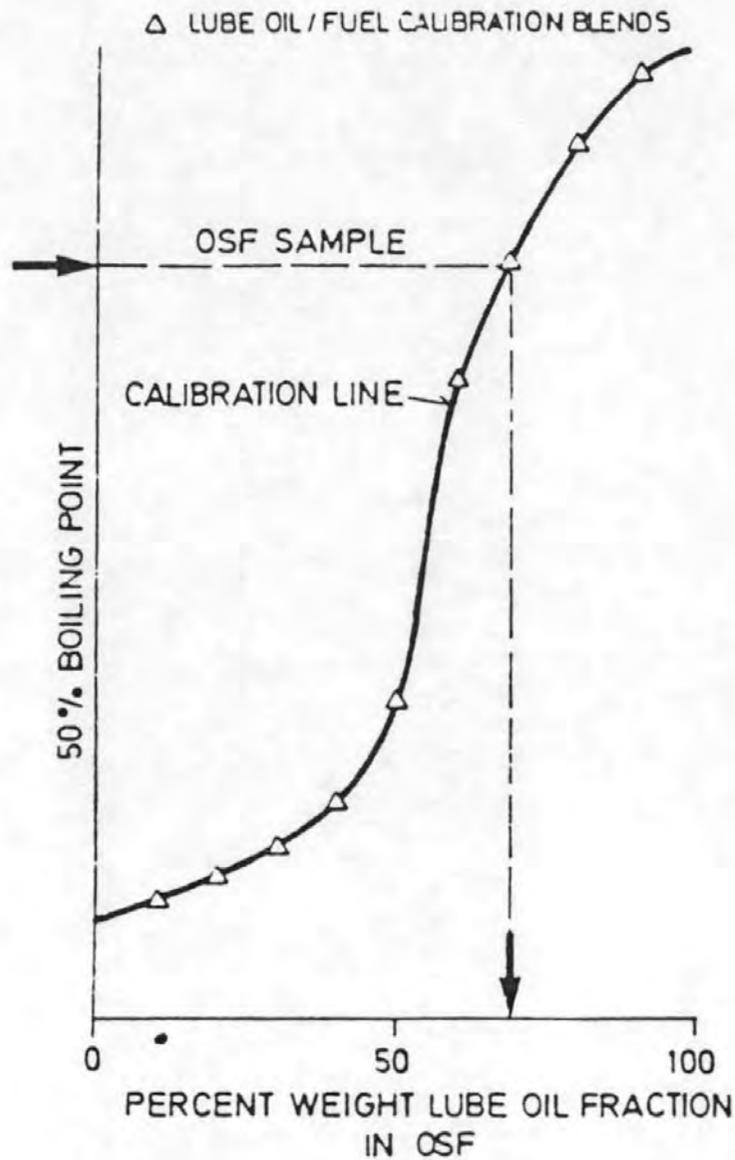
Fig. 6 - TGA interfaced with an HFID - weight loss and HC curves for a soot sample

Fig 2.1 Results from a TGA Coupled with an HFID Showing Weight Loss and HC Curves, (from Cuthbertson et al.1979. Reprinted with permission 1979 Society of Automotive Engineers, Inc.)

plotted against the lubricating oil percentage in the corresponding calibration blend. The resulting calibration line enables the lubricating oil contribution of a diesel particulate SOF fraction to be calculated once the 50% boiling point for the SOF is determined by SIMDIS the method is illustrated in Fig 2.2. The method requires a separate calibration line to be plotted for each different fuel and engine oil used in engine tests. It is also based on the assumption that the lubricating oil type material in the SOF (by boiling point) is substantially unchanged from the original lubricating oil in the sump, and assumption supported by the radio-labelled experiments by Mayer et al. (1980) discussed above.

A later paper by Cuthbertson et al. (1987) describes a similar use of packed column GC with a novel solid sample injection which enables portions of dilution tunnel filters to be thermally desorbed onto the column without prior extraction. A simpler interpretation of the results of analyses from diesel particulate filters assigned all material eluting from the column after a certain retention time as originating from the lubricating oil, demonstrated in Fig 2.3.

It is apparent from Fig 2.3, that packed column GC gives very poor resolution of fuel or lubricating oil, both of which contain many thousands of discrete compounds. This imposes a severe limitation on the information available from the methods described above. Furthermore the methods describe the total FID response only in terms of either



Calibration line to determine the percent lube oil fraction in the organic soluble fraction of particulate matter.

Fig 2.2 SIMDIS Curve Based on Boiling Point Range of Sample, (from Cartellieri and Tritthart 1984. Reprinted with permission 1984 Society of Automotive Engineers, Inc.)

Sample details : Engine - Heavy duty DI diesel
Cycle - U.S. Federal heavy duty transient
Fuel - '1995' Canadian
Injection timing - 6° retarded from standard
Sample size - 20° segment
Attenuation : 512

1925/18

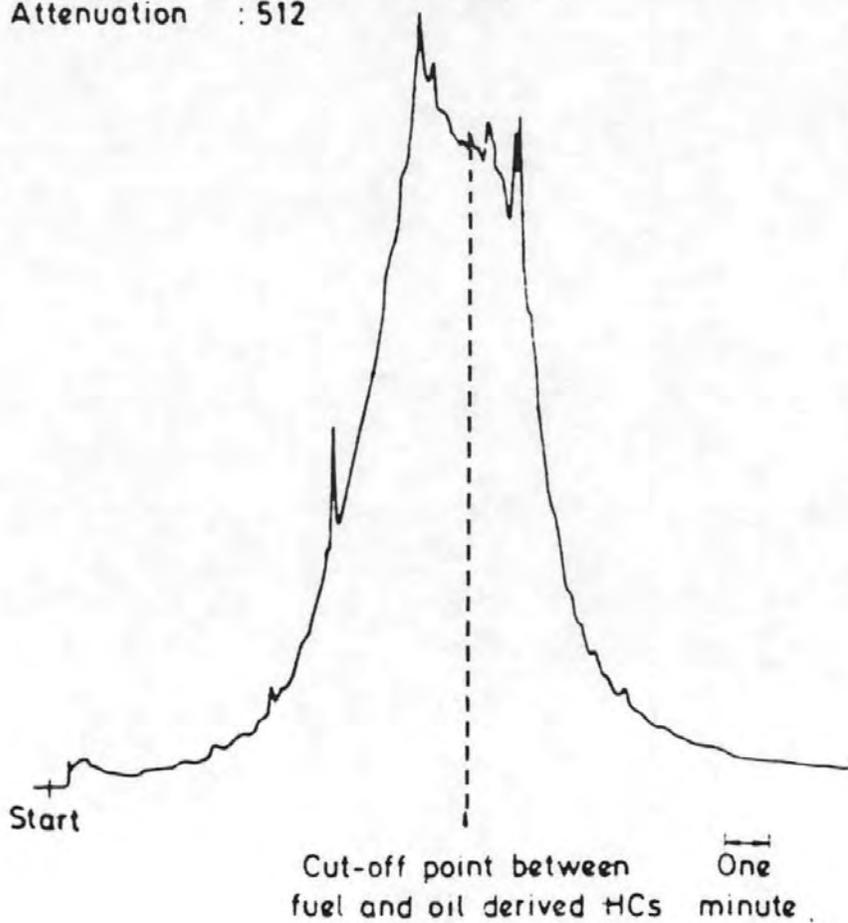


Fig 2.3 GC Packed Column Analysis of Dilution Tunnel Filter with a Novel Solid Sample Injection Technique, (from Cuthbertson et al. 1987. Reprinted with permission 1987 Society of Automotive Engineers, Inc.)

fuel or oil, whereas, in some circumstances pyrolysis products will make a significant contribution to the boiling point range typical of the lubricating oil. Since these pyrolysis compounds may originate from either fuel or lubricating oil, the methods described may overestimate the lubricating oil contribution.

2.4 Objectives of Research Undertaken and its Relevance to Previous Work.

Previous sampling systems for diesel exhaust gaseous and particulate emissions have all had shortcomings with respect to the quality of information they have yielded on the fundamental questions relating to the combustion processes. The reasons for this have been principally, their vulnerability to the formation artifacts of sampling, along with an inability to effectively sample the low relative molecular mass more volatile compounds in the exhaust.

The origins of the hydrocarbons and other species in the exhaust have not been fully elucidated, particularly the extent of contribution from lubricating oil and products of partial combustion. With the availability of a range of modern analytical instruments, it is possible for the chemist to make a new contribution to the research field of diesel exhaust emissions. In this way, the additional information may provide new insights into the problems of diesel combustion and the formation of soot and PAH.

The objectives of the current research described hereafter can be summarised as follows:

1/ To design, build and validate a suitable new sampling system for the solvent extractable fraction of diesel exhaust emissions, avoiding the limitations of some existing systems detailed in section 2.2.

2/ To use the new system to collect representative samples of the solvent extractable fraction from diesel exhaust, and with the aid of sophisticated analytical techniques to develop further the detailed interpretation of these samples obtained, with the intention of elucidating the origins of compounds within the complex mixture. To use these results to understand more fully the processes occurring within the combustion chamber of the IDI diesel that cause the emission of PAC.

3/ To develop a method to assess the contribution that lubricating oil makes to the solvent extractable fraction from diesel exhaust emissions.

4/ To draw conclusions, which may be of use to the diesel engineer, concerning the effectiveness of sampling systems for the solvent extractable fraction of diesel exhaust currently used by the motor industry, and to indicate where further research effort can fruitfully be applied.

CHAPTER 3.

Experimental Techniques and Facilities Available.

Analytical techniques for PAH have been well-developed in the past and comprehensively reviewed, (Lee et al.1981, Bartle et al.1981, Bjorseth 1983). Work conducted by the Chemical Characterisation Panel (CCP) of the Air Pollution Research Advisory Committee Coordinating Research Council's Diesel Composition Group (US) has developed and evaluated specific techniques for the analysis of the unregulated diesel engine emissions, which include PAC. The recommended methodology has periodically been published, (Perez et al.1980, 1984, 1987, Eisenberg et al.1984). Other researchers have focused on the characterisation of the diesel exhaust SOF and specific groups of compounds within it, (Funkenbusch et al.1979, Lies et al.1983, Schuetzle 1983, Obuchi et al.1984). These general techniques have been adapted for the identification of PAH in the SOF from diesel particulates, (Grimmer et al.1973, Schuetzle et al. 1981, Breuer 1984, Williams et al.1986).

An appropriate methodology for the present research was developed, with reference to the previously published research mentioned above, and is described below.

3.1 Preliminary Procedures for Sample Preparation.

Diesel exhaust samples invariably contain a very complex mixture of compounds for analysis. Furthermore, the

samples can include traces of carbon particulates or fine fibres from filters. Preliminary analytical procedure therefore includes extraction and clean-up of samples, followed by fractionation and concentration to simplify analysis.

3.1.1 Extraction and Concentration of Dilution Tunnel Filters.

Extraction of diesel particulates on filters can be satisfactorily achieved by either soxhlet extraction or ultrasonication, (Perez et al.1984). Although ultrasonication is more rapid, it involves additional analytical steps to remove suspended soot and filter fibres. Unused filters invariably have extraneous organic material adsorbed to them, even with solvent extraction before use. Ultrasonication breaks-up the filters which may increase this background contamination, on the otherhand soxhlet extraction can be left unattended overnight, and several filter samples can be extracted simultaneously, (Petersen and Chuang 1982).

The CCP has defined the SOF as the fraction of the total particulate mass removed by soxhlet extraction using DCM, (Perez et al.1987), and this methodology has been used in the current research.

Diesel particulate filter samples from a dilution tunnel system were obtained from Ricardo Consulting Engineers Ltd as part of a collaborative study. All filter samples were

sealed in polythene bags, after equilibrating to a constant weight for 24 hours in the dark, wrapped in aluminium foil to exclude light, and stored in a fridge at 0°C prior to soxhlet extraction with DCM as the solvent. Initially, glass fibre thimbles, pre-extracted by soxhlet for 24 hours, were used to hold the filters, but it was found that the contamination remaining in the thimbles, even after extensive pre-extraction, could be significant if particulate loading on the filters was light. Consequently, the filters were folded in on themselves and soxhlet extracted without using thimbles. The dilution tunnel filters, which had been pre-extracted before use, gave less contamination, for most of the samples this was not practicably possible.

The filter sample to be extracted was weighed prior to being placed in the soxhlet extractor. The filter was only handled with clean tweezers during these procedures. DCM (150 cm³) was added to the system and heated to reflux. The extraction was carried out for a period of 12 hours with the apparatus enclosed in aluminium foil to exclude light. At the end of the extraction the apparatus was allowed to cool and any DCM retained in the soxhlet extractor transferred to the round-bottom flask (RBF). The contents of the RBF were then rotary evaporated, under reduced pressure, and the sample concentrated, weighed, and fractionated, before final dilution for HRGC analysis, in the manner described below using open-column chromatography, section 3.1.4.

3.1.2 Extraction and Concentration of Sample from TESSA.

The sample mixture obtained from the collecting reservoir of TESSA after a run was in two phases, aqueous methanol and DCM (see section 4.1 for further details). The particulate material was filtered under reduced pressure using Whatman filters (GF/F 5cm). The filters were placed in a muffle furnace at 400°C for 24 hours prior to use. The two phases were isolated by liquid/liquid partition in a separating funnel (2 litres). The DCM fraction, which was the lower layer, was removed and the remaining aqueous phase further extracted with three aliquots of DCM (50 cm³), to maximise recovery of the sample; these aliquots were combined with the main DCM fraction. The whole procedure was repeated three times in order that the large volume of solvent extract (4.5 litres) could be processed.

The resulting DCM fraction (approx. 1.2 litres), which contained the organic compounds of interest, was reduced by rotary evaporation (reduced pressure, 30°C) to a small volume (150 cm³). The sample was then dried by adding anhydrous sodium sulphate (3 g), filtered, and further rotary evaporated to remove most of the DCM (leaving ca. 1 cm³), before being transferred quantitatively, by pasteur pipette, with a small amount of DCM (1 cm³), to a preweighed glass vial. The DCM was evaporated from the sample by gently passing a stream of dry nitrogen gas over the sample, before the vial was weighed to a constant weight. Concentration steps are generally a major source

of compound loss through adsorption, evaporation, incomplete transfer between containers and/or reaction with other constituents, (Petersen and Chuang 1982). Extreme care was taken to minimise losses of the more volatile sample components during the rotary evaporation and nitrogen blowdown concentration steps.

3.1.3 Removal of Particulates from Used Lubricating Oil.

The analysis of used lubricating oil presents a particular problem. A large amount of carbon particulates from combustion accumulate in the lubricating oil of diesel engines, and only the largest of these are removed by the oil filter. Most of the particulates are too small to be filtered due to a detergent additive in the lubricating oil. This acts as a dispersant to keep the particulates evenly dispersed throughout the oil, in a colloidal suspension, preventing the agglomeration into large particles or the build up of a sludge that could increase engine wear. Some of these particulates are so fine that they will pass right through a silica column. These particulates will then present a problem for the capillary column, since on-column injection is very efficient at delivering the whole sample, including particulates, onto the top of the column. Any particulates, so introduced, will remain at the top of the column and have a detrimental effect on the chromatography. It is therefore necessary to remove particulates from the used lubricating oil in a clean-up step before column fractionation.

Initially, extraction of the aromatic hydrocarbons from lubricating oil was achieved using dimethyl sulphoxide, which has a strong affinity for aromatics (Natusch and Tomkins 1978, Lee et al.1981), followed by back-extraction into hexane with an excess of water. This liquid/liquid partition method was only partially successful because the detergent additives in the oil prevented a clean separation between layers. A better technique was devised in cooperation with another researcher at Plymouth (Gough 1985).

A sample of used lubricating oil (0.5 g) was weighed into a stoppered flask (50 cm³). To this were added chloroform (10 cm³), propan-2-ol (10 cm³) and concentrated hydrochloric acid (0.5 cm³). The mixture was shaken and left to stand for 10 minutes before being passed through a preweighed Whatman GF/F filter under reduced pressure. A visual inspection confirmed that the particulates were fully retained on the filter. The filter was rinsed with two aliquots of chloroform (5 cm³) and an excess of distilled water (20 cm³) was then added to the filtrate. The hydrocarbon compounds of the lubricating oil were recovered by liquid/liquid partition using three successive extractions with hexane (10 cm³). The cleaned-up sample of used lubricating oil, dissolved in hexane, was then subjected to the same concentration and fractionation steps, prior to analysis by HRGC, that were described for the TES above.

The clean-up technique for used lubricating oil, which has

been described, is effective because the concentrated acid destroys the dispersant additive, thereby allowing the carbon particulates to agglomerate into larger particles which can be filtered effectively.

3.1.4 Sample Fractionation by Silica Gel Open-Column Chromatography.

Column chromatography has been widely used as a method of fractionating samples (Bartle et al.1981). The TES was fractionated on a silica gel column, using a standard technique (Robbins and McElroy 1982), into aliphatic and aromatic fractions by sequential elution with solvents of increasing polarity (Williams et al.1987). In their review Lee et al. (1981) comment that both alumina and silica suffer the disadvantage of high adsorptivity which can lead to losses of trace constituents, as well as poor fractionation of higher relative molecular mass PAC. Variations in water content also can result in poor reproducibility. Notwithstanding these limitations, the technique is still extensively used (Eisenberg et al.1984), and Later et al. (1985) have optimised the column chromatography class fractionation of PAC. They have shown that the optimum activity for silica is obtained with 5-8% water (w/w), and this can be achieved routinely by storing the silica at a constant 50°C.

The silica gel was first cleaned by soxhlet extraction with DCM for 24 hours, before being used in column chromatography and then oven-dried to fully activate it,

(1 hour, 120°C). It was then stored in an incubator at a constant temperature (50°C). To prepare a column silica (3 g) was placed in a small beaker and then covered with hexane (20 cm³), (to ensure good fractionation the weight of silica must be 30 times the sample weight). The silica was stirred with a glass rod to remove any bubbles of air. The empty glass column was three quarters filled with hexane and lightly plugged at its lower end, close to the stopcock, with solvent-extracted cotton wool. The silica gel slurry was rapidly transferred to the column (stopcock open) with the aid of a glass funnel and spatula. At the same time the sides of the glass column were lightly tapped with a short length of rubber tubing. In this way a compact bed of silica was achieved, free from any fractures, several centimetres in depth..

A layer (1 cm) of coarse grade sand was added to the top of the silica bed; this ensured that the top of the silica column was not disturbed when the sample was added. The stopcock was fully closed, leaving a thin layer of solvent (3 mm) covering the top of the sand; the top of the column was never allowed to run dry.

Routine procedure was as follows: Hexane (1 cm³) was added to the sample in a vial and this was ultrasonicated (5 mins). In this way, even the most polar sample components, which were not readily soluble in hexane, became suspended in the solvent and were therefore quantitatively transferred for fractionation. The sample was placed on the top of the prepared column with a pasteur

pipette; the vial was rinsed twice with hexane (0.5 cm³) and the washes added to the column.

The column was first eluted with hexane (10 cm³) to collect the aliphatic hydrocarbon fraction, then with DCM (15 cm³) to collect the aromatic hydrocarbon fraction; methanol (15 cm³) was used to remove remaining sample material, inevitably some strongly adsorbed polar material remained on the column. Recovery weights indicated that this loss amounted to between 6 - 15% of the original sample weight. Each fraction was collected in an RBF, rotary evaporated to dryness, and then transferred to a pre-weighed vial with DCM (1 cm³). The solvent was removed with gentle nitrogen blowdown and the sample weight for each fraction recorded. The final step was to dilute each fraction for HRGC and GC/MS analyses; normal procedure was to use a standard concentration (2 mg/cm³) for all samples, this was sufficient to give a satisfactory FID response without exceeding the capacity of the capillary column.

3.2 Analytical Techniques Applied to Samples.

The principal analytical techniques in this research have been HRGC and GC/MS, details of the instrumentation and operating conditions follow:

3.2.1 High Resolution Gas Chromatography.

Samples were analysed by HRGC, carried out on a Carlo Erba HRGC 5360 equipped with cold on-column injection and flame

ionisation detector (FID). The FID response was recorded and integrated by a Shimadzu CR3-A integrator. Gas chromatographic details are summarised in Table 3.1.

Once the carrier gas flow had been set ($2\text{cm}^3/\text{min}$ at 250°C), the combustion gases were then optimised using Simplex, a computer program run on an Apple IIe computer (Miller and Miller 1984). This involved thirty five repeat analyses of a naphthalene standard to find the optimal settings of air and hydrogen. The optimal gas settings gave a peak height for the naphthalene standard as 69000 units, measured on the integrator; this contrasted with the original combustion gas settings which gave a peak height for the naphthalene standard of only 43600 units. Having made these measurements the carrier gas flow was routinely checked, at the beginning of the day, with a standard mixture that included naphthalene, without removing the detector.

Great care was taken so that the same injection technique was always used. A comparison was made between 5.0 and 0.5 mm^3 syringes, using samples with an internal standard (n-undecane). The result showed that the coefficient of intersample variation, for repeated injections, with the 5.0 mm^3 syringe was considerably larger (8.5%) than it was for the 0.5 mm^3 syringe (2.3%); the 0.5 mm^3 syringe gave more reproducible results and was used routinely for all analyses except where a larger volume of sample was required, for example, in co-injection of sample and standards for the calculation of retention indices.

Column Type	DB-5 (J&W Scientific SE-54 equivalent) fused silica capillary
Length	30 metres
I.D.	0.32 mm
Film Thickness	0.025 mm
Injector	On-column
Injection Volume	0.5 mm ³
Carrier Gas	Hydrogen
Detector Temp	320°C
Solvent	DCM
Chart Speed	5 mm/min
GC Oven Temperature Program:	Initially 50°C held for 5 mins, followed by temperature ramp of 10°C/min, from 50°C to 300°C, final temperature of 300°C held for 25 mins.
Carrier gas flow:	2 cm ³ /min
Detector H ₂ flow:	25 cm ³ /min
Detector air flow:	320 cm ³ /min

Table 3.1
Details.

High Resolution Gas Chromatographic

3.2.2 Gas Chromatography/Mass Spectrometry.

GC/MS analyses were performed on a Carlo Erba HRGC 5160 coupled to a Kratos MS25 double focussing magnetic sector mass spectrometer. The gas chromatograph was fitted with a fused silica capillary column (30 m x 0.32 mm I.D., DB-5 J&W Scientific) which was positioned directly into the ion source of the mass spectrometer. Cold on-column injection and helium carrier gas were used throughout. The temperature program of the column oven started at 50°C, maintained for 5 minutes, then was raised at 5°C/min to a final temperature of 300°C which was held for 25 minutes. Low resolution electron impact MS was used, with an ionisation potential of 40eV, filament emission current 600A, and source temperature maintained at 250°C. Data were collected after 4 minutes with complete mass spectra recorded every 1.5 seconds using a Data General Desktop-30 data handling system. A plot of the combined intensity of the ions against scan number, over the mass range (40-532 mass units), provided a Total (Reconstructed) Ion Chromatogram (TIC); a mass fragment of a single selected ion against scan number could also be plotted using the Selected Ion Recording (SIR) mode.

3.3 Analysis of Nitro-PAC.

Various techniques have been developed for the analysis of nitro-PAC. They usually involve a fractionation procedure, since the diesel exhaust extract is a highly

complex mixture of compounds, some of which might interfere with the analysis of nitro-PAC. Fractionation has been achieved usually by silica column chromatography (Campbell and Lee 1984) or semipreparative normal phase silica column HPLC (Schuetzle et al.1982). Nitro-PAC have been reduced to the amino- PAC and subsequently analysed by HPLC with fluorescence detection (Shore et al.1987, Hartung et al.1984). Alternatively nitro-PAC have been successfully analysed directly, after pre-fractionation, by HRGC and a flame ionisation detector (Tong et al.1983); other workers have used HRGC with electron capture detector (Draper 1986), or nitrogen specific detectors (Paputa-Peck et al.1983, Nielson 1983, Hartung et al.1984, Williams et al.1986). Additional information can be obtained by GC/MS analysis (Schuetzle et al.1982, Newton et al.1982, Henderson et al.1983, Schuetzle and Jensen 1985).

After consideration, the method developed by Campbell and Lee (1984) was used for this present work because it included a concentration step, which was considered important, since only trace levels of nitro-PAC are present in diesel exhaust. Furthermore the reduction and derivatization of the nitro-PAC enabled the products to be analysed by HRGC with an enhanced FID response. Since HRGC was already one of the principle analytical systems available, this was very convenient and also allowed subsequent analysis by GC/MS, when required, without additional preparation of the sample. These results are presented in section 5.5.

3.3.1 Fractionation, Reduction and Derivatization of TES.

Silica gel (60-120 mesh) was heated in an oven (150°C) overnight, to drive off any adsorbed water; distilled water was then added (5% by weight) and the silica shaken mechanically for several hours. Two silica columns were then made up in the manner described previously (section 3.1.4). The TES was dissolved in DCM and then blown down to dryness with a gentle stream of nitrogen before being redissolved in hexane (1cm³). The compounds in the TES were not all soluble in hexane, but by sonicating the vial briefly (30 secs), they were all either dissolved or suspended in the hexane, and, thus, were transferred quantitatively to the top of the silica column.

The nitro-PAC, along with other compounds, were eluted with n-hexane/benzene (17 cm³, 1:1 v/v). This fraction also included aliphatic and aromatic hydrocarbon compounds from the TES, but excluded the most polar compounds, which were retained on the column and subsequently discarded. The hexane/benzene fraction containing the nitro-PAC compounds was collected in an RBF (50 cm³) and rotary evaporated to dryness before being redissolved in methanol (15 cm³); to this was added distilled water (1 cm³), an 0.05% aqueous solution of copper(II)chloride (1 cm³), and potassium borohydride (0.1 g). The mixture was shaken and then allowed to stand at room temperature in the dark for one hour. By this time the reduction of nitro-PAC to the corresponding amino-PAC was completed, and distilled water

(5 cm³) was added.

A liquid/liquid partition was carried out, by extracting the nitro-PAC and other hydrocarbons from the solution, with three portions (10 cm³ each) of n-hexane/benzene (1:5 v/v). The extracts were combined in a RBF and reduced in volume by rotary evaporation before being transferred to a reactor vial (2 cm³). The remaining solvent was removed with a gentle stream of high purity nitrogen and the extract redissolved in benzene (0.5 cm³); to this was added 0.05M trimethylamine in benzene (0.1 cm³), followed by trifluoroacetic anhydride (0.01 cm³). At this point the vial was sealed and heated in a bath of paraffin oil, maintained at a constant temperature of 50°C, for 15 minutes.

The reactor vial was then cooled for several minutes before adding 5% aqueous ammonia solution (1 cm³) and shaken for five minutes to terminate the derivatization reaction. The organic and aqueous phases were allowed to separate, and the benzene layer, containing the derivatized amino-PAC, was recovered.

The benzene layer was blown down to dryness with nitrogen gas, redissolved in 1:1 n-hexane/benzene (1 cm³), and placed onto the top of the second silica column, previously prepared. Aliphatic and aromatic compounds, less polar than the derivatized amino-PAC were eluted in the first fraction with n-hexane/benzene (1:1 v/v, 28 cm³). Finally the derivatized amino-PAC were eluted in the second

fraction with benzene (30 cm³): this fraction was then rotary evaporated, transferred to a vial, weighed and then dissolved in DCM to a suitable dilution (2 cm³) for HRGC analysis.

The technique described removes all the compounds more polar than nitro-PAC in the first column fractionation. In the next step, the reduction of nitro-PAC to amino-PAC increases their polarity. In the second column fractionation these compounds, with their increased polarity, can now readily be separated from all the other compounds, including oxygenated and nitrogen heterocyclic species which normally co-elute with the nitro-PAC. The method is therefore effective at concentrating the nitro-PAC and removing any interference from other species in the analysis. The derivatization with trifluoroacetic anhydride not only increases the GC detector response (esp. ECD) for the nitro-PAC, but also ensures the stability of the compounds since the poly halogenated derivative is much more stable than the amino-PAC. (Campbell and Lee 1984, Jager 1978, Later et al.1982)

3.4 Use of Standards to Aid Identification.

A mixture of 12 PAC compounds was used routinely as a beginning-of-day standard for the HRGC; this monitored the carrier-gas flow, the resolution of the capillary column and the FID response. The PAC standard was also used for confirmatory identification of the 12 parent PAC in samples. Several other standard mixtures were also used,

where the individual compounds were available, which included: A range of alkanes from n-C18 to n-C30 plus pristane, a mixture of specific alkyl naphthalene isomers, and a mixture of nitro-PAC. Table 3.2 lists the individual compounds in each of the standards. HRGC chromatograms for four of the standards are shown in Figs 3.1 and 3.2.

In addition to the use of these standards for direct comparison with a sample, the Lee retention index mixture of naphthalene, phenanthrene, chrysene and benzo(g,h,i)perylene were also used, by co-injection with a sample aliquot, to calculate the relative retention times for sample components (Lee et al.1979, Vassilaros et al.1982). Benzo(g,h,i)perylene was used in the place of picene which was unobtainable; it has a relative retention time almost identical to that of picene. The calculation was facilitated by a Fortran program written on the Prime mainframe computer, in the Polytechnic Computer Centre, which enabled retention data to be rapidly entered from the HRGC integrator printout and from which the relative retention data could be calculated for all the sample peaks present.

3.5 General Laboratory Practice.

All glassware was cleaned by soaking in a 5% solution of Decon 90 overnight, and rinsing each item six times with tap-water, followed by a final rinse with distilled water. Glassware was then either oven dried (200°C), or rinsed

1/	PAH Standard	2/	Alkane Standard
	Naphthalene		Pristane
	Phenanthrene		Octadecane
	Anthracene		Eicosane
	9-Methylanthracene		Heneicosane
	Pyrene		Docosane
	Benz(a)anthracene		Tetracosane
	Chrysene		Pentacosane
	Benzo(a)pyrene		Hexacosane
	Perylene		Triacontane
	Dibenz(a,h)anthracene		
	Benz(g,h,i)perylene		
	Coronene		
3/	Alkyl-PAH Standard	4/	Nitro-PAC Standard
	1-Methylnaphthalene		2-Nitrofluorene
	2,6-Dimethyl-naphthalene		9-Nitroanthracene
	2,3,5-Trimethyl-naphthalene		1-Nitropyrene
	1-Methylphenanthrene		7-Nitrobenz(a)-anthracene
			6-Nitrochrysene
			6-Nitrobenz(a)pyrene

Table 3.2 List of Individual Compounds Making Up Four Different Analytical Standard Mixtures.

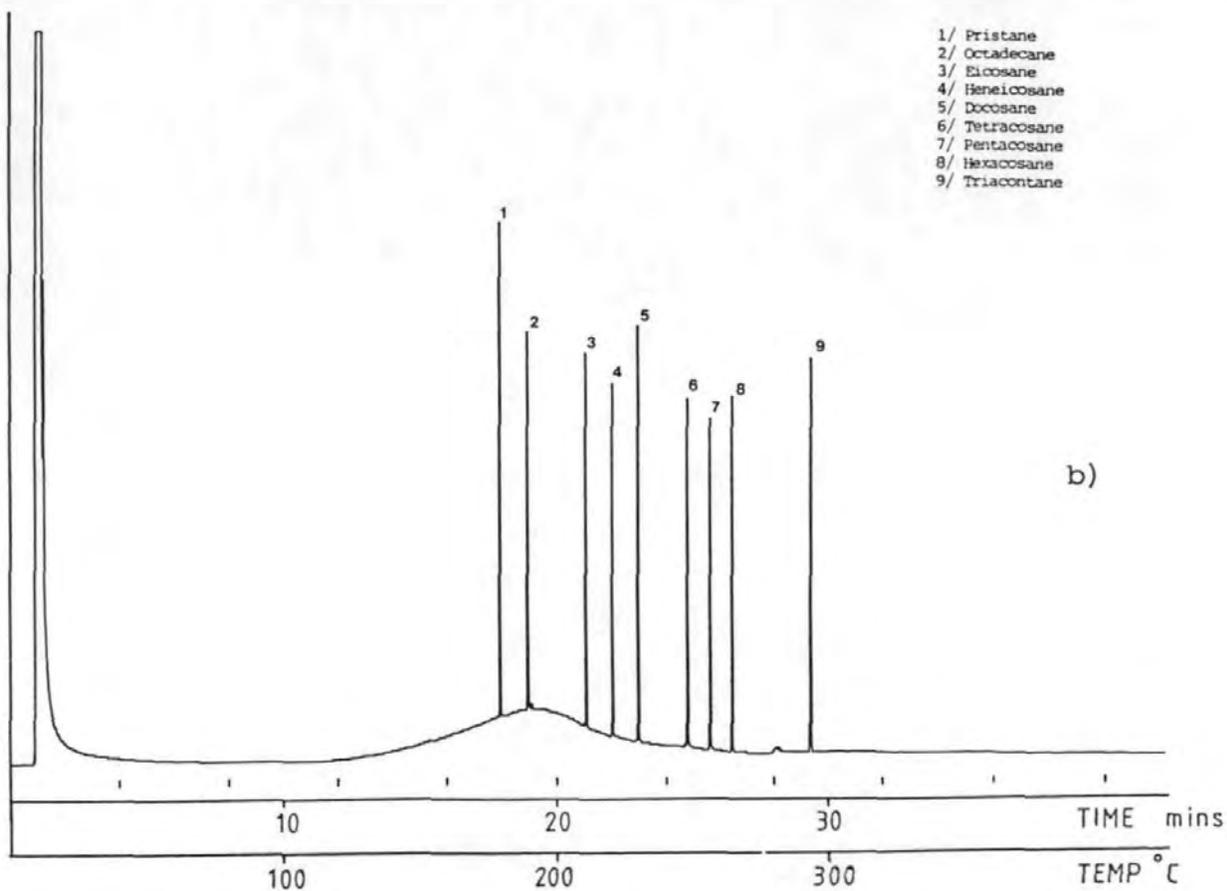
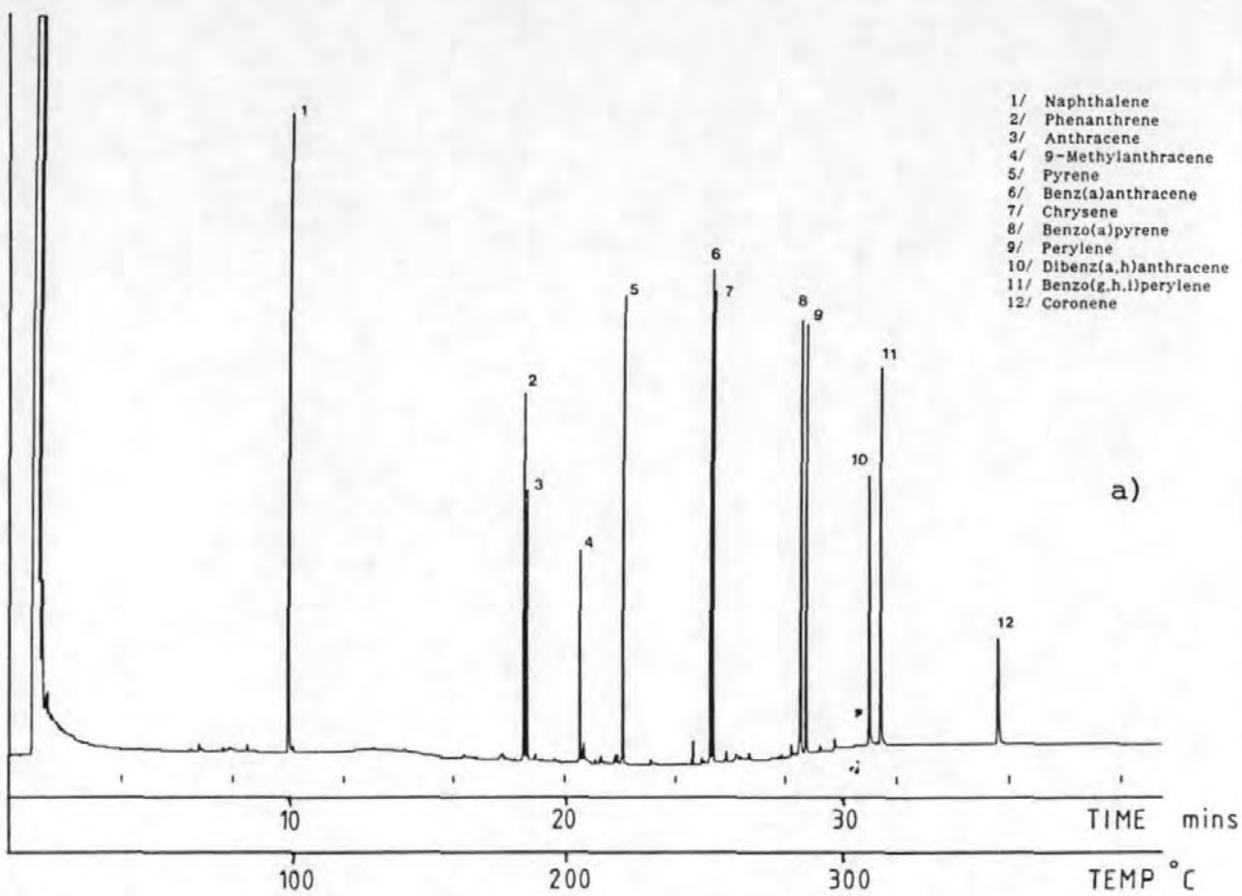


Fig 3.1 Analytical Standards: a) PAH Standards.
 b) Alkane Standards.

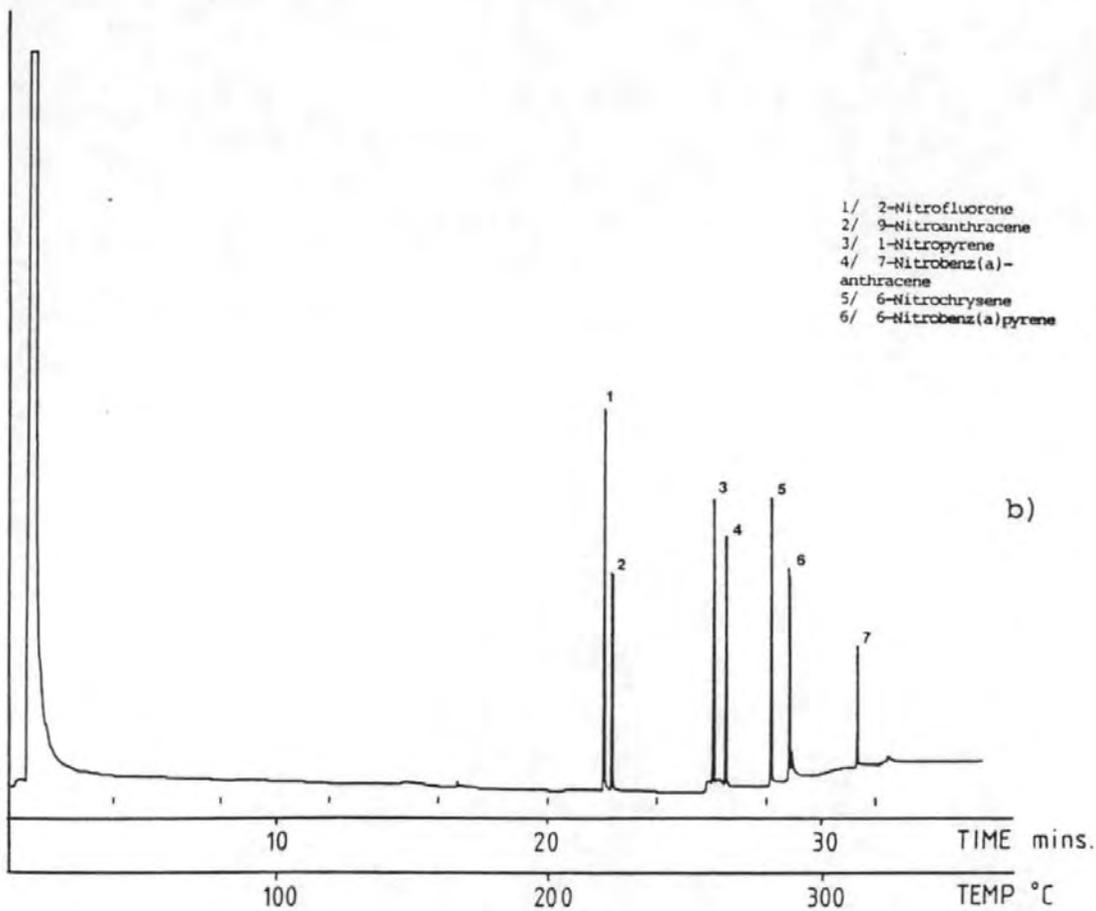
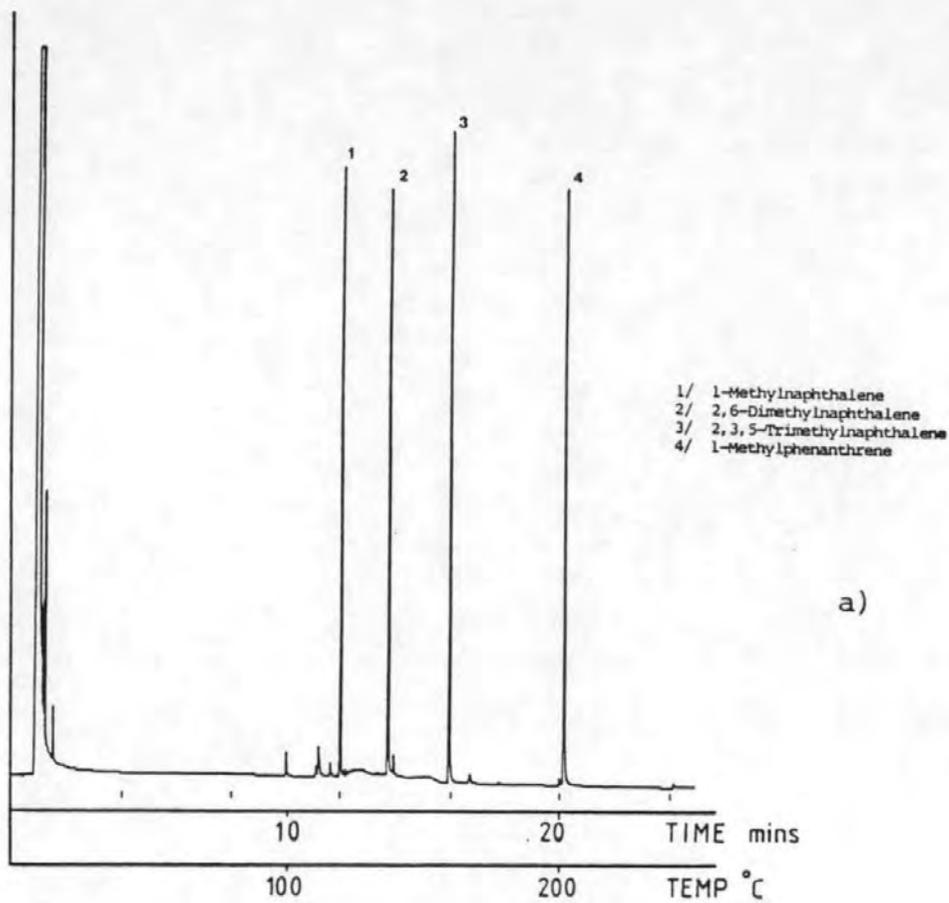


Fig 3.2 Analytical Standards: a) Alkyl-Naphthalenes and Phenanthrene Standards.
 b) Nitro-PAC Standards

with distilled acetone to remove water and left to drain.

General purpose solvents used in this work (hexane, dichloromethane, methanol, propan-2-ol and acetone) were redistilled in an all-glass apparatus (Walker 1979). The appropriate drying agents (Vogel 1956) were used in the crude solvents before distillation to remove any water present. In the experimental work with TESSA, large volumes of solvents were used (3.5 litres), and DCM was recovered from the waste solvents that resulted. Once-used DCM was redistilled twice to achieve an acceptable high standard of purity. The purity of each solvent was routinely tested by reducing a sample of the solvent (150cm³), using rotary evaporation, to a small volume (50mm³) and analysing this by HRGC. Small quantities of AnalaR grade chloroform and dimethyl sulphoxide were used during clean-up techniques on a used lubricating oil, without being redistilled.

Samples were stored in airtight glass vials in the freezer compartment of a refrigerator, and were protected against light. Silica gel, cotton wool, anhydrous sodium sulphate, anti-bumping granules, PTFE cord and GF/F filters were all extracted overnight in a soxhlet apparatus with DCM, in order to remove contamination.

3.6 Details of Engine Facilities.

The following facilities were available for the research described.

3.6.1 Test Engine Ricardo E.6/T.

The engine used for the present research was a Ricardo E.6/T single cylinder, four-stroke, poppet valve, reciprocating internal combustion engine with compression ignition and a compression ratio of 22:1. The cylinder head includes a Ricardo Comet Mk.V swirl chamber. It has a top half in a spherical form and the lower half in a truncated cone which communicates with the cylinder by means of a narrow passage or throat which was thermally insulated from the rest of the cylinder head. On the compression stroke, air was forced into the Comet chamber, and was given a rotating motion by the shape of the chamber. The air picks up a certain amount of heat from the lower insulated half of the combustion chamber thus serving to raise the compression temperature without loss of volumetric efficiency. Special cavities are cut into the crown of the piston. All the arrangements described are standard for the particular engine, no modifications have been made on site.

The cylinder, which was cast-iron, was fitted with a hardened high-phosphorus cast-iron liner. The lubricating system was of the wet-sump type and the oil was delivered direct to the crankshaft and the big-end by means of a pump driven by the crankshaft. The engine was water cooled.

The engine was coupled to a swinging field electric

dynamometer, the whole being mounted on a combination bedplate. Switch gear enables the dynamometer to be operated as a motor to start the engine, or in order to motor the engine during tests. The fuel pump injects the fuel into the Comet chamber via a pintle-type nozzle. Fuel consumption was measured by noting the time taken for a set volume (50 cm³) to be consumed by the engine.

Before sampling, the engine was conditioned by running at 3000 rev/min and 7.6 kW for one hour. The standard engine conditions are 2000 rev/min and 3.4 kW load; a period of 15 minutes was allowed, at the test conditions, before sampling. The cooling water for the engine was maintained at a temperature of 80°C, and that of the engine oil to around 75°C. The cooling water for TESSA was kept at 4°C before sampling.

3.6.2 Ancillary Equipment for Emission Mapping.

The Ricardo engine was fitted with the following monitoring devices:

- a/ Inductive needle lift transducer (Cussens).
- b/ Degree marker system for engine timing (Cussens).
- c/ Piezo pressure transducer placed in the cylinder (Cussens).

This equipment was backed up with a Transient Recorder (Datalab) which captured single shot or low repetition events and presented them for continuous display; a Gould

Oscilloscope and Apple IIe micro were available for data display and recording. A programmable data acquisition system, Fluke 2280A Datalogger, was used to enable simultaneous multichannel recording of measurements from a series of 20 thermocouples mounted in TESSA, section 4.3.2.

Exhaust gas analysis was performed with a Lamdascan (Cussens) which gives a continuous and direct measurement of mass air:fuel ratio, equivalence ratio, and residual oxygen, along with a Long Line Emissions Trolley loaned by Perkins Engineering, which gives continuous and direct measurements of CO, NO, and HC in the exhaust.

The Emissions Trolley was fitted with a heated soot filter immediately after the sample probe and an 8 metre sample line, both operated at between 180° and 190°C. The heated line connects directly to the hydrocarbon analyser oven which diverts some of the sample gas for concurrent NO and CO analysis. The HC analyser was a hot FID system, NO analysis was achieved with a chemiluminescence system, whilst the CO was analysed by non-dispersive infra-red.

3.6.3 Emission Maps for the Ricardo E.6/T.

A variety of engine parameters were measured for the full range of the Ricardo E.6/T engine. Apart from the exhaust emissions of UHC, NO and CO, the following were also measured, air/fuel ratio, oxygen, fuel consumption, injection timing, and smoke Bosch number. The results are presented in Table 3.3. The exhaust emissions, along

SPEED r. p. m.	LOAD kW	HC ppm	NO ppm	CO ppm	AFR	LAMBDA	OXYGEN %	FUEL cm3/min	INJECTN Start degBTDC	TIMING Finish degATDC	FILT. No	80% No
3000.0	0.5	490.0	120.0	330.0	48.4	3.3	14.3	19.4	4.0	37.0	6	0.7
3000.0	2.9	165.0	329.0	220.0	32.5	2.2	11.3	27.8	4.0	38.0	5	1.1
3000.0	4.3	95.0	431.0	210.0	26.6	1.8	9.2	34.1	4.0	40.0	4	1.5
3000.0	5.7	75.0	503.0	220.0	22.4	1.6	7.3	41.1	3.0	42.0	3	5.6
3000.0	7.2	50.0	586.0	420.0	18.3	1.2	4.0	50.0	3.0	43.0	8	3.2
3000.0	7.6	25.0	718.0	800.0	16.4	1.1	2.1	55.6	3.0	43.0	7	4.6
2750.0	0.5	330.0	120.0	235.0	53.2	3.7	14.9	16.3	5.0	32.0	6	0.6
2750.0	2.6	250.0	347.0	160.0	35.2	2.4	12.3	23.6	7.0	34.0	5	0.8
2750.0	4.0	170.0	515.0	60.0	29.3	2.0	10.2	28.8	6.0	35.0	4	1.0
2750.0	5.3	110.0	550.0	150.0	24.0	1.6	7.9	35.7	5.5	36.0	3	1.7
2750.0	6.6	60.0	718.0	220.0	19.3	1.3	4.8	43.5	5.0	38.0	2	2.9
2750.0	7.5	50.0	888.0	900.0	17.1	1.2	2.8	49.2	5.0	39.0	1	3.6
2500.0	0.4	230.0	120.0	250.0	60.0	4.0	15.6	13.4	8.0	28.0	1	0.3
2500.0	2.4	220.0	347.0	160.0	36.5	2.5	12.9	20.3	8.0	30.0	2	0.5
2500.0	3.6	205.0	461.0	230.0	31.3	2.1	10.8	23.3	8.0	30.0	3	0.8
2500.0	4.8	105.0	539.0	270.0	25.0	1.8	8.7	31.2	8.0	31.0	4	1.6
2500.0	6.0	60.0	680.0	200.0	21.0	1.4	6.1	37.0	7.0	33.0	5	2.3
2500.0	7.1	45.0	652.0	875.0	17.3	1.2	3.2	44.1	7.0	34.0	6	4.1
2250.0	0.4	235.0	138.0	210.0	62.0	4.3	15.7	11.5	8.0	23.0	6	0.2
2250.0	2.2	260.0	371.0	195.0	38.0	2.6	12.6	18.3	9.0	25.0	5	0.7
2250.0	3.2	220.0	461.0	230.0	31.7	2.2	10.9	22.6	9.0	26.0	4	1.0
2250.0	4.3	140.0	627.0	265.0	26.2	1.8	9.0	27.3	9.0	27.0	3	1.1
2250.0	5.4	115.0	556.0	210.0	21.6	1.5	8.5	32.6	8.0	29.0	2	1.9
2250.0	6.3	70.0	634.0	250.0	18.9	1.3	4.6	37.5	7.0	30.0	1	3.3
2000.0	0.3	260.0	144.0	170.0	64.0	4.3	15.9	9.9	9.0	18.0	1	0.1
2000.0	1.8	190.0	455.0	140.0	38.7	2.7	12.9	16.0	10.0	19.0	2	0.7
2000.0	2.9	225.0	503.0	220.0	32.0	2.2	11.1	19.9	10.0	20.0	3	0.8
2000.0	3.8	125.0	574.0	210.0	26.5	1.8	9.1	23.8	10.0	22.0	4	0.8
2000.0	4.8	80.0	574.0	240.0	23.2	1.6	7.4	27.8	10.0	24.0	5	1.5
2000.0	6.0	50.0	562.0	380.0	18.0	1.2	3.6	36.1	10.0	25.0	6	2.7
1750.0	0.3	310.0	203.0	170.0	65.0	4.5	16.1	8.7	11.0	12.0	6	0.1
1750.0	1.7	165.0	514.0	110.0	38.5	2.7	12.7	14.2	12.0	16.0	5	0.2
1750.0	2.5	145.0	532.0	120.0	32.6	2.2	11.3	16.8	13.0	16.0	4	0.3
1750.0	3.3	110.0	568.0	135.0	27.4	1.9	9.4	20.4	13.0	17.0	3	1.5
1750.0	4.2	100.0	503.0	195.0	23.5	1.6	7.8	23.8	13.0	19.0	2	1.7
1750.0	5.1	105.0	503.0	375.0	19.8	1.4	5.4	28.8	14.0	21.0	1	3.1
1500.0	0.2	90.0	273.0	105.0	60.3	4.7	16.3	7.1	15.0	12.0	1	0.1
1500.0	1.4	95.0	473.0	95.0	43.3	3.0	13.7	11.0	17.0	10.0	2	0.1
1500.0	2.2	75.0	485.0	100.0	35.7	2.5	12.2	13.5	17.0	12.0	3	0.6
1500.0	2.9	75.0	449.0	170.0	30.0	2.1	10.3	16.4	16.0	14.0	4	1.7
1500.0	3.6	70.0	407.0	225.0	25.6	1.8	8.7	19.4	15.0	16.0	5	2.7
1500.0	4.3	95.0	323.0	460.0	20.4	1.4	5.9	24.6	15.0	20.0	6	4.5
1250.0	0.2	90.0	263.0	110.0	71.7	4.8	16.5	5.6	19.0	7.0	2	4.3
1250.0	3.4	180.0	437.0	205.0	22.4	1.5	6.9	20.0	18.0	16.0	1	0.1
1000.0	2.8	120.0	443.0	190.0	21.3	1.5	6.4	16.1	19.0	12.0	2	4.5
											1	0.1

* = Badly spotted, discounted.

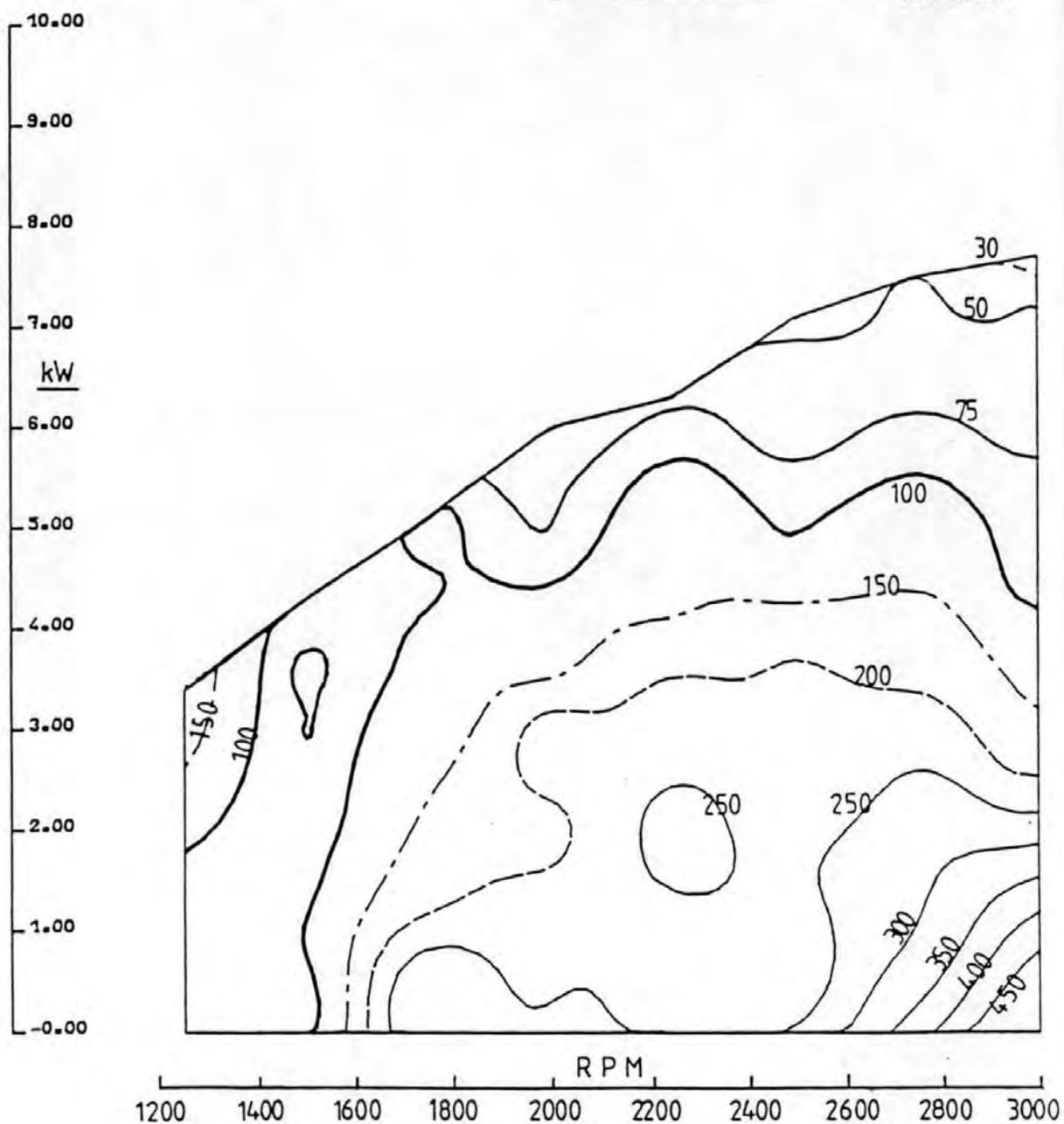
Table 3.3 Engine Parameters Measured Over a Wide Range of Speed and Load on a Ricardo E.6/T IDI Diesel Engine.

with Bosch smoke, are also plotted on contour maps shown in the Figs 3.3, 3.4, 3.5 and 3.6.

These measurements have been an important aid in choosing suitable sampling conditions for different experiments. For example in an experiment to assess the formation of nitro-PAC, the engine conditions which produced high levels of NOx could easily be selected. They also confirmed the sound condition of the test-engine. Indeed, an earlier engine map was used as a diagnostic tool to correct an engine fault which gave anomalous emission levels.

KEY TO PROFILE VALUES

-----	30.000
=====	50.000
=====	75.000
=====	100.000
- - - - -	150.000
=====	200.000
=====	250.000
=====	300.000
=====	350.000
=====	400.000
=====	450.000

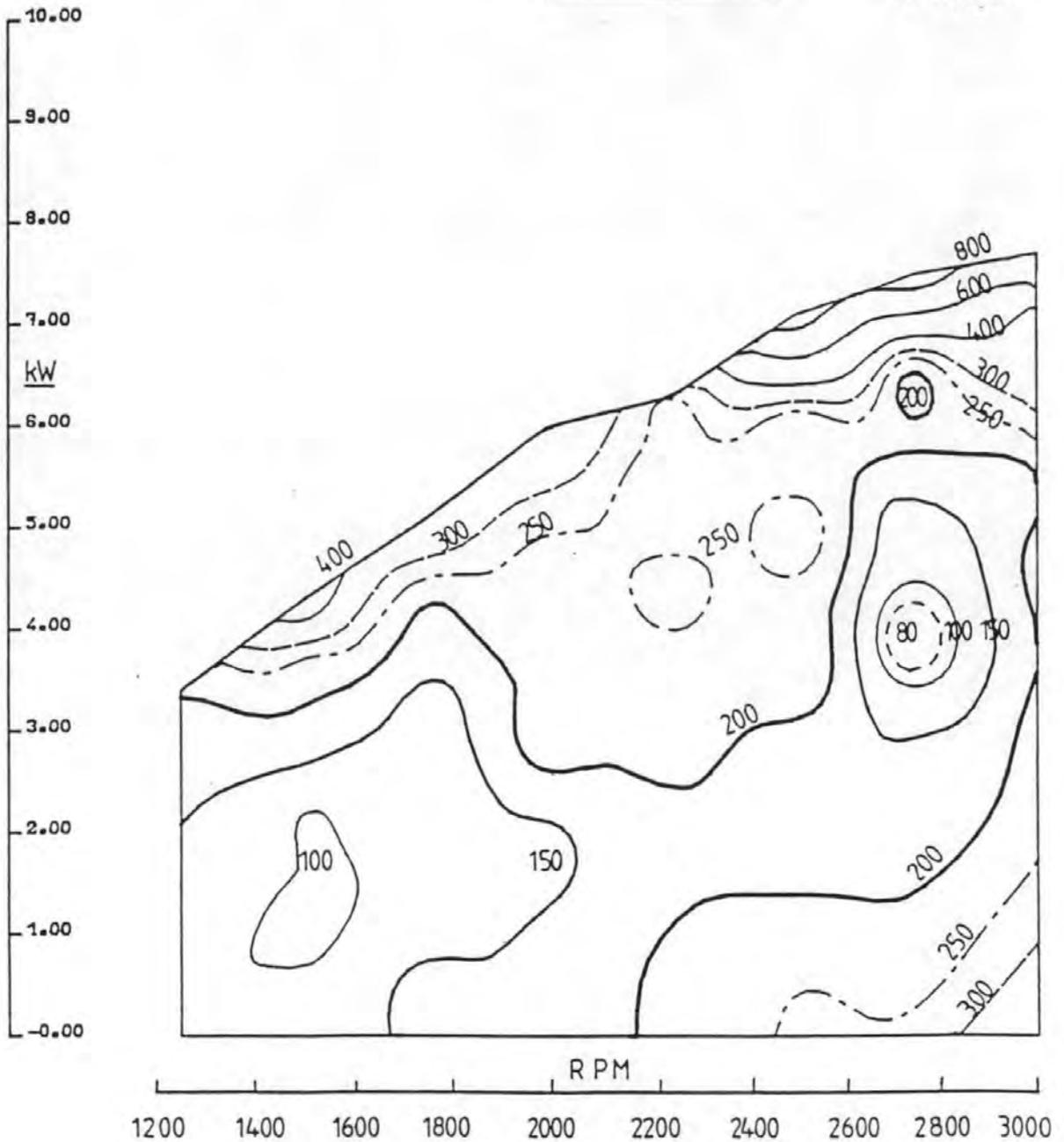


ISO-HC EMISSIONS VPM. RICARDO E6 ENGINE.

Fig 3.3 Contour Map for UHC Emissions from Ricardo E.6/T IDI Diesel Engine, (courtesy Perkins Engines Ltd).

KEY TO PROFILE VALUES

-----	80.000
=====	100.000
=====	150.000
=====	200.000
-----	250.000
-----	300.000
=====	400.000
=====	600.000
=====	800.000

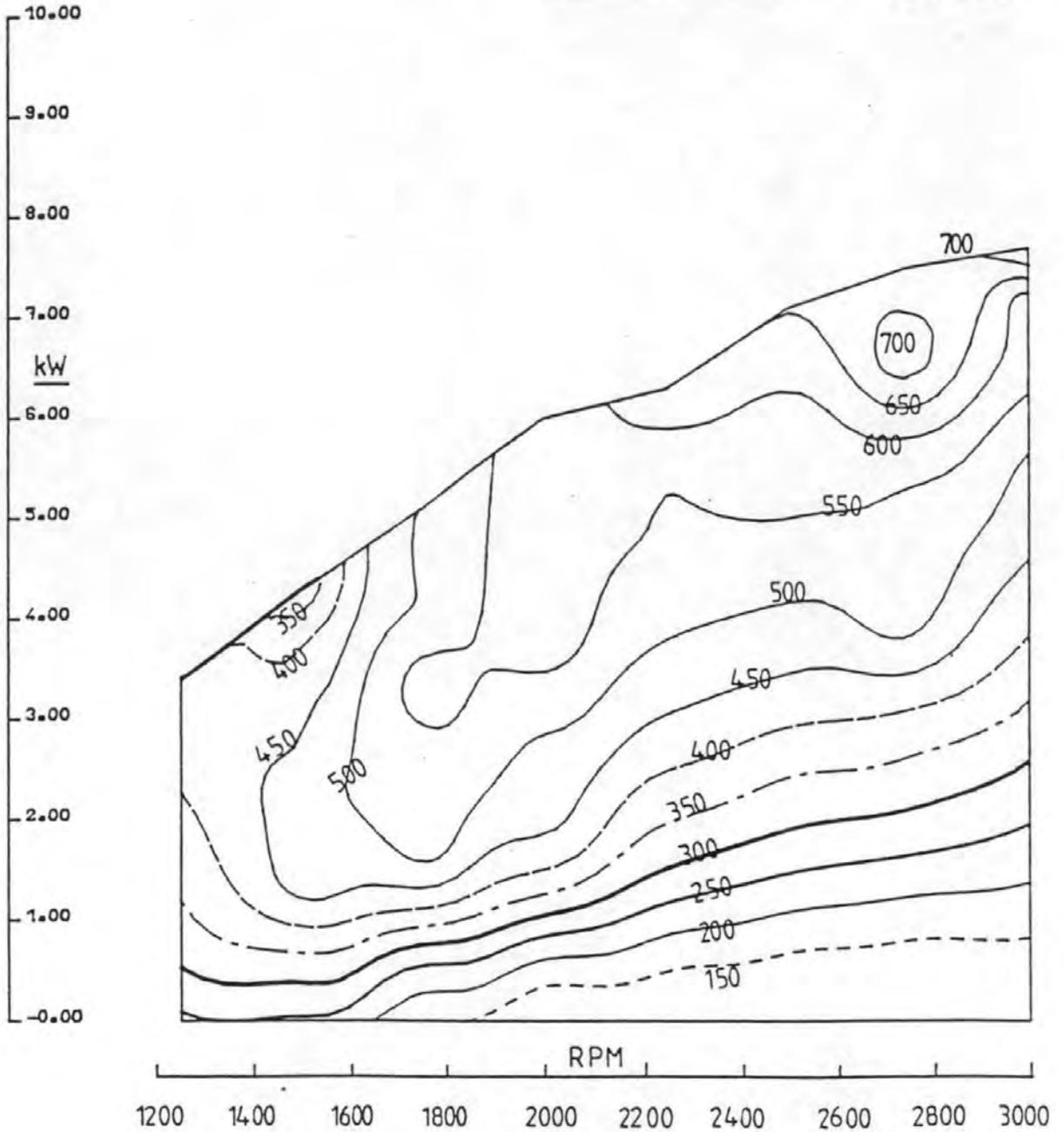


ISO-CO EMISSIONS VPM RICARDO E6 ENGINE.

Fig 3.4 Contour Map for CO Emissions from Ricardo E.6/T IDI Diesel Engine, (courtesy Perkins Engines Ltd).

KEY TO PROFILE VALUES

-----	150.000
=====	200.000
=====	250.000
=====	300.000
- - - - -	350.000
-----	400.000
=====	450.000
=====	500.000
=====	550.000
=====	600.000
=====	650.000
=====	700.000

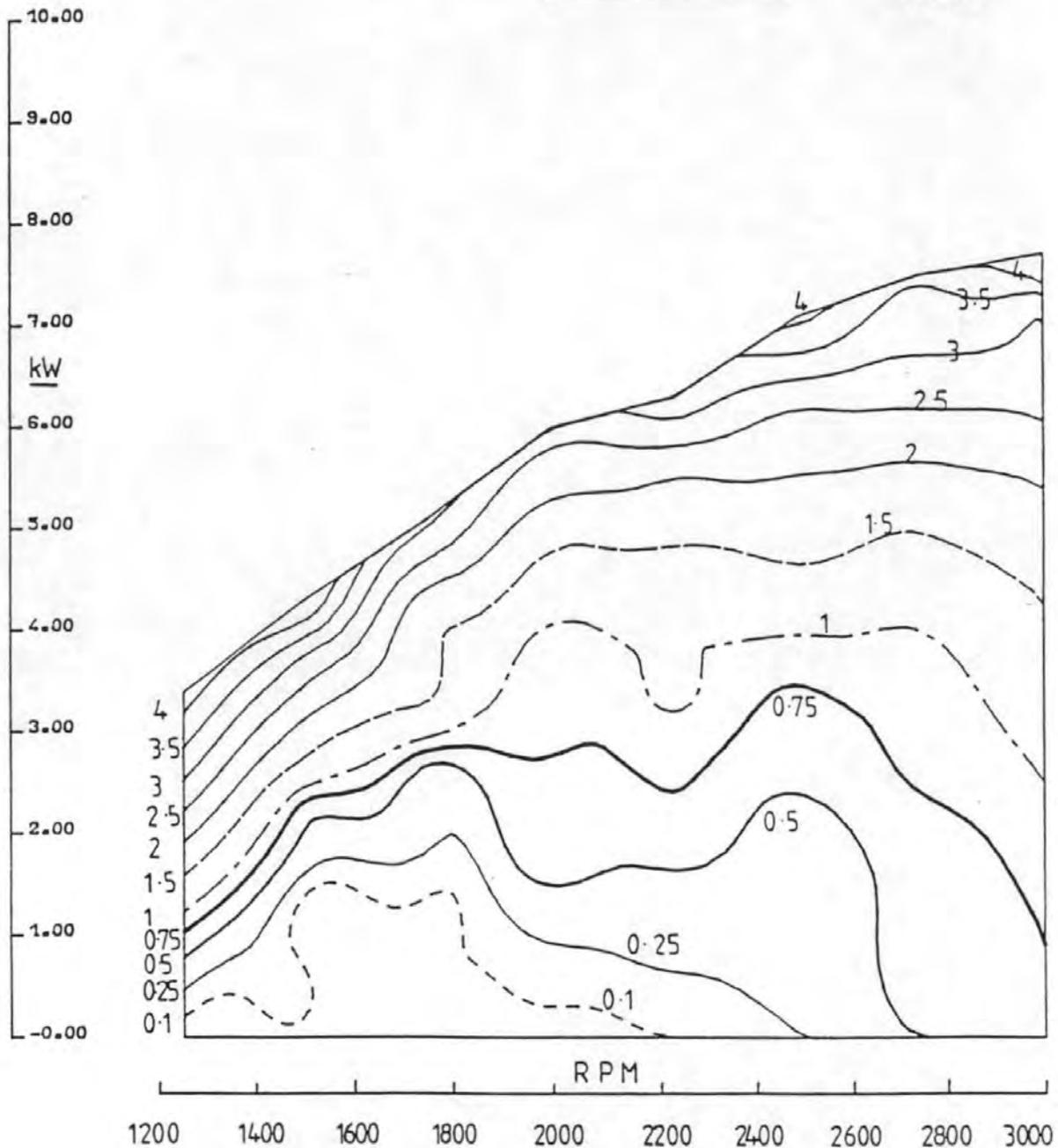


ISO-NOX EMISSIONS VPM RICARDO E6 ENGINE.

Fig 3.5 Contour Map for NO Emissions from Ricardo E.6/T IDI Diesel Engine, (courtesy Perkins Engines Ltd).

KEY TO PROFILE VALUES

-----	0.100
=====	0.250
=====	0.500
=====	0.750
-----	1.000
-----	1.500
=====	2.000
=====	2.500
=====	3.000
=====	3.500
=====	4.000



ISO-BOSCH SMOKE RICARDO E6. PLYMOUTH POLYTECHNIC

Fig 3.6 Contour Map for Bosch Smoke Measurements from Ricardo E.6/T IDI Diesel Engine, (courtesy Perkins Engines Ltd).

CHAPTER 4

The Development and Validation of a New Sampling System for Diesel Exhaust.

A new sampling system for undiluted diesel exhaust has been designed, and constructed working in close cooperation with Dr G.S.Petch. It has been fully tested and is described in this chapter.

4.1 The Need for a New Sampling System.

The intention of this research has been to investigate the origins of the extractable organic material in exhaust emissions from diesel engines. To this end, a method was required which would effectively sample exhaust emissions as close to the engine as possible. Any resulting sample had to be representative of the exhaust gas composition in the very early part of the exhaust system, immediately after the exhaust port of the engine.

In reviewing existing diesel exhaust sampling systems (section 2.2), none of the systems adequately met the present research requirements. There were several reasons for this: Firstly, the most widely used system, the dilution tunnel and filter, was originally developed for the purpose of testing engine emissions in the context of air pollution legislation, rather than more fundamental research into ascertaining the combustion processes that cause soot and PAH formation. Secondly, most of the systems appeared prone to the formation of artifacts of the

sampling. In addition to these limitations, research involving radiochemicals concurrent with the experiments described in this thesis, required the ability for a system to be able to sample the total exhaust, in order that a minimum of ^{14}C -labelled PAH could be used in any experiment, (Petch et al.1988).

4.1.1 Criteria for the Design of a New Sampling System.

The criteria for the design of a new exhaust sampling system were defined as follows:

a) To sample as close as possible to the engine.

The present research is concerned with the chemical reactions within the combustion chamber rather than those that may have occurred by the time the exhaust gases have mixed with the atmospheric environment, beyond the exhaust pipe. It follows that the residence time on any pre-sampling, transfer line had to be kept to a minimum.

b) To halt further reactions between exhaust constituents within the sample as rapidly as possible.

Thermal decomposition and chemical reactions of PAC occur very rapidly in raw exhaust at elevated temperatures above 200°C (Nielson 1984). The rate of chemical transformation is a function of temperature, reactant concentration and contact time (Williams et al.1985). At the end of combustion, the exhaust gases expelled from the combustion

chamber include high concentrations of radicals; these are highly reactive and unstable intermediate species of chemical chain reactions. It is not possible to sample these radicals intact, but the sampling system must cause existing radicals to reach a chain terminating step as quickly as possible, producing relatively stable products, thereby preventing further radical formation. To achieve this end, the exhaust gases, once sampled, had to be cooled and quenched as quickly as possible.

c) To sample for as short a period of time as possible.

A short sampling time minimises the possibility of artifact formation. It also facilitates repeated sampling within an engine test cycle. In practical terms the minimum sample time is governed by the time required to gain sufficient weight of sample for analysis. Therefore the system had to have the capacity to sample a large proportion, or the total volume of the exhaust during sampling.

d) To protect the sample compounds, once trapped by the sampling system, from further exposure to exhaust gases.

Prolonged exposure of sampled compounds to exhaust gases has been shown to increase the potential for artifact formation, (Schuetzle 1983). Therefore, the sampled compounds had to be removed continuously to a stable, unreactive reservoir, remote from sampling.

e) To sample all the organic compounds present in diesel exhaust that were condensable at standard temperature and pressure.

The sampling system had to effectively trap gas-phase organics, as well as those associated with carbon particulates, with the minimum of sample losses; this would allow reasonably accurate quantitative calculations to be made.

f) To avoid chemical artifacts of the sampling technique.

In particular, the sampling system had to prevent reactions involving the nitration of PAH from occurring, once the PAH had been sampled.

4.2 The Development of a New Sampling System.

In the development of a new sampling system a direct substitution of air dilution for dilution with an inert gas, such as argon, was considered, but, although a gas such as argon could have effectively quenched chemical reactions (Chew et al. 1968), since a gas has a low thermal capacity it would have required a large volume to cool the sample, and consequently would have been very expensive. Instead a solvent-based system was chosen, which quenched, dissolved, and cooled the organic compounds in the exhaust, and then transported them to a reservoir remote from the sampling.

In the design envisaged, the hot exhaust gases would meet a countercurrent, downward flow of cool solvent which would act as a scrubbing device to strip out of the exhaust the solvent-extractable organic compounds. In order to maximise the surface area interaction between the exhaust gases and the solvent, the system would incorporate a very large internal surface area of glass which would be covered by a thin film of solvent flowing constantly over it. Particulates would lose kinetic energy by impacting with the solvent, and then be carried downward suspended in the solvent stream. It was intended that the sampling system would be mounted close enough to the exhaust port to ensure that most of the organic compounds could be sampled whilst they were still in the gas-phase, before the bulk of them had had the time to adsorb or condense onto particulates. The flow of solvent would need to be continually replenished with a fresh supply, from the top of the device, and, after sampling, to be channelled to a remote reservoir from the bottom end. In this way continued exposure of the sample to exhaust gases would be avoided.

Initially, a prototype solvent scrubbing tower was constructed from Quickfit glassware. A large glass column was packed to half its volume with randomly placed, small pieces of broken glass in dense formation. Above the column, a water-cooled condenser was fitted, to minimise loss of sample out of the top exit, from which the remaining gases were vented. A controlled flow of solvent was released down the tower, from the top, wetting the

large surface area of glass. On entering from the base, the exhaust gases interacted with the thin film of solvent on the surface of the glass with the result that, as expected, the condensables and particulates were successfully stripped out into solution. The solvent solution, with the sample, drained to a separate collecting flask.

The prototype demonstrated that the basic design of a scrubbing apparatus could sample diesel exhaust emissions effectively. Nevertheless, it could only cope with a fraction of the total exhaust, and the cooling provided by the condenser was inadequate to prevent some losses from the top of the apparatus.

4.2.1 The Final Design: TESSA.

After trials with the prototype, a full-scale system was constructed with the capability of sampling the total exhaust flow from the experimental engine. A vertical, stainless steel tower was constructed, in a modular form of three sections, for ease of dismantling, with an overall height of 1.5 metres. Stainless steel was chosen for its robustness, relative inertness and high thermal capacity. The joints between the three sections were sealed with PTFE cord. The design is illustrated in Fig 4.1 and is supplemented by photographs in appendix A.

The lowest section was a small chamber with an inlet pipe to introduce exhaust from the engine. This inlet pipe was

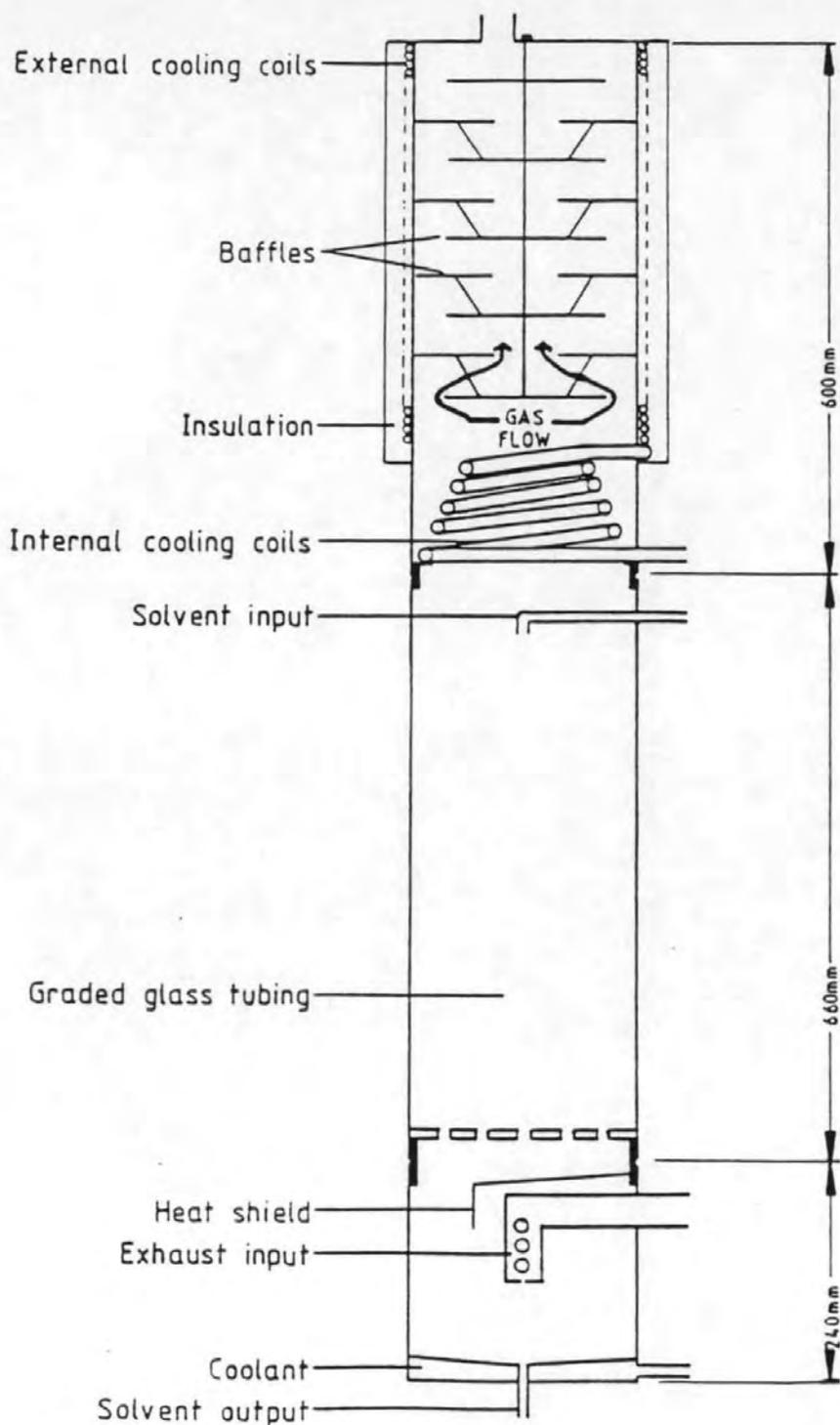


Fig 4.1

Final Design Chosen for New Sampling System.

protected, from above, by a heat shield, to prevent solvent falling directly onto its very hot surfaces. The base of the chamber was constructed with a slight decline to a central drain hole, through which the solvent and sample mixture drained; it was cooled by chilled water circulated through a channel underneath.

The middle section was filled with graduated layers of glass (Pyrex), thin wall tubing, 50 mm in length and varying in external diameter: 13 mm, 26 mm, and 38 mm. Each layer was divided from the next by a circular metal grid. A pipe, at the top of this section, fed solvent into the system, from an external solvent reservoir (2 l.) mounted on the side of the tower with a valve to regulate flow. Below the input pipe for the solvent, a metal grid covered the top layer of glass tubing; this acted as an impactor and caused the solvent to be evenly dispersed, in droplets, onto the top layer of the glass. Solvent droplets were better than a fine spray, which would have been carried upwards too rapidly by the ascending exhaust gases.

In the top section, 4 metres of coiled stainless steel tubing provided internal cooling from an external, chilled, water reservoir maintained at 4°C. Additional cooling was provided, at this point, by external cooling coils, wrapped round the outer surface of the steel tower and fully lagged on the outside. Above the cooling coil, a series of baffles was placed, which acted as impactors to trap out solvent droplets, carried up by the scrubbed exhaust gases. A fine steel mesh was wound round the baffles to aid the

impaction of very fine solvent spray. Above the baffles, an exit port allowed the scrubbed exhaust gases to be vented to atmosphere.

TESSA, when it was completed, had an internal volume of 0.0736 m³, and a total internal surface area, including that provided by the glass tubing, of approximately 10 m².

In operation, the solvent reservoir was opened a short time (15 sec) before the the exhaust gases were diverted into TESSA, at the start of sampling; in that time the solvent had wetted all the glass surfaces. Thus, the exhaust gases always interacted with solvent, rather than the solid surfaces, so that, gas-solid adsorption and the possibility of surface-catalysed reactions was avoided. Hot exhaust gases entering TESSA were cooled and quenched rapidly by the solvent. In so doing, some of the solvent was vapourised, and carried upwards into the top section, where it condensed on the cooled surfaces. The residence time of solvent and sample, not including vapour-phase solvent, was very short, in the order of a few seconds, (Petch et al.1987).

4.3 Validation of TESSA as a Sampling System.

Once the construction was completed, TESSA was thoroughly assessed to see how well it met the intentions of its design, with particular reference to the integrity of the sample collected, the avoidance of sampling artifacts, and the efficiency of the collection. A number of

experimental refinements were then made to the system.

4.3.1 Choice of Solvent.

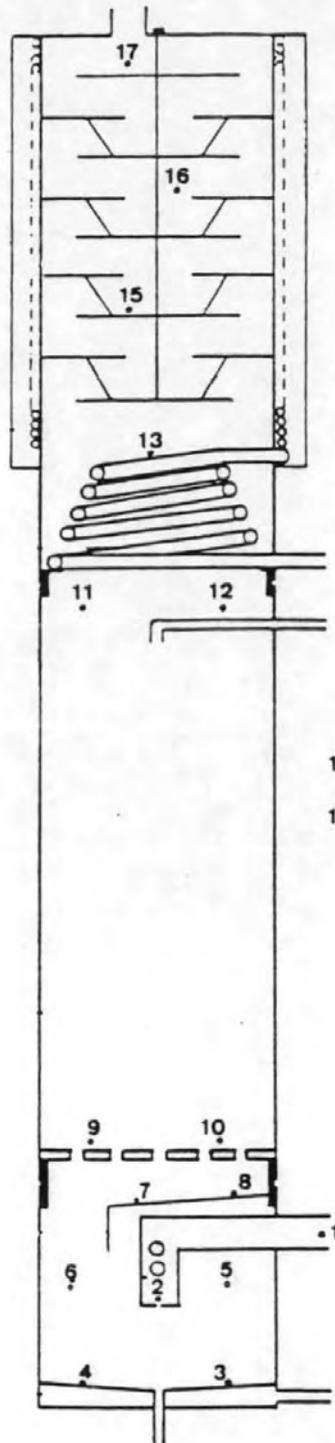
During the initial work with the prototype tower the solvent mixture had been propan-2-ol and hexane (50:50 v/v), until it was found that a rinse of DCM down the tower, after a run, removed a considerable amount of material that had remained behind in TESSA. The high boiling point of propan-2-ol also had proved inconvenient during the analytical concentration step. Methanol was tried on its own, but it failed to quantitatively trap the aliphatic compounds.

The final choice of solvent was a mixture of DCM and methanol (50:50 v/v). This solvent mixture proved to be suitable for the removal of exhaust compounds having a wide range of polarity; furthermore it had sufficient miscibility with water, over a limited range of composition, to ensure that a single phase was maintained, in spite of the inevitable presence of combustion generated water vapour in the exhaust gases. At higher proportions of water the mixture separated into two layers, an upper, aqueous methanol layer, and a lower, DCM layer containing the PAC and other organic compounds. The immiscibility of DCM with water (DCM is 2% soluble in water) and its low boiling point allowed efficient recovery of the TES using rotary evaporation under reduced pressure. Any water remaining in the sample was removed with anhydrous sodium sulphate in the analytical work-up, (Section 3.1.2).

Immediately after each sampling run, TESSA was rinsed with more of the solvent mixture (DCM/methanol, 1.5 litres), and any additional sample resulting was added to the previously collected sample, as a precautionary measure; in practice, very little additional material was collected in this way. The rinse was separately analysed on several occasions to confirm this, and the only circumstances when the rinse did contain significant additional material, was when the capacity of TESSA had been exceeded during sampling, for instance, at extremes of high speed and load. The inner surfaces of TESSA were regularly inspected, between runs, but remained remarkably clean. On the rare occasion that a run did contaminate the system, or as a matter of routine every six months, TESSA was dismantled, and the glass tubing soaked in a solution of Decon overnight; the inner surfaces of the tower were similarly cleaned.

4.3.2 Temperature Map of TESSA.

The heavy stainless steel construction of TESSA ensured that it had a massive thermal capacity, and the whole structure aided in the cooling of the sample. If the local temperature fluctuations in the lowest section of TESSA had been high enough, on occasion they might have caused thermal degradation of the DCM. Temperature variation throughout TESSA was investigated by fitting sixteen thermocouples at various points inside TESSA (the positions of the thermocouples fitted in TESSA are illustrated in Fig 4.2). The temperature fluctuations



- 18 Ambient Temp.
- 19 Cooling Water Temp.

Fig 4.2 Position of Thermocouples Fitted Inside TESSA.

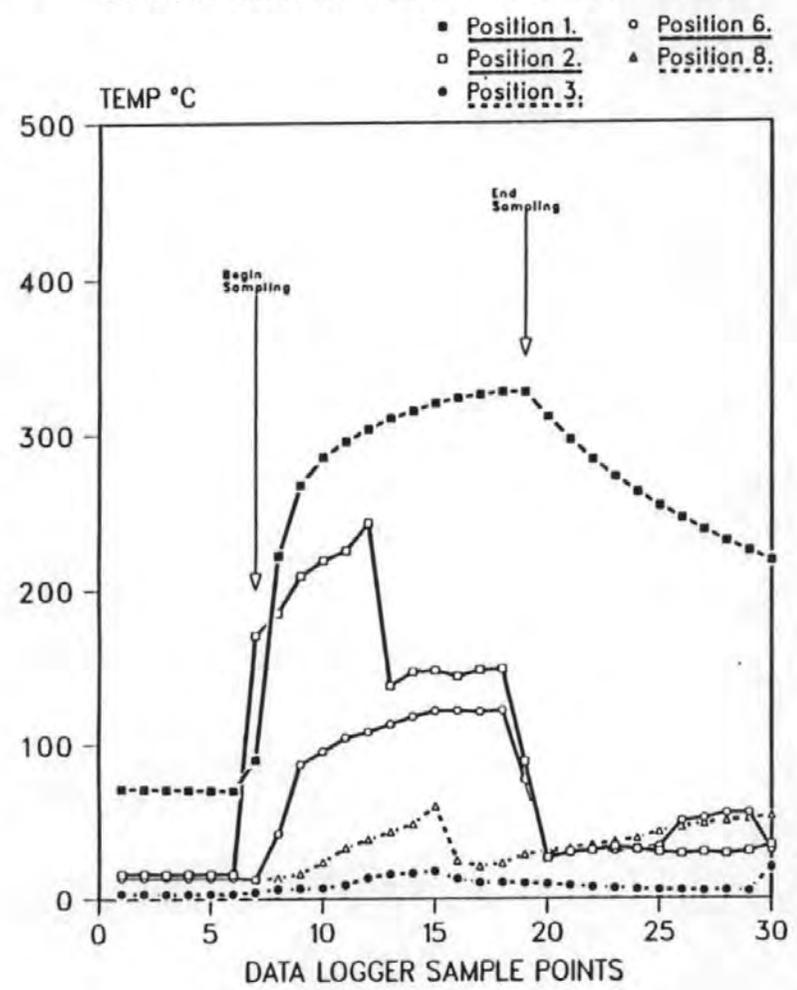
were recorded for each of the thermocouples every 15 seconds, throughout a three minute TESSA run, with the aid of a computerised Data Logger (details given section 3.6.2). The measurements were first made under standard conditions, (2000 rev/min, 3.4kW), and then repeated under conditions of high speed and load, (2750 rev/min, 7.0 kW). The results for the two runs are plotted in Figs 4.3(a+b) and 4.4(a+b). The most extreme fluctuations occurred at the exhaust inlet, in the lowest section of the tower, but even at this position the temperature remained below 350°C, except for a momentary very high temperature recorded for the high speed and load run, which probably reflected an unevenness in the solvent flow. There was a very steep gradient of decreasing temperature going up TESSA and at the exit port the temperature did not exceed 40°C at any time.

4.3.3 The Influence of Acidic Gases on the Sample.

There are two sources of acidic gases in the exhaust of a diesel engine. One is from the high temperature oxidation of N₂ gas, present in air, to form NO within the combustion chamber. The other is from sulphur, which may be present in diesel fuel, and can result in low levels of sulphuric acid in the exhaust. The significance of acidic gases in TESSA, was the possibility that they might promote the nitration or oxidation of PAH in the sample; the resulting compounds would have been artifacts of the sampling.

This problem of acidic gases was assessed by substituting

a) TEMPERATURE MAP FOR TESSA:
LOWER SECTION 2000 RPM MID-LOAD



b) TEMPERATURE MAP FOR TESSA:
UPPER SECTION 2000 RPM MID-LOAD

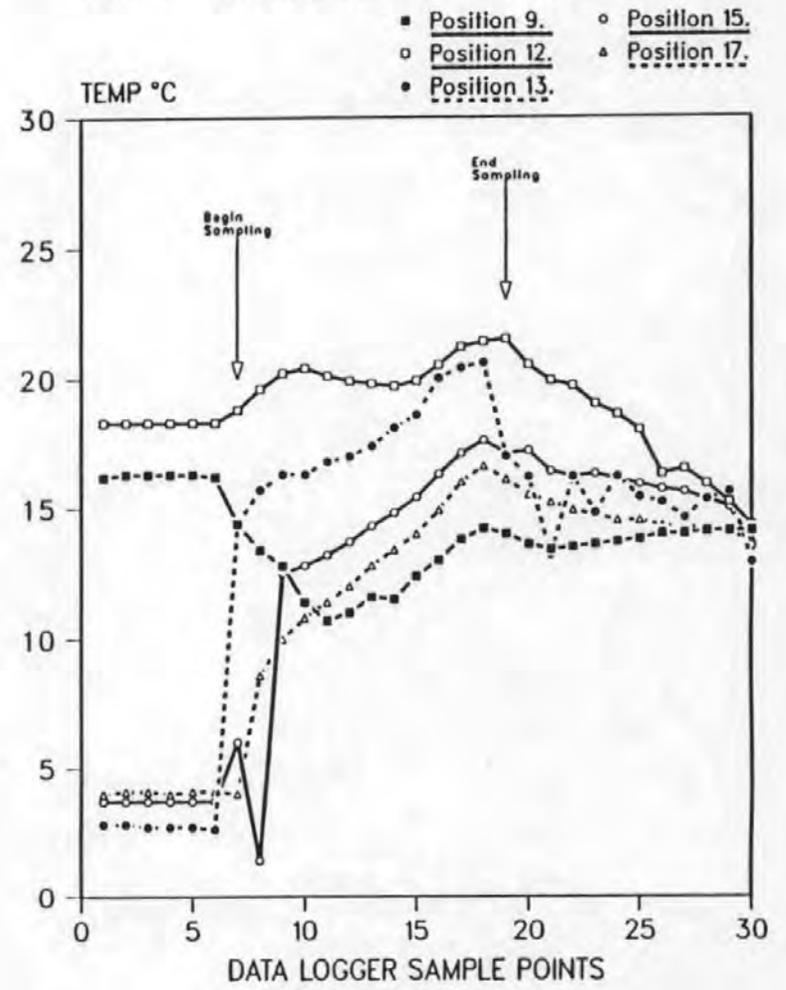
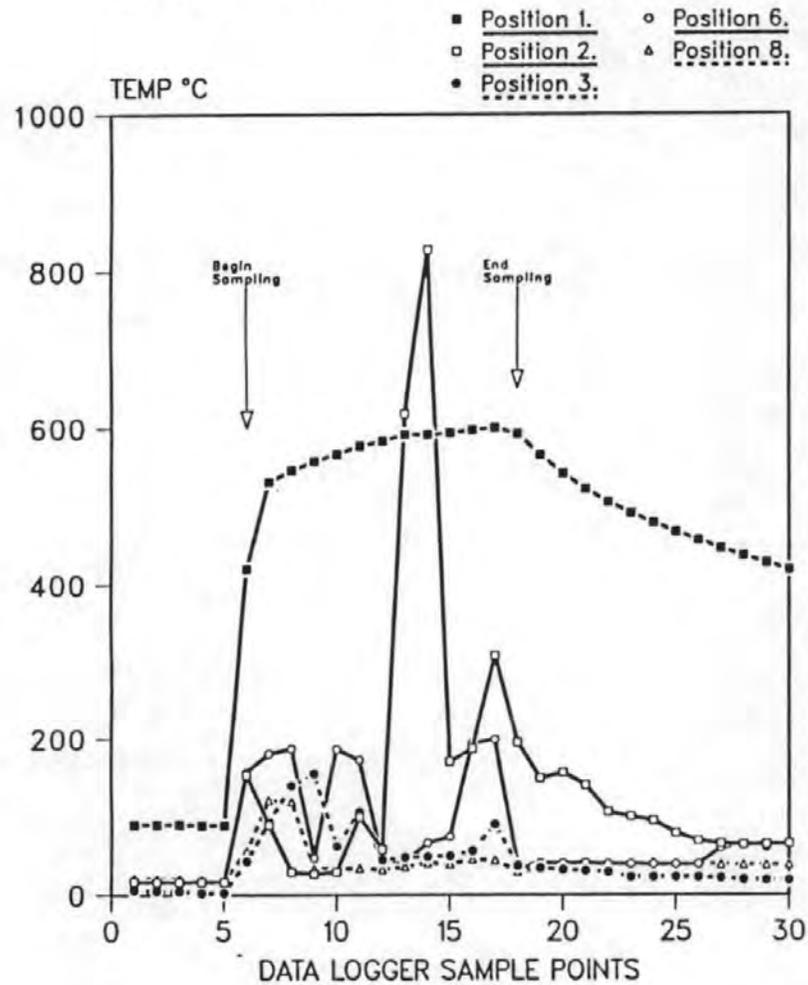


Fig 4.3 Temperature Fluctuations in TESSA During Sampling, 2000 rev/min 3.4 kW.
a) Lower Section b) Upper Section.

a) TEMPERATURE MAP FOR TESSA:
LOWER SECTION 2750 RPM HIGH-LOAD



b) TEMPERATURE MAP FOR TESSA:
UPPER SECTION 2750 RPM HIGH-LOAD

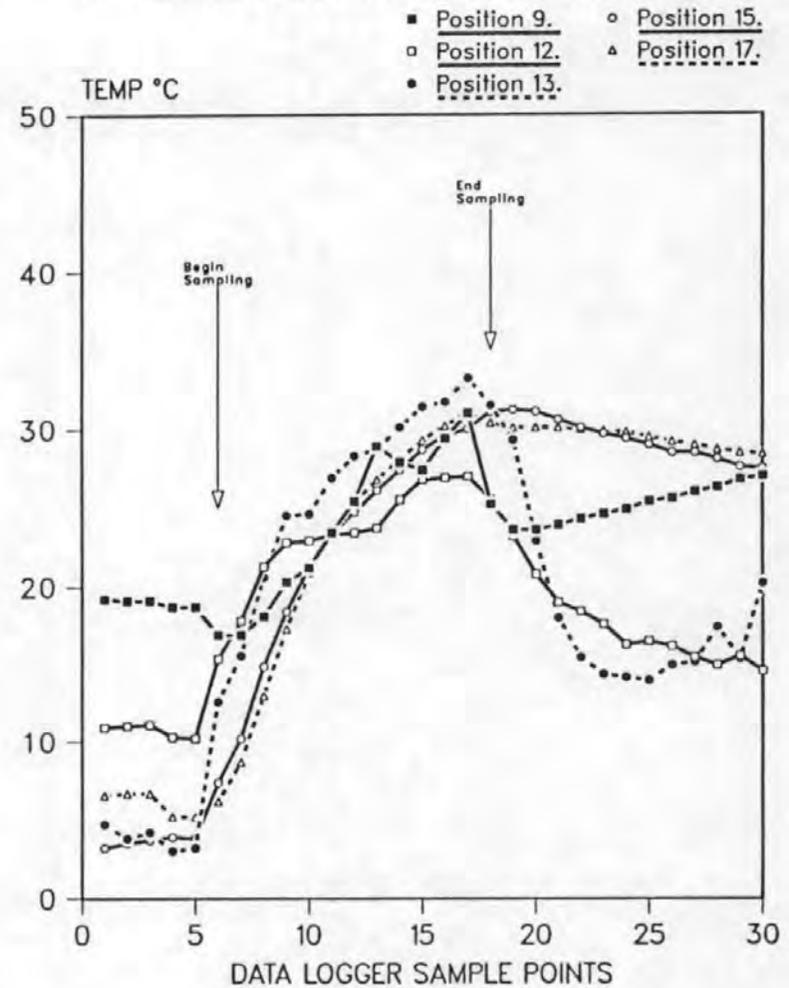


Fig 4.4 Temperature Fluctuations in TESSA During Sampling, 2750 rev/min 7.0 kW.
a) Lower Section b) Upper Section.

distilled water (2 litres) for the normal solvent mixture, and taking a three minute TESSA sample, under standard engine conditions. At the end of the run, the water had a pH of 1.9, measured with a pH meter; this indicated that there was a strongly acidic environment in TESSA. One solution would have been to add a buffer to the solvent mixture; but this was likely to have altered the equilibrium between the solvents, particularly if the buffer had been aqueous-based, and also might have affected sampling, adding another uncertainty to an already complex situation.

The residence time of solvent and sample in TESSA was calculated to be in the order of a few seconds, and it was decided that the real danger of nitration reactions was in the collecting reservoir. Consequently, rather than adding a buffer to TESSA, distilled water (2 litres) was added to the collecting reservoir before sampling began. The distilled water was present in sufficient excess, to cause the solvent mixture to separate into two phases, as soon as it entered the collecting reservoir from TESSA; the acidic species dissolved in the upper aqueous methanol layer, whilst the PAC and other organic compounds remained in the DCM layer underneath, with which they have a strong affinity.

4.3.4 Recovery of Particles.

It was the intention in the design of TESSA that it should trap PAC and other organic compounds from the exhaust

before they had had time to adsorb to the carbon particles invariably present with a diesel engine. Carbon particles from the engine were efficiently scavenged in TESSA, by collision with solvent droplets, and were transported by the solvent, along with the dissolved part of the sample, into the collecting reservoir. After the end of sampling the solvent mixture was filtered, under reduced pressure, (details in Section 3.1.2). The solvent mixture caused the particles to coalesce into larger particles, which consequently were completely trapped by the filters, no breakthrough of the filter was observed; the mean particle size within diesel exhaust is $0.02 \mu\text{m}$ (Ross et al.1982), which would have been too small to filter efficiently without coalescence.

Along with the particles, there was also a considerable amount of other material visible on the filter. This was mainly debris that had been picked up from either TESSA or the transfer pipe and consisted of fine fragments of glass, grit and rust. This material made a sufficiently large contribution by weight to prevent quantitative weighing of the diesel particles. The material was almost completely inorganic in nature (electron microscope analysis was undertaken by another researcher, Horn 1985)

The extent that organic material, within the exhaust, had already adsorbed onto the particles prior to entering TESSA, and subsequently had remained adsorbed after the particles had been trapped by the solvent, was assessed. A filter containing particles, filtered from a typical

TESSA run, was subjected to soxhlet extraction, and the resulting extract prepared for HRGC analysis (details in Section 3.1.1). The weight of the solvent soluble material that was extracted by this means was small (0.4 mg), and when compared to the total sample weight (60 mg), represented less than 1% of the TES. This was considered an insignificant amount, since the weights recorded were of the same order of magnitude as the typical level of contamination remaining on a filter, even after it had been heated in a muffle furnace.

The HRGC chromatogram of the unfractionated solvent soluble sample from the filter is shown in Fig 4.5. It is quite different from a TES in that it contains relatively more material with a high retention time beyond 24 minutes. Nor does it resemble lubricating oil, since it is without the characteristic UCM hump between 24 and 32 minutes (c.f. Fig 5.7a showing chromatogram of a lubricating oil). In fact, many of the components can be matched with the extract from a clean filter. These results suggested two possible explanations: Either the PAC and other organic compounds, present in the diesel exhaust, were being trapped successfully by TESSA, before they could adsorb onto the particle surfaces; which would be expected at the elevated temperatures- above 300°C- of the transfer pipe. Or, alternatively, some adsorption of organic compounds to the particles might have already occurred, but these were extracted from the surfaces, once the particles entered the solvent system. In any event, the end result was acceptable.

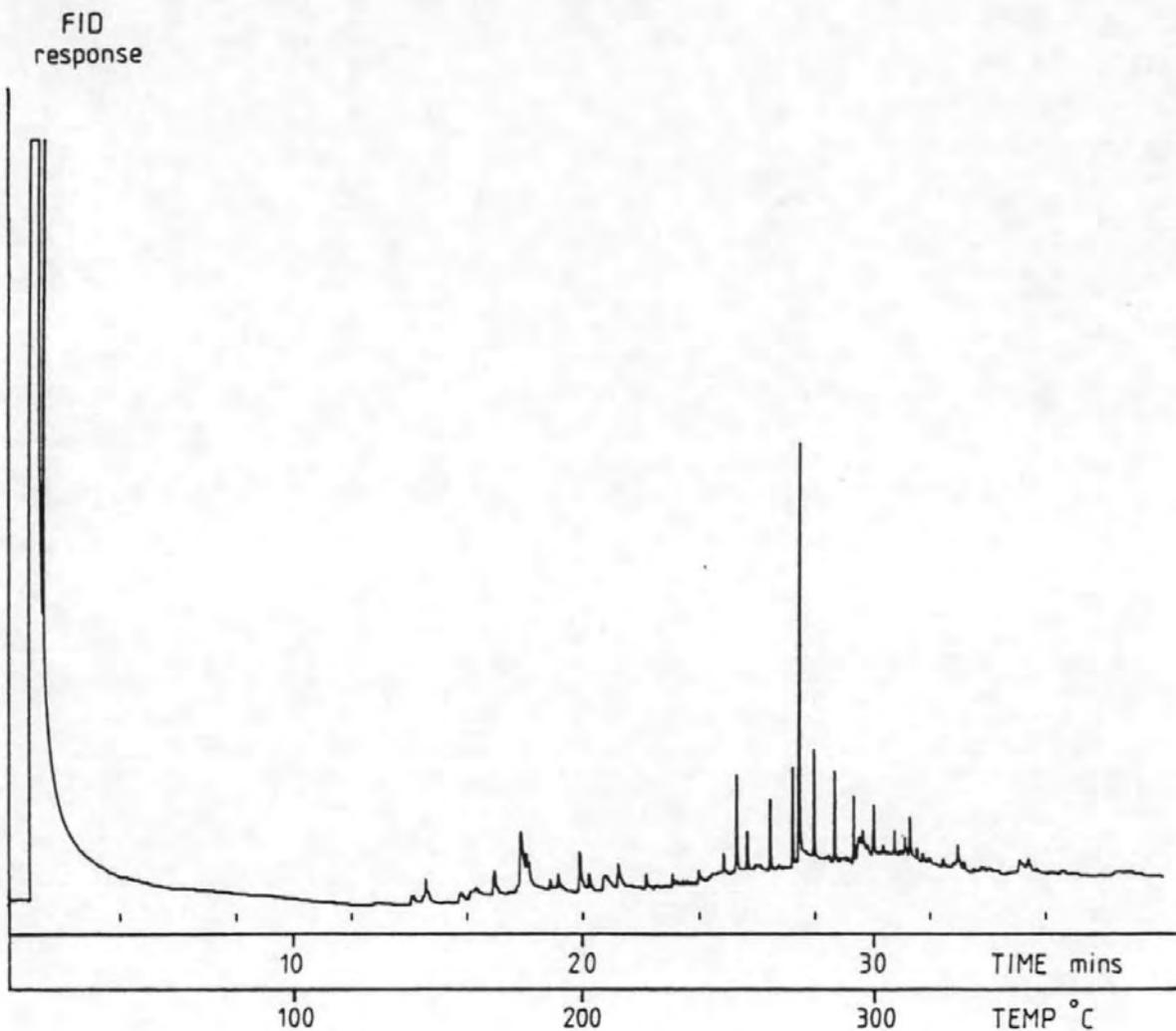


Fig 4.5

Gas Chromatogram of Soxhlet Extracted Filter
of Particulates from TESSA.

4.3.5 Losses from the Top Exit of TESSA.

During a sampling run with TESSA, the exhaust gases were vented from the exit port, having been stripped of solvent soluble organic material and the particles. The exhaust products which were gaseous at STP, N₂, NO, NO₂, CO, CO₂, and O₂, also included vapour from water and DCM. It was found that up to 20% of the DCM could be vented from the exit port in a vapour state; this was due to the relatively low boiling point (40°C) of DCM compared to that of sample components.

The proportion of potential TES not trapped by TESSA, but vented from the exit port, was ascertained by sampling a portion (6-10%) of the effluent gases with a liquid nitrogen trap. The bulk of material trapped by the nitrogen cold-trap was found to be water from combustion, DCM and methanol. The organic material was extracted from this mixture by liquid/liquid partition, after adding an excess of distilled water (15 cm³); 3 extractions of DCM (5 cm³) removed any organic compounds of interest. These washes of DCM were collected together and concentrated by rotary evaporation and nitrogen blow-down before fractionation and HRGC analysis. Recovery weights were too low to get accurate masses for the aliphatic hydrocarbon (0.2 mg) and aromatic (0.2 mg) fractions. The results of the HRGC analysis Fig 4.6(a+b), show a similarity with a typical gas chromatogram from a TES (c.f. Fig 5.10), suggesting that some fine droplets of DCM passed

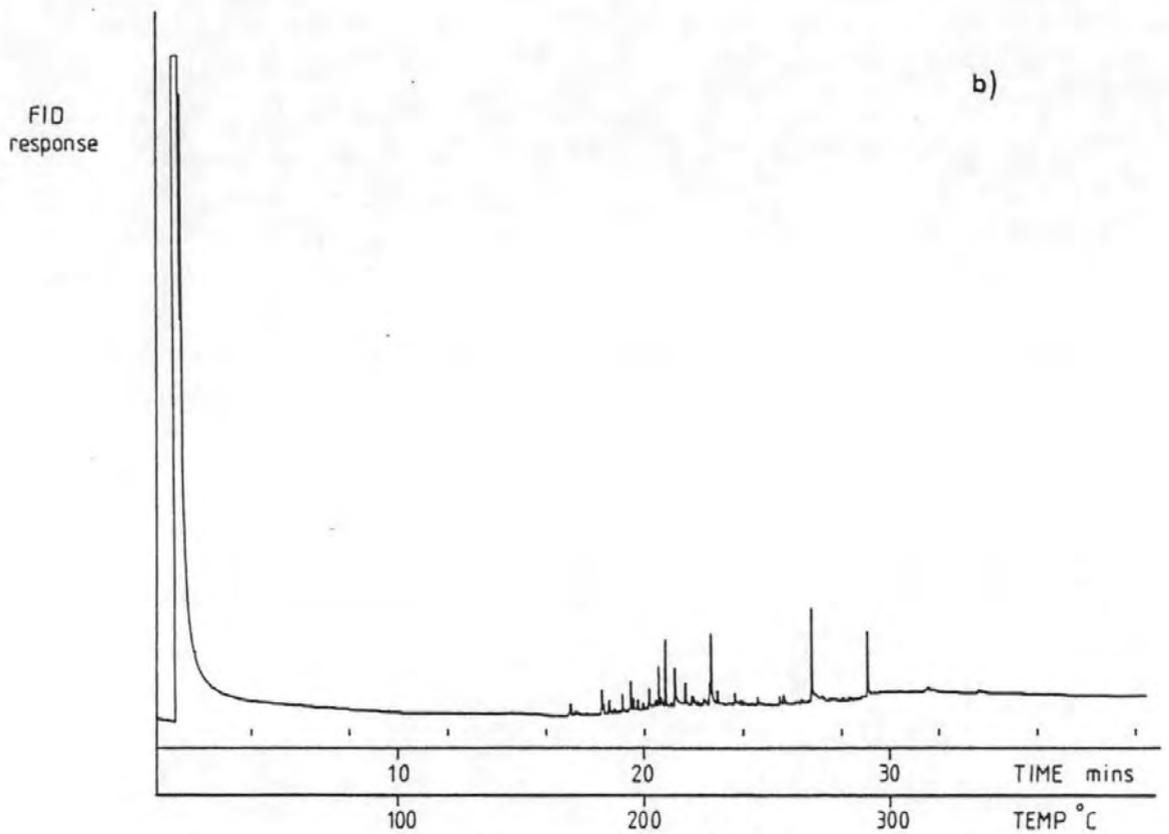
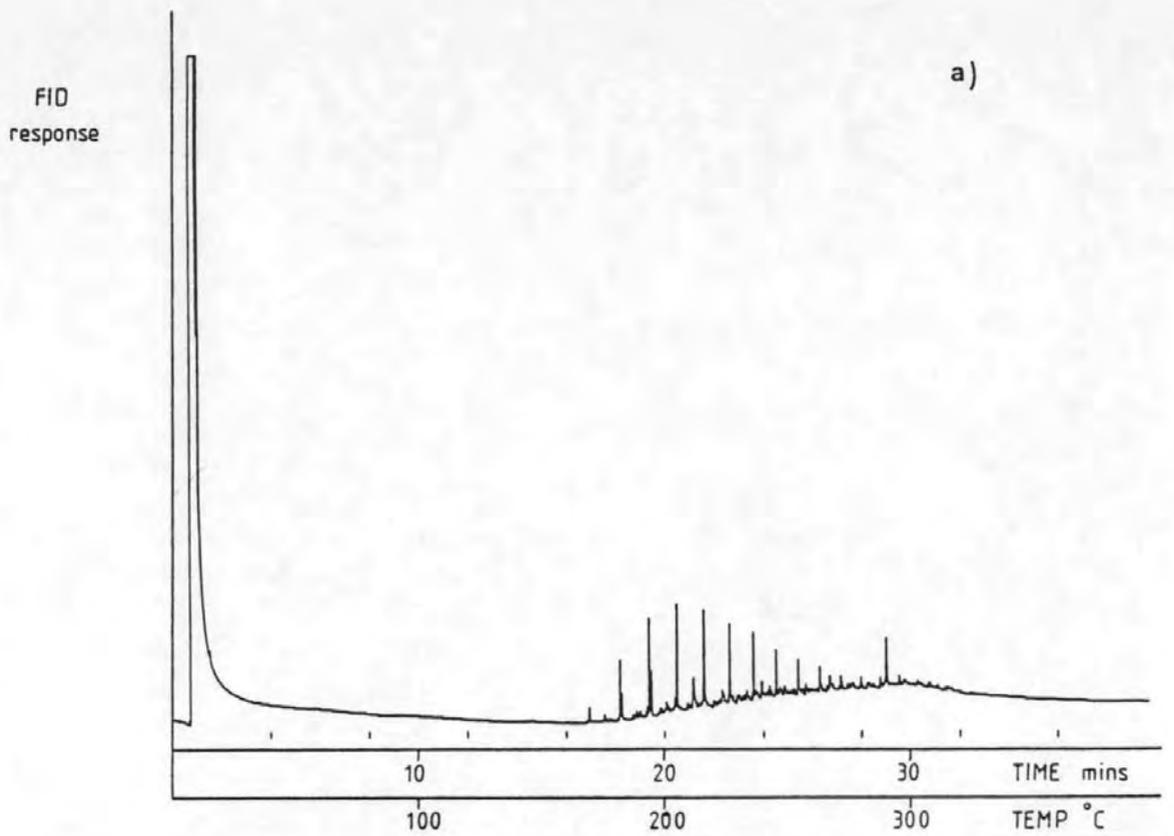


Fig 4.6

Gas Chromatograms of Organic Material
 Sampled at Exit Port from TESSA by Nitrogen
 Cold-Trap: a) Aliphatic Hydrocarbon
 Fraction b) Aromatic Fraction.

out of the system as well as DCM vapour; the amount was very small.

This experiment was repeated several times, and from these results, the total losses were calculated to be 5-6% of the total TES and, as such, were acceptable. The breakthrough of sample components increased at high load and speed when the capacity of TESSA was exceeded. Nevertheless, sampling at high load and speed could easily be achieved, quantitatively, by taking only a portion of the total exhaust through TESSA. Proportional sampling would only be a problem if experiments using radioactive tracers required a complete recovery.

4.3.6 Recovery Efficiency Achieved with TESSA.

An experiment was undertaken to assess the recovery efficiency of TESSA by adding 11 PAH standards to the solvent mixture before a sampling run with TESSA. From the standard solution containing the 11 compounds, each at an approximate concentration of 2 mg/cm³, two aliquots of equal volume (1 cm³) were taken. One of the aliquots was added to the 2 litres of solvent mixture in preparation for a sampling run with TESSA, and the other was placed in a clean vial. The percentage recovery of the 11 PAH, after passing through TESSA and being subjected to the routine analytical clean-up and fractionation procedure, described in section 3.1.2, was assessed by direct comparison with the GC/FID response from the analysis of the second aliquot. This second aliquot, therefore, represented the

original concentration of the 11 PAH added to the solvent mixture. The gas chromatograms of the aromatic fraction of the TES with the additional PAH, and that of the 11 PAH on their own, is shown in Fig 4.7(a+b).

The percentage recoveries of the 11 PAH were calculated and are shown in Table 4.1. Many of the PAH standards used, were also present in the fuel and TES, consequently, adjustments had to be made by the subtraction of the normal values that had been measured for these compounds in previous runs. The concentration of each PAH standard was chosen to minimise the influence of the same PAH present in the TES which were at much lower levels than the standards. Naphthalene was the only PAH standard whose recovery was unacceptably low. The low recovery, in this case, was due to the low relative molecular mass, high volatility, and high solubility in water for this two-ring aromatic compound.

Naphthalene	40%
Phenanthrene	91%
Anthracene	96%
Fluoranthene	93%
Pyrene	92%
Chrysene	95%
Benzo(e)pyrene	93%
Benzo(a)pyrene	79%
Perylene	76%
Benzo(ghi)perylene	77%
Coronene	81%

Table 4.1 Recovery Percentages for 11 PAH Added to Solvent in TESSA.

The recovery percentages indicated that TESSA was effectively trapping the PAH from diesel exhaust. The recoveries included the losses that had occurred during the

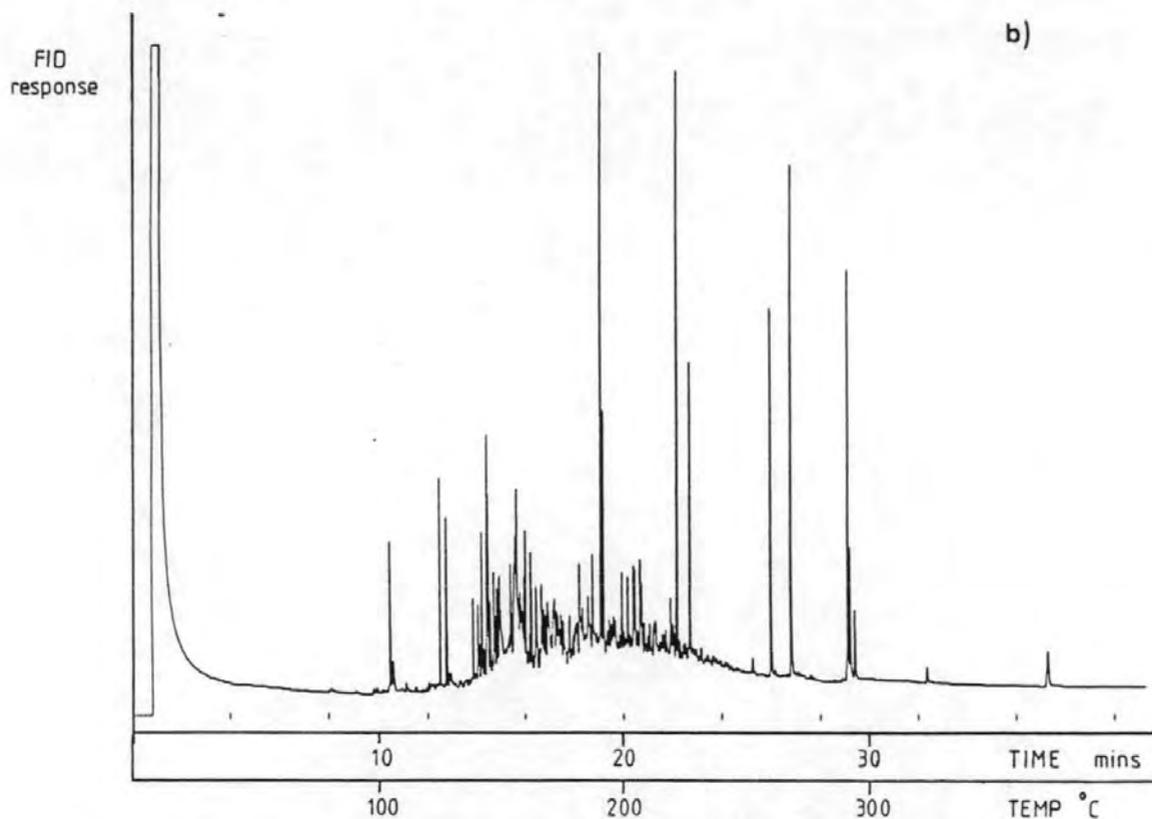
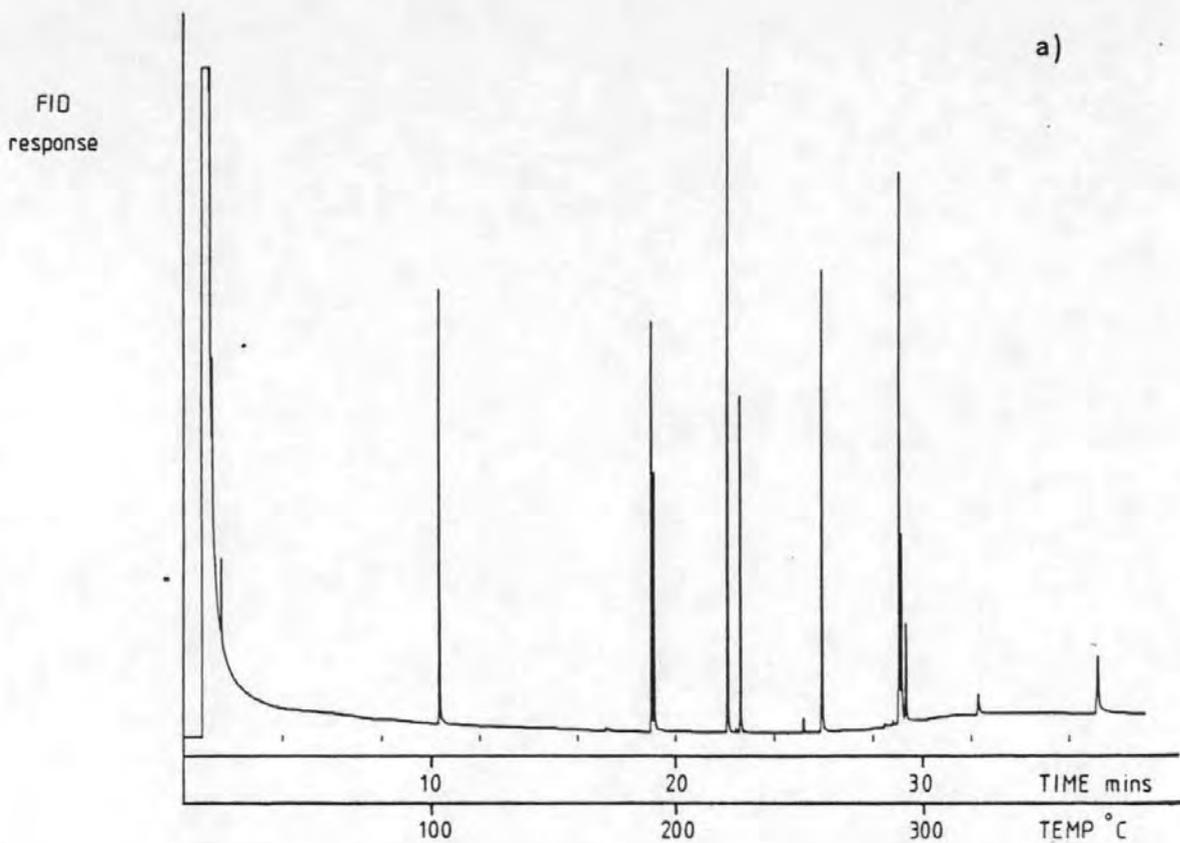


Fig 4.7

Gas Chromatograms from Recovery Experiment:
 a) 11 PAH Standards b) Aromatic Fraction
 of TES Showing the Recovery of the PAH
 standards.

various stages of the analytical work-up after the sampling. These analytical losses were assessed in another experiment in which a solvent mixture identical to the one used in TESSA was made up to a similar volume (3.5 litres) and was then spiked with 2-ring, 3-ring, 4-ring and 5-ring PAH standards (at a concentration of 0.2 mg/cm³ for each PAH). This solvent mixture was not put through TESSA, but was subjected to an analytical work-up identical to that for a TES. The resulting sample was suitably fractionated and diluted for HRGC analysis. The quantification of the relevant peaks, in the chromatogram for the aromatic fraction, indicated the losses occurring during analytical preparation, after sampling with TESSA, but prior to gas chromatographic analysis (Table 4.2).

Naphthalene	59%
Phenanthrene	96%
Pyrene	95%
Perylene	97%

Table 4.2 Recovery Percentages of PAH Through Analytical Procedure.

The nitrogen blow-down step in the analytical procedure was subsequently found to be the cause of the greatest losses of naphthalene; when this step was performed with increased care the losses were minimised. The experiment described above also tested the degree of purity of the solvents that were being used routinely. In the event, the solvent mixture showed only low levels of background contamination, which did not become significant because the sample masses (typically 70 mg), recovered from a 3 minute duration sampling run of TESSA, were much larger.

4.3.7 Sources of Contamination in TES.

Background contamination, from solvents and other possible sources, was monitored throughout the experimental period. For the most part, the inevitable levels of contamination, associated with reducing the volume of the solvent mixture from 4.5 l. to 1 cm³, remained insignificant, because of the large weight of the actual sample. Contamination levels remained at a fraction of 1 percent of the sample weight and consequently did not interfere with the analysis of PAC and other organic compounds.

There were several exceptions to the general circumstances where contamination became a problem. Throughout the experimental work, there was frequently a representation from two compounds, commonly associated with plastics. The first was 2,6-Bis(1,1-dimethyl ethyl)-4-methyl phenol, commonly known as butylated hydroxy toluene (BHT), which is widely used as an anti-oxidant in plastics and other products. The second was the di-isooctyl ester of 1,2-benzenedicarboxylic acid, a typical phthalate ester used as a plasticiser. GC/MS spectra were used to identify these two compounds and are shown in Fig 4.8(a+b). The types of compounds represented by these two are ubiquitous and invariably were present, at low concentrations, in samples.

A more specific contamination arose from various materials used within the steel tower and the transfer pipe. Some

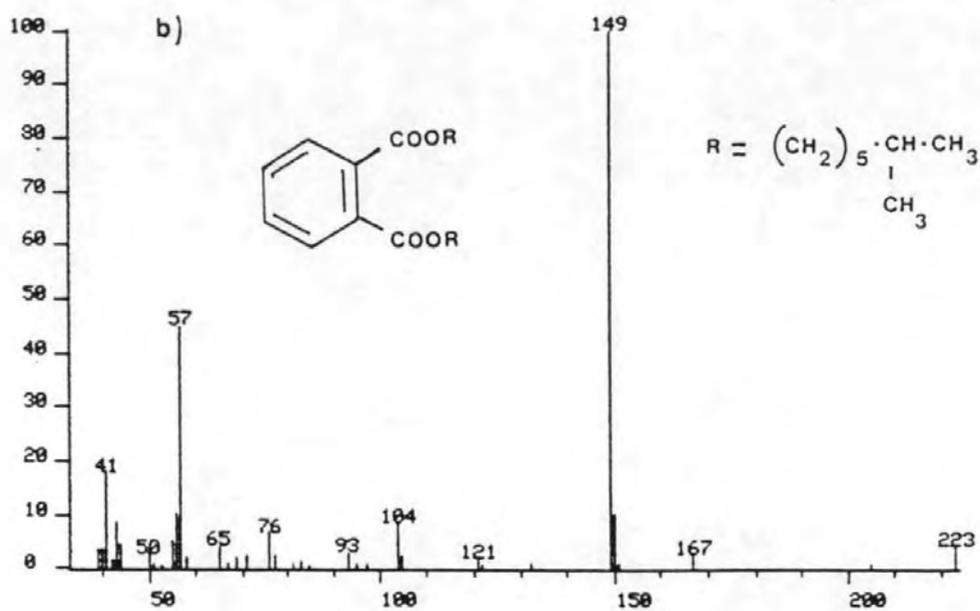
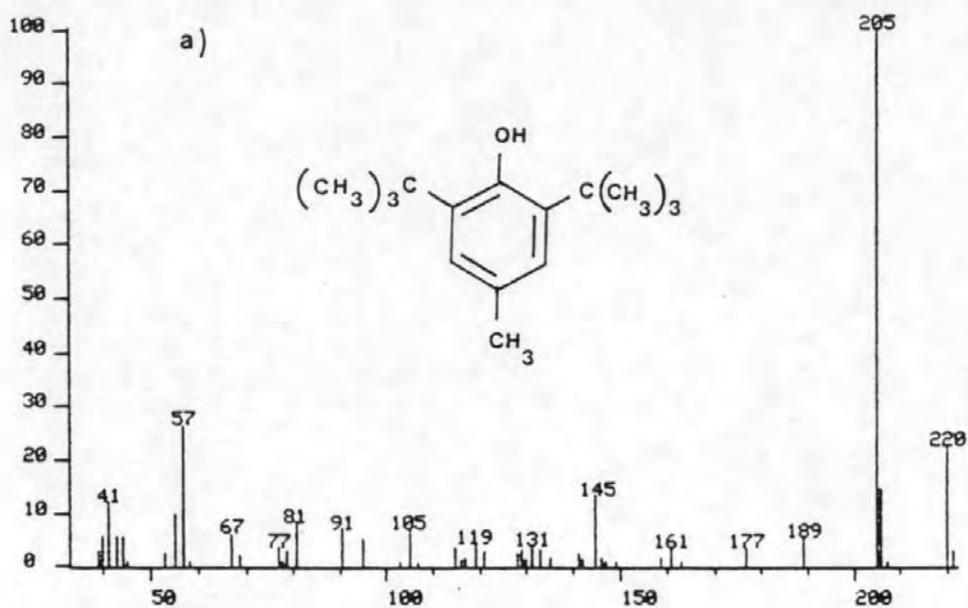


Fig 4.8

GC/MS Spectra Identifying Contaminants:

a) Butylated Hydroxy Toluene

b) A Phthalate Ester of Benzene

Dicarboxylic Acid.

gas chromatograms revealed the presence of a background level of high relative molecular mass n-alkanes typical of lubricating greases (Fig 4.9a). Lubricating oil itself is dewaxed and does not contain these compounds, and they were probably introduced during the various engineering adjustments made to the Ricardo E6.T engine or exhaust transfer system.

The PTFE sealant cord used in TESSA was soxhlet extracted (12 h. with DCM) and yielded a fine petroleum based oil which comprised 3.5% of the cord by weight. HRGC analysis of this extracted material showed that it was highly dewaxed and comprised for the main part unresolvable complex material contributing to a distinct hump (Fig 4.9b). It is worth noting that soxhlet extraction is a viable means of cleaning this cord before using it on the TESSA joints, but that the process causes an approximate. 10% shrinkage in length so that correct lengths should be cut after pre-extraction.

The worst contamination problems occurred after small amounts of epoxy resin glue were used to fix thermocouples to the inside surfaces of TESSA, in order to measure temperature fluctuations. The strength of the solvent mixture was sufficient to render the adhesive qualities of these substances ineffective. Small particles from the glue were dislodged and became trapped between parts of TESSA, so that, each time solvent was passed down TESSA during a run, further polymeric material originating from the glue fragments was extracted. The problem was solved

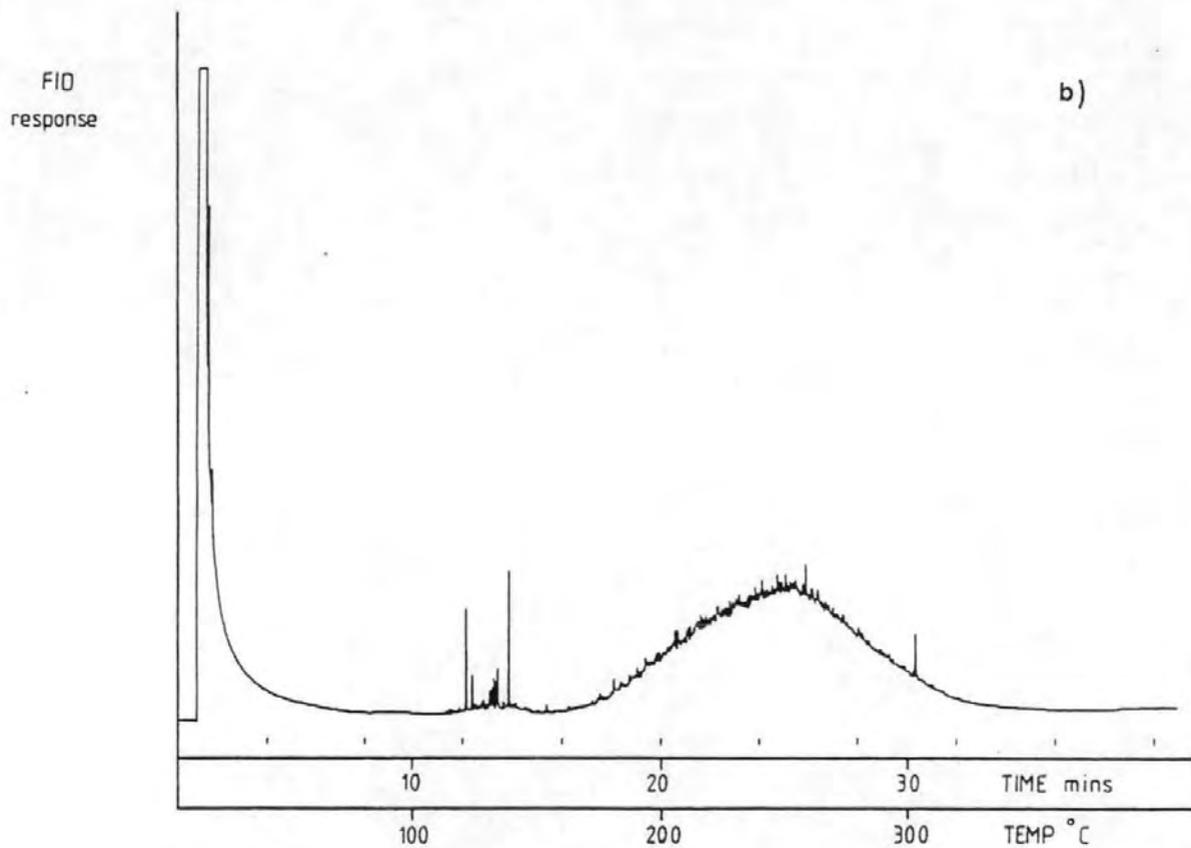
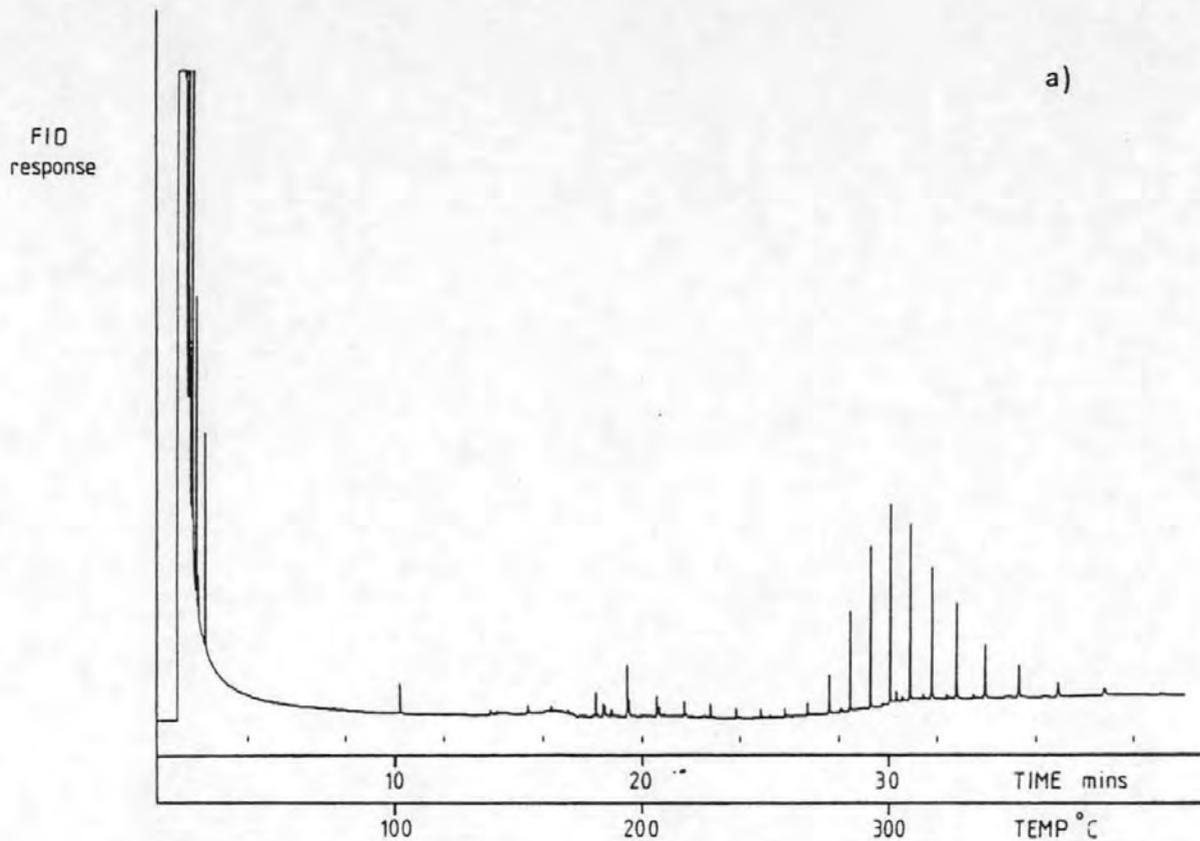


Fig 4.9

Gas Chromatograms Showing Contamination Present in TESSA: a) Lubricating greases, High Molecular Weight Alkanes. b) Soxhlet Extract of PTFE cord.

by dismantling TESSA, removing all the glass packing and cleaning the inside surfaces.

On dismantling TESSA after six months of use, a white substance was noticed collected around the lower part of the mesh as it meets the baffles in the top section of TESSA. At first, it was feared that this material might include high relative molecular mass, organic compounds from the exhaust sample. After extensive analytical tests, including solvent extraction and analyses by HRGC, UV fluorescence and IR spectroscopy, it was concluded that the material was totally inorganic and originated from the corrosion of the wire mesh itself.

4.3.8 Routine Sampling Procedure with TESSA.

1/ The cooling system is turned on 3 hours before sampling; at the end of this time, ice is added to the cooling reservoir to bring the temperature down to 4°C.

2/ The engine is started and run at high speed and load for 1 hour. It is then throttled down to the specific sampling conditions selected and run for a further 15 mins to warm up and condition the engine before sampling begins.

3/ The collecting reservoir is placed in position with distilled water (2 l.) added. Solvent mixture (2 l. of DCM/Methanol) is added to the solvent reservoir.

4/ Oil and water temperatures in the engine are

routinely monitored. The time for the engine to consume 50 cm³ of fuel is measured for the test conditions immediately before or after the sampling run.

5/ Solvent flow is started 15 secs. before sampling begins in order to wet glass surfaces.

6/ Exhaust gases are diverted to TESSA via a transfer pipe at the beginning of sampling.

7/ Sampling continues for 3mins., during which time the solvent flow is carefully monitored.

8/ At the end of sampling, the exhaust gases are diverted back to the main exhaust.

9/ A rinse of the solvent mixture (1.5 l.) is put through TESSA and collected with the rest of the solvent/sample in the collecting reservoir.

10/ The solvent and sample in the collecting reservoir are then filtered, under reduced pressure, to remove the particulates, and the DCM layer of the extract isolated by liquid/liquid partition. The analytical steps involved in preparing the TES are more fully described in the analytical section 3.1.2.

4.4 Conclusions.

The validation of TESSA has confirmed that it is a useful

and effective new sampling device, flexible in use, which enables additional chemical information to be obtained from raw diesel exhaust. The comprehensive nature of the TES is more representative of the exhaust than the samples from other sampling systems previously reported. The intention in TESSA's development was not to replace any of the other sampling systems but to construct a system that could meet specific research needs and thereby supplement existing equipment. This end has been achieved successfully.

The limitations of TESSA were fully explored, and the effects of acidity, excessive temperature, and the possibility of excessive sample losses from the exit port assessed satisfactorily.

CHAPTER 5

Results and Discussion of Experiments Undertaken with TESSA and the Ricardo E.6/T Diesel Engine.

This chapter describes the HRGC and GC/MS analyses of the fuel and lubricating oil and the comparison between them and the TES obtained from three separate experiments with TESSA: Sampling under standard conditions, sampling at high speed and load, and sampling further down (3m) the exhaust tailpipe.

5.1 Analysis of the Fuel.

The fuel used throughout the experiments undertaken at Plymouth was a standard BP Gas Oil, A2 Derv with a boiling point range of 200-360°C (c.f. diesel with boiling point range of 150-250°C), specific gravity 0.845, approximately 0.25% sulphur, and an aromatic content of 25-30%, (David 1988). An aliquot of the fuel was taken and fractionated into aliphatic and aromatic fractions using silica column chromatography described in chapter 3.1.4. These were then suitably diluted with DCM (2 mg/cm³) and analysed by HRGC, Fig 5.1(a+b).

The aliphatic hydrocarbon fraction shows a dominance from the homologous series of straight chain n-alkanes starting with n-C9 and going up to beyond n-C27. In the fuel the n-alkanes are in approximate normal distribution around n-C16. Pristane and phytane, the branched alkane

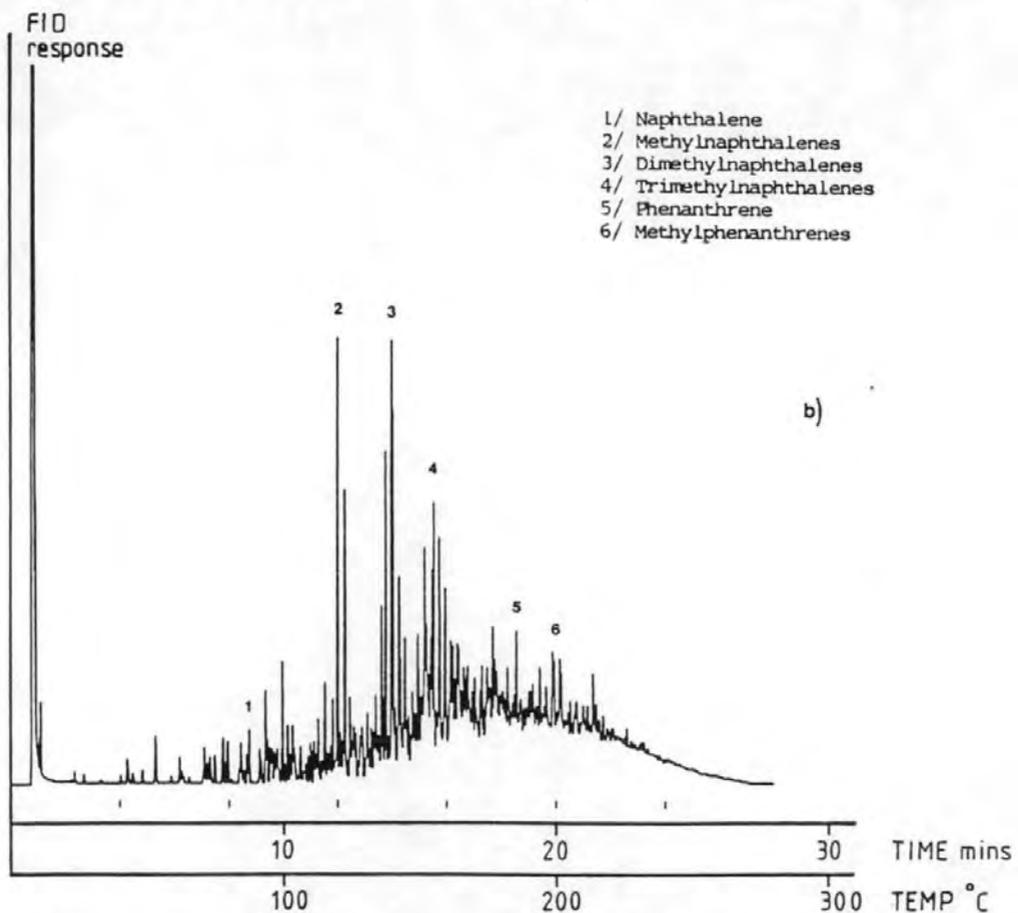
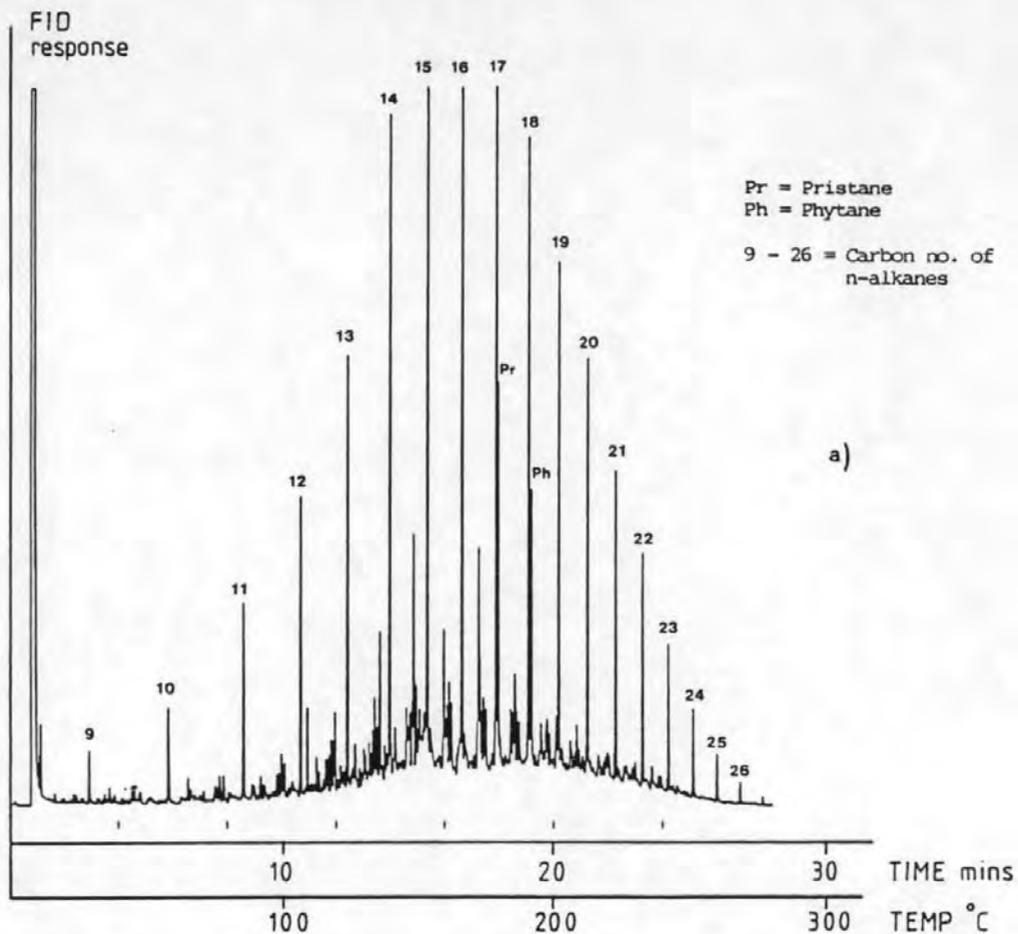


Fig 5.1 Gas Chromatograms of Fuel, a) Aliphatic Hydrocarbon Fraction. b) Aromatic Fraction.

isoprenoids closely associated with n-C17 and n-C18 enable these to be identified.

The aromatic fraction shows a prominent representation from alkyl naphthalenes and phenanthrenes, but the higher relative molecular mass (RMM) PAC (5 ring or more) such as benzo(a)pyrene, are not detectable at significant levels using HRGC, without further fractionation and concentration. In both fractions the bulk of the material elutes within a retention time window between 8 and 24 minutes, and there is a small amount of unresolved complex material which forms a hump under the resolved material.

5.2 Analysis of the Lubricating Oil.

Samples of both the used lubricating oil in the test engine and a sample of unused oil were subjected to the clean-up procedure, described in section 3.1.3, in order to destroy the dispersant additives and remove, by filtration, the accumulated soot in the used oil. Aliquots of the two samples were then fractionated on a column of silica.

Table 5.1 details the clean-up and fractionation, and gives the percentage recoveries for the two techniques. The difference in weight of residue for the clean-up procedure, between the unused and used oil, was very small. The residue of the unused oil, retained by the filter, had a significant contribution from high relative molecular mass polymeric material, even though it contained no particulate carbon. The additional contribution made by

particulates, in the used oil, was not very great, amounting to 2% of the oil. The clean-up technique gave a good percentage recovery; it was slightly lower for the used oil, probably due to the accumulation of highly polar material which was removed into the aqueous phase during liquid/liquid extraction.

The percentage recovery in the fractionation procedure was better than 90%, for both the unused and used oils. Percentage weights in each of the fractions were very similar for the two samples; the bulk of the oil (85%+) eluted with hexane in the aliphatic hydrocarbon fraction. There was no discernible percentage increase in the aromatic fraction for used oil.

The gas chromatograms for the two samples, Figs. 5.2(a+b) and 5.3(a+b), show that the material in the aliphatic hydrocarbon fraction is made up predominantly by an unresolved complex mixture of compounds that forms a hump beneath the resolved material. The lubricating oil shows a normalised distribution within a retention time window of 24 and 36 minutes for 95% of the compounds.

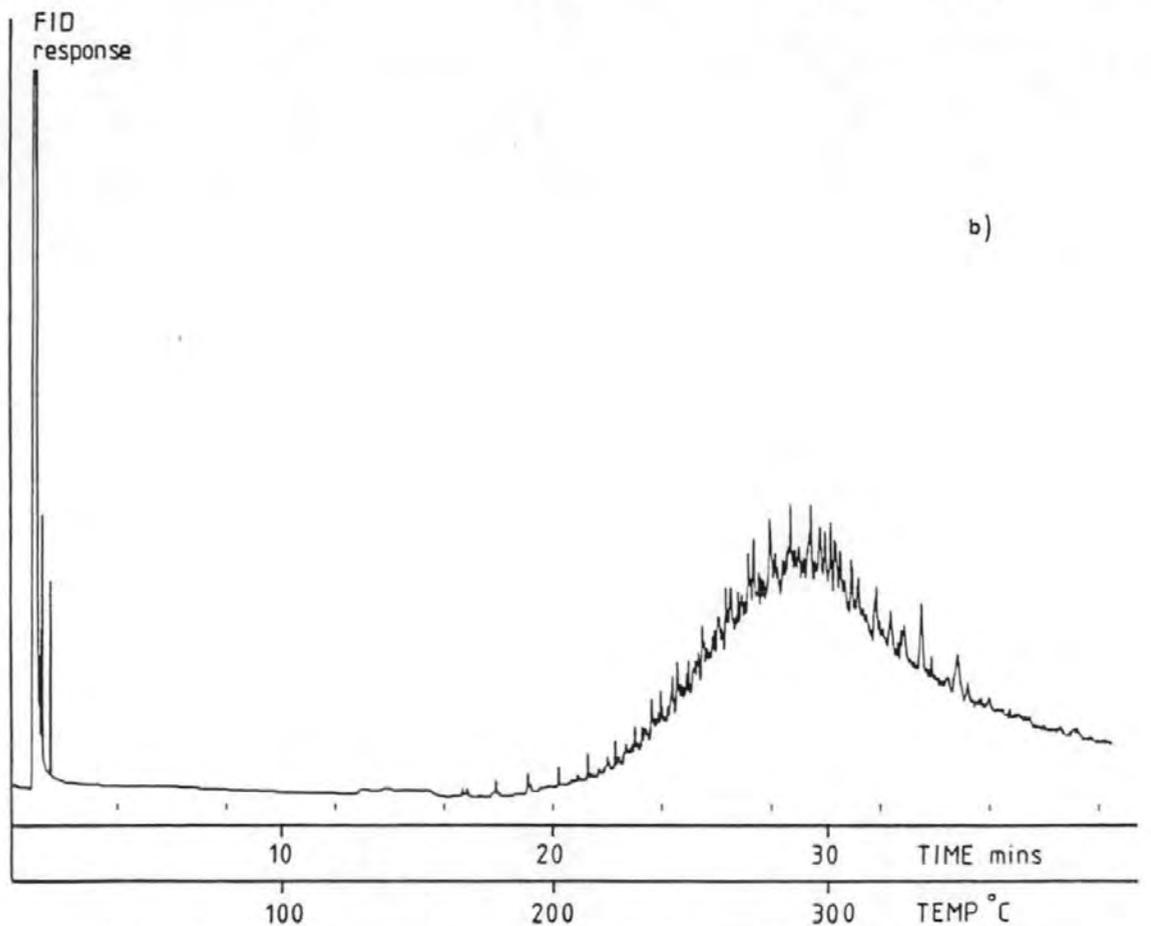
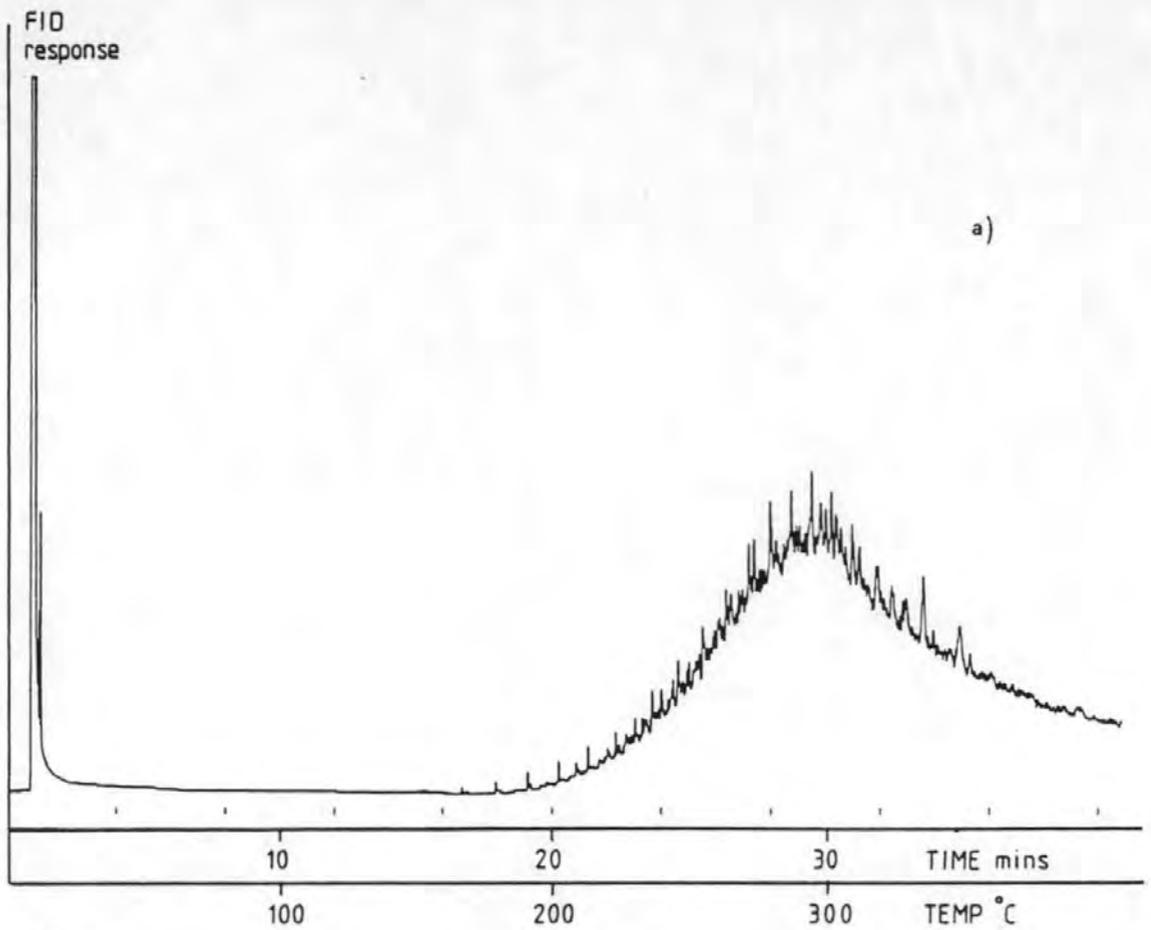


Fig 5.2 Gas Chromatograms of Aliphatic Hydrocarbon Fractions from Lubricating Oil. a) Unused Oil. b) Used Oil.

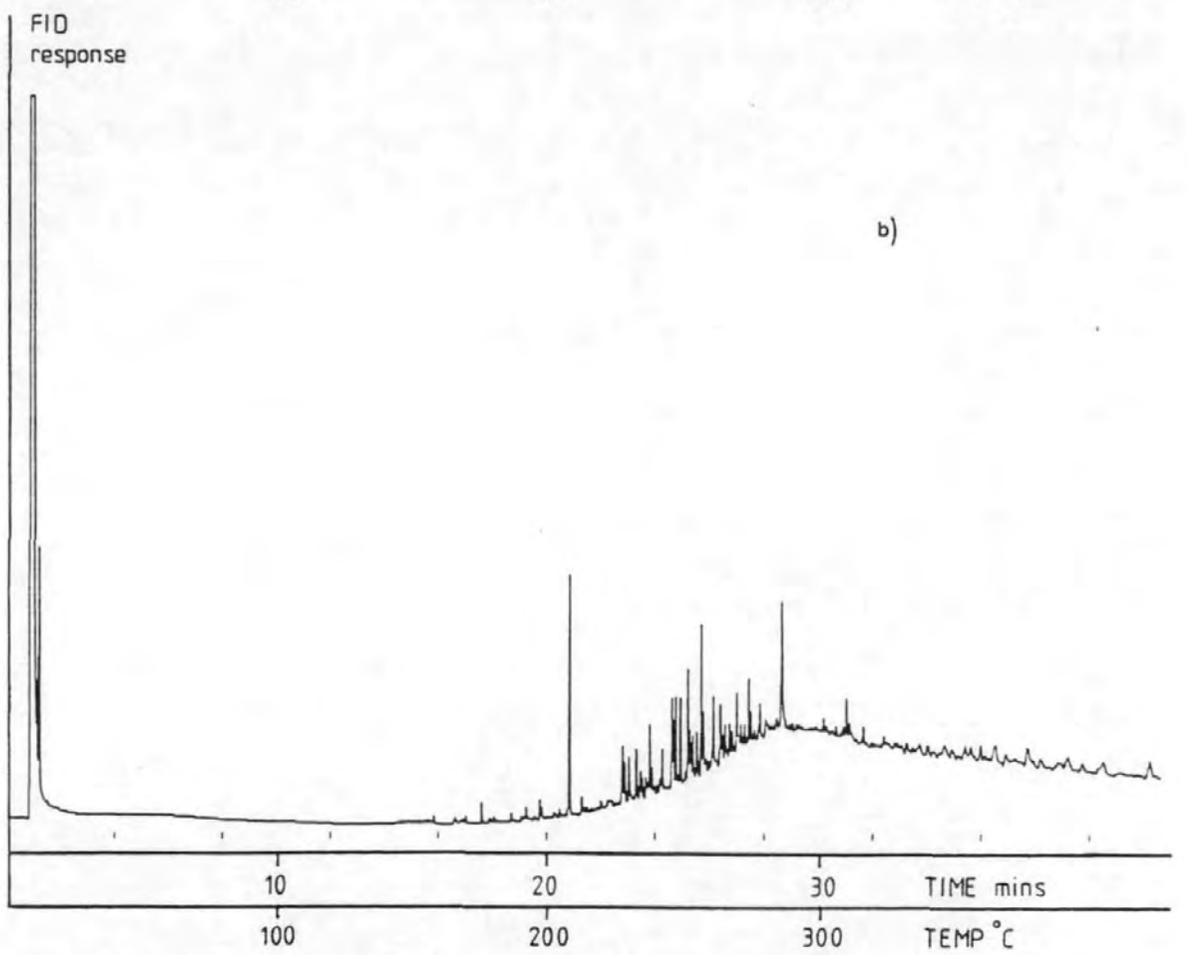
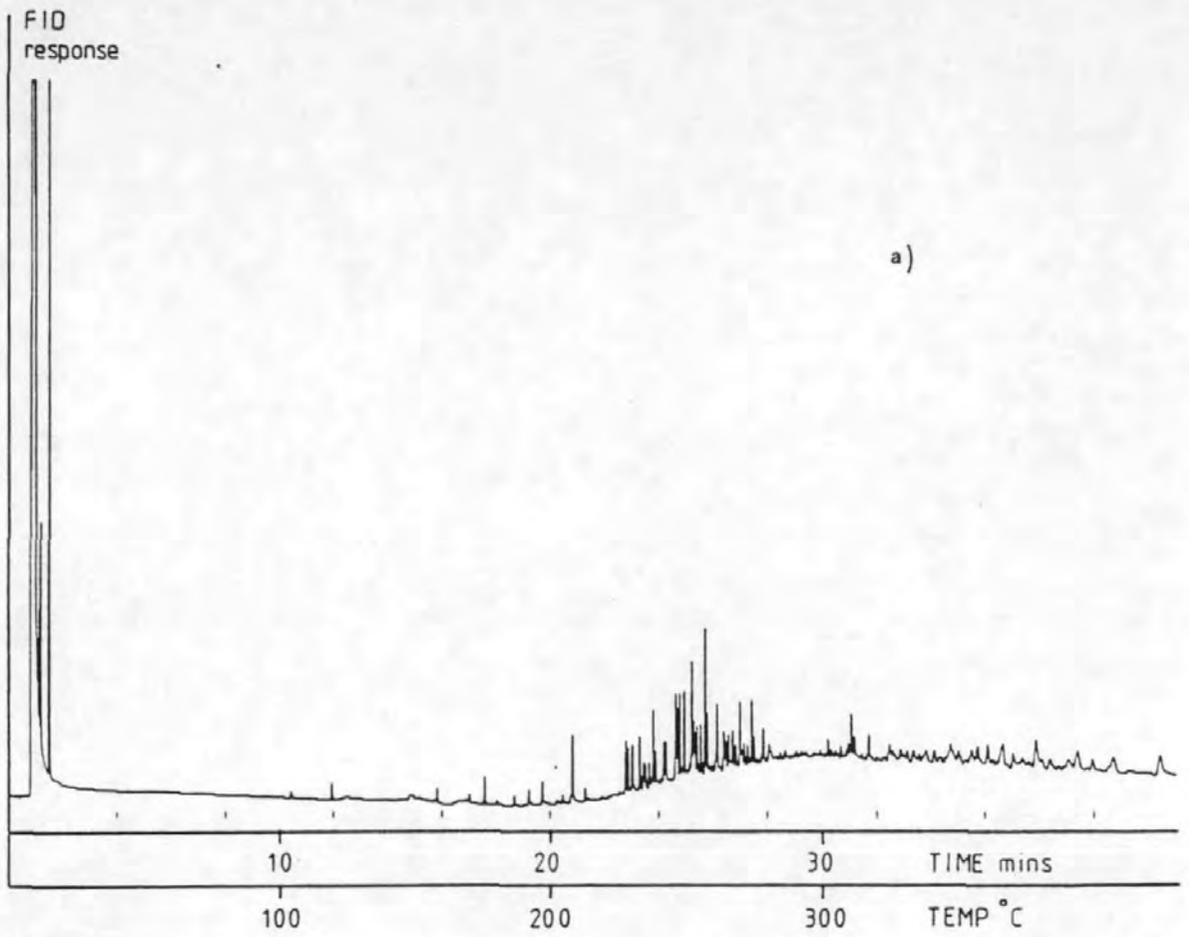


Fig 5.3 Gas Chromatograms of Aromatic Fractions from Lubricating Oil. a) Unused Oil. b) Used Oil.

Weight of:	UNUSED OIL		USED OIL	
	(mg)	%	(mg)	%
Initial oil	620.5	100.0	510.8	100.0
Residue	13.2	2.1	21.7	4.2
Recovered oil	606.4	97.7	474.4	92.9
Aliquot	84.2	100.0	23.4	100.0
Aliphatic fn.	72.1	85.6	20.7	88.5
Aromatic fn.	3.4	4.0	1.0	4.3
Polar fn.	3.7	4.4	0.8	3.4

Table 5.1. Recovery Weights and Percentages for Unused and Used Lubricating Oil, Clean-up, and Fractionation.

Visually, there is an overwhelming similarity between the HRGC chromatograms for both the aliphatic and aromatic fractions of the clean and used lubricating oil; the used oil had had about 40 hours of use within the engine. The results of the HRGC analyses support the conclusions of the work by Grimmer et al. (1981), in which it was reported, that, whereas PAC accumulate in the lubricating oil of gasoline engines with increasing hours of use, they do not do so to anything like the same extent for diesel engines. A lubricating oil which had been used in a diesel engine run continuously for 200 hours was also analysed in a similar manner by another researcher (Gough 1987). No significant build-up of PAC in the lubricating oil was detected at the end of the 200 hours test.

It is interesting to note that similarities between clean and used lubricating oil suggest that high temperature transformation of lubricating oil within the combustion chamber, either by pyrolysis or incomplete combustion, and

the subsequent return of the changed oil to the sump, is negligible. A method to estimate the contribution of lubricating oil to the solvent soluble organic fraction of diesel exhaust is described in section 7.1.

Diesel fuel and lubricating oil, along with the corresponding solvent soluble exhaust extracts, contain many thousands of compounds. Previous research has focused on the identification of these compounds and this has not been repeated here, (e.g. Schuetzle et al.1982, Xu 1982, Mills 1983, Risby 1983, Tong et al.1984, Williams et al.1985). Instead tentative identification has been made where necessary by the calculation of relative retention times from the retention time data obtained from an integrator. Further identification was made with authentic standards, section 3.5, and GC/MS data.

5.3 The TESSA Extracted Sample (TES).

The procedure adopted to obtain a TES has already been described, section 3.1.2, i.e. sampling close to the engine with standard engine conditions, followed by a rigorous analytical work-up involving the whole sample. Over the period of six to eight months there are inevitably variations introduced to the system as a whole which ultimately affect the TES. These variations include atmospheric conditions, i.e. barometric pressure, humidity and temperature, along with wear and tear in the engine, fuel injector pump, and other parts.

At the same time, in circumstances where the fuel used for the experiments comes from a bulk tank which is regularly replenished with fresh deliveries of fuel, which will never be absolutely identical in make up to a previous fuel, and where the tank itself may have accumulated residues, some variation in fuel quality must be anticipated. The sampling runs, described in detail in this chapter, were all undertaken within a short period of time, in order to minimise the influence of external factors and facilitate direct comparison between samples.

In order to assess the reproducibility of TESSA, independently of the variables mentioned above and which vary even from day to day, it would be necessary to do 5 repeat TESSA runs in the same day to generate sufficient data to calculate statistically a coefficient of variation between runs. At this time, this has not been attempted, requiring, as it would, considerable time, resources, and manpower.

In the first of a series of sampling runs with TESSA, the engine was operated at the standard conditions detailed in Table 5.2.

Engine Speed (rev/min)	2000
Load (kW)	3.5
Fuel Consumption (cm ³ /min)	22
Sampling Time (min)	3
Solvent Volume (litre)	2
Cooling Water Temp. (°C)	80
Oil Temp. (°C)	77
TESSA Cooling Water (°C)	4

Table 5.2 Standard Engine Conditions for a TESSA Sampling Run.

The TES was subjected to the clean-up and fractionation procedure already described in detail, section 3.1. The HRGC chromatograms of the TES are shown in Fig 5.4(a+b).

Several important features can be seen in the aliphatic fraction. The compounds in TES fall within the retention time windows of both fuel (ca. 8-24 mins.) and lubricating oil (ca. 24-36 mins.). The homologous series of n-alkanes with the associated isoprenoids can be readily identified. Nevertheless the distribution has changed somewhat when compared with the fuel, with less of a presence from the lighter relative molecular mass n-alkanes (C9-C13), whilst the survival of the higher relative molecular mass members of the series (C23-C26) follows more closely the pattern of relative peak height in the fuel.

The similarity of the n-alkanes present in the fuel and TES suggest that these compounds have originated from the fuel. The compounds eluting between 24 and 36 minutes have a close similarity with the lubricating oil: in the shape of the UCM hump, by the retention time of resolved compounds

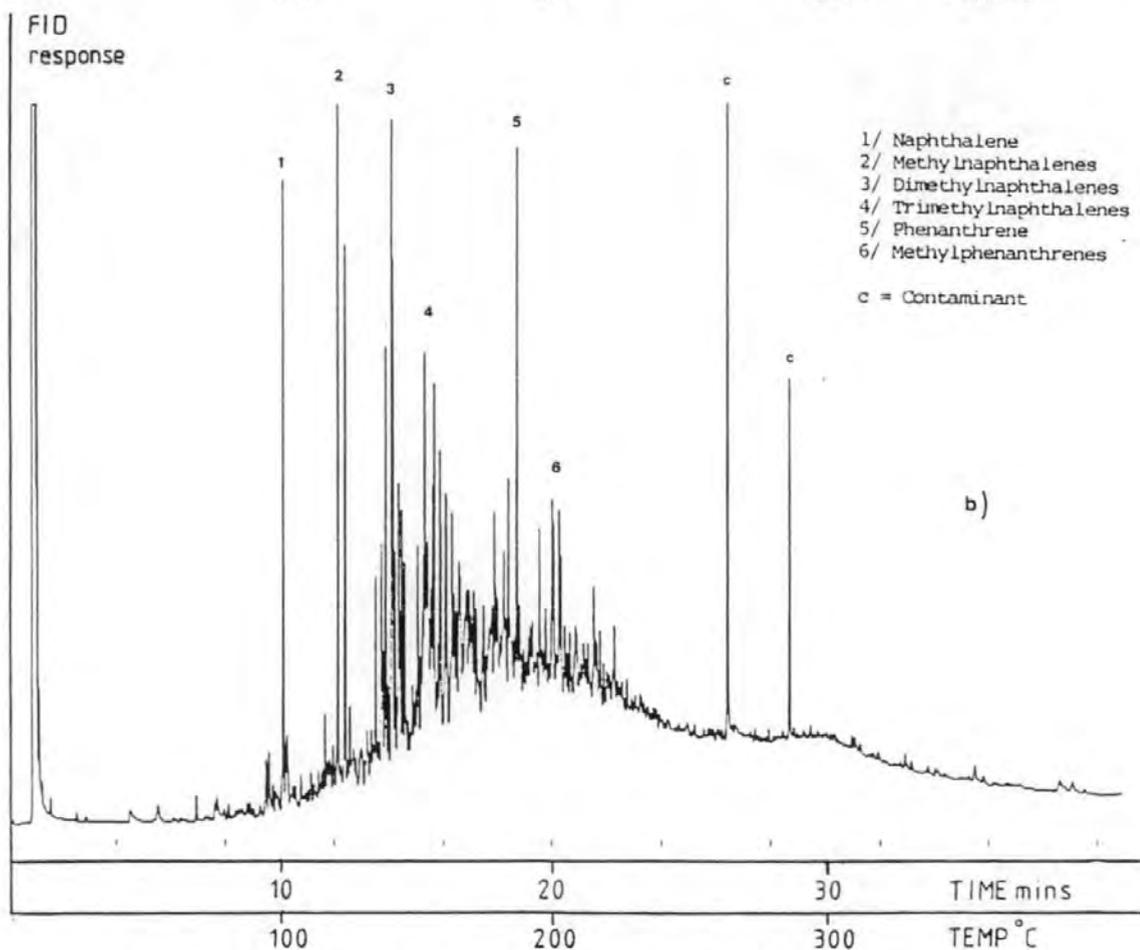
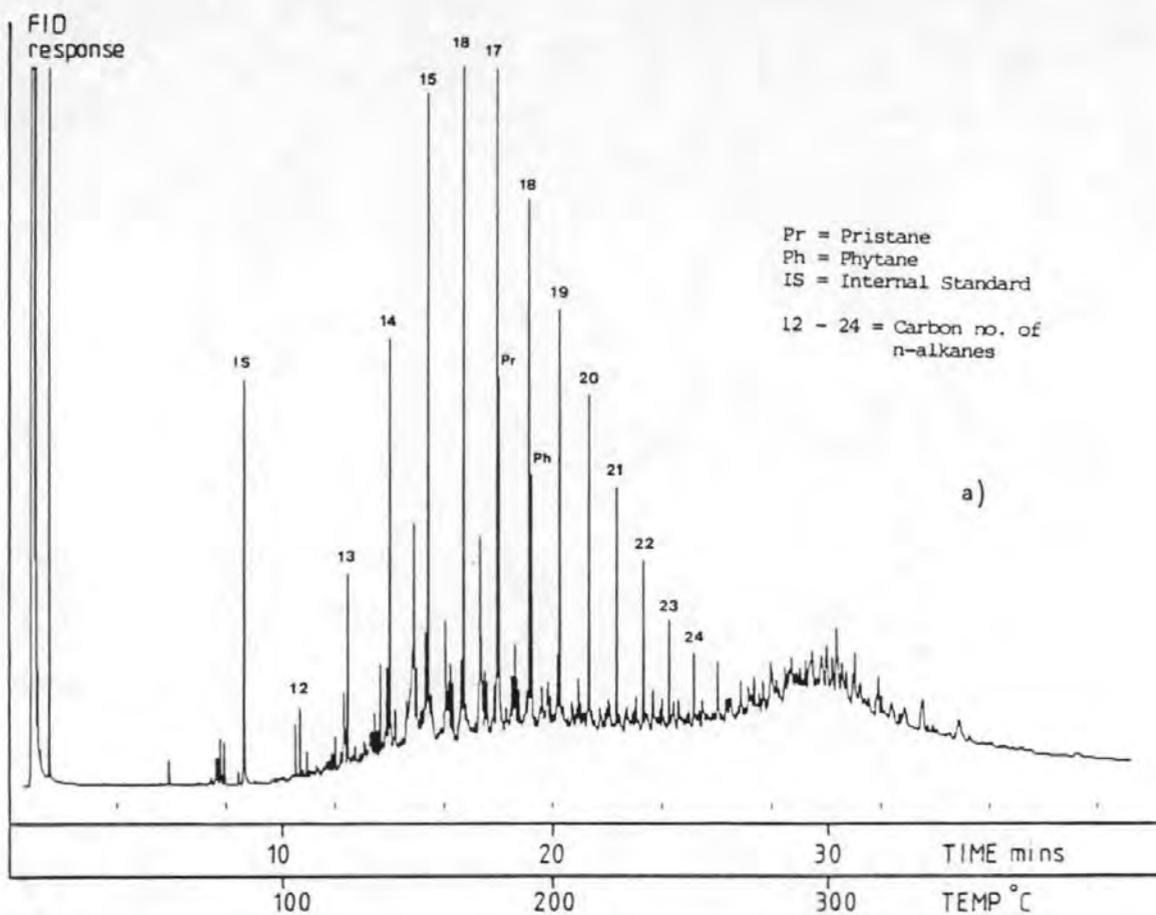


Fig 5.4 Gas Chromatograms for a TES Taken at Standard Conditions: 2000 revs/min and 3.4 kW. a) Aliphatic Hydrocarbon Fraction. b) Aromatic Fraction.

and by the ratios of peak heights of this resolved material. These similarities are investigated at greater depth in section 5.7 and section 7.1 respectively.

When the chromatogram for the aromatic fraction is considered, there is, again, a recognisable similarity in the prominent contribution from the alkyl naphthalenes and phenanthrenes between the TES and the fuel. The presence of the parent PAH's, naphthalene and phenanthrene, are enhanced in the TES with respect to their presence in the fuel, when compared to their alkyl derivatives. GC/MS analysis of the aromatic fraction, presented in section 5.7, bears out the direct relationship between the fuel and TES.

Initial inspection of a typical TES indicates a contribution from fuel and lubricating oil along with some additional features which cannot be assigned to either of these sources. These other compounds originate from the combustion chamber and are products of the pyrolysis or incomplete combustion of the fuel and/or lubricating oil. Specific contaminant peaks were identified by running analytical blanks, and, in this way, could be identified and discounted.

5.4 Tessa Sampling at High Speed

An experiment was undertaken to use TESSA to sample the exhaust from the E.6/T Ricardo engine, operated at high speed, whilst varying the load to three positions: high

load, medium load and low load. The higher engine speed took TESSA close to its capacity (nominal maximum exhaust flow 500 l./min) and consequently it was decided to sample for a shorter time. The sampling time was reduced from 3 minutes to 1 minute, whilst the solvent volume was reduced from 2 to 1 litre. Details of the sampling conditions are presented in Table 5.3

	TESSA at High Load	TESSA at Medium Load	TESSA at Low Load
Engine Speed (rev/min)	2750	2750	2750
Load (kW)	7.5	5.3	2.6
Fuel Consumption (cm ³ /min)	50.8	35.7	24.0
Sampling Time (min)	1	1	1
Solvent Volume (litre)	1	1	1
All other conditions standard. (Section 5.3)			

Table 5.3 Engine and Sampling Conditions Used for TESSA Run at High Speed and Load.

The chromatograms from this experiment contrasted with previous results sufficiently to require an explanation in addition to the changed engine conditions. As an example the HRGC chromatograms from the aliphatic and aromatic fractions for the high load result are presented in Fig 5.5(a+b). The aliphatic fraction for this sample is dominated by a very considerable UCM hump which neither corresponds with the UCM humps for the fuel or lubricating oil. When this chromatogram is compared to that of the extracted PTFE cord, Fig 4.9b, there is a striking similarity. In fact the PTFE seal for the joints in TESSA had been replaced just prior to this experiment, and it

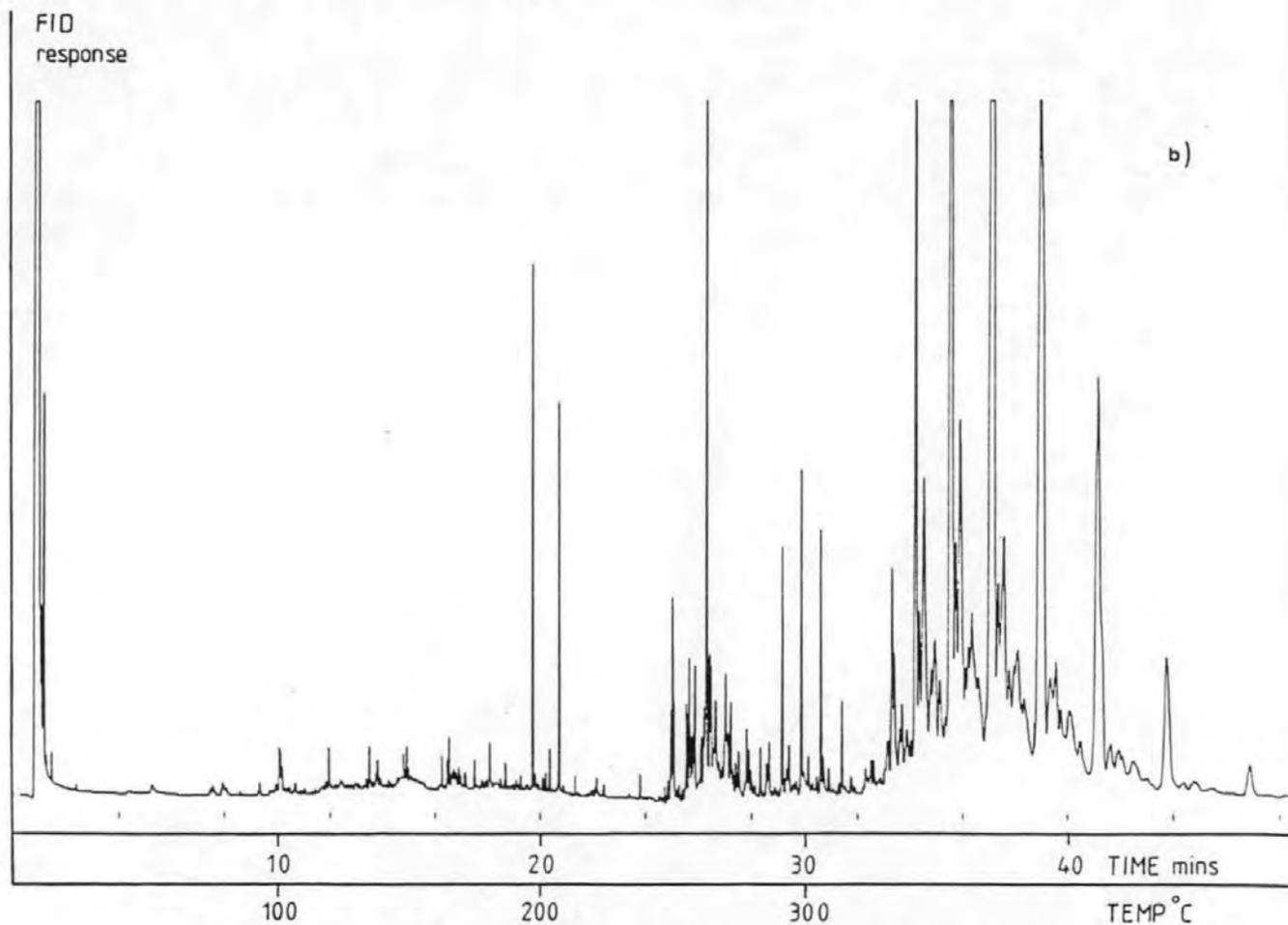
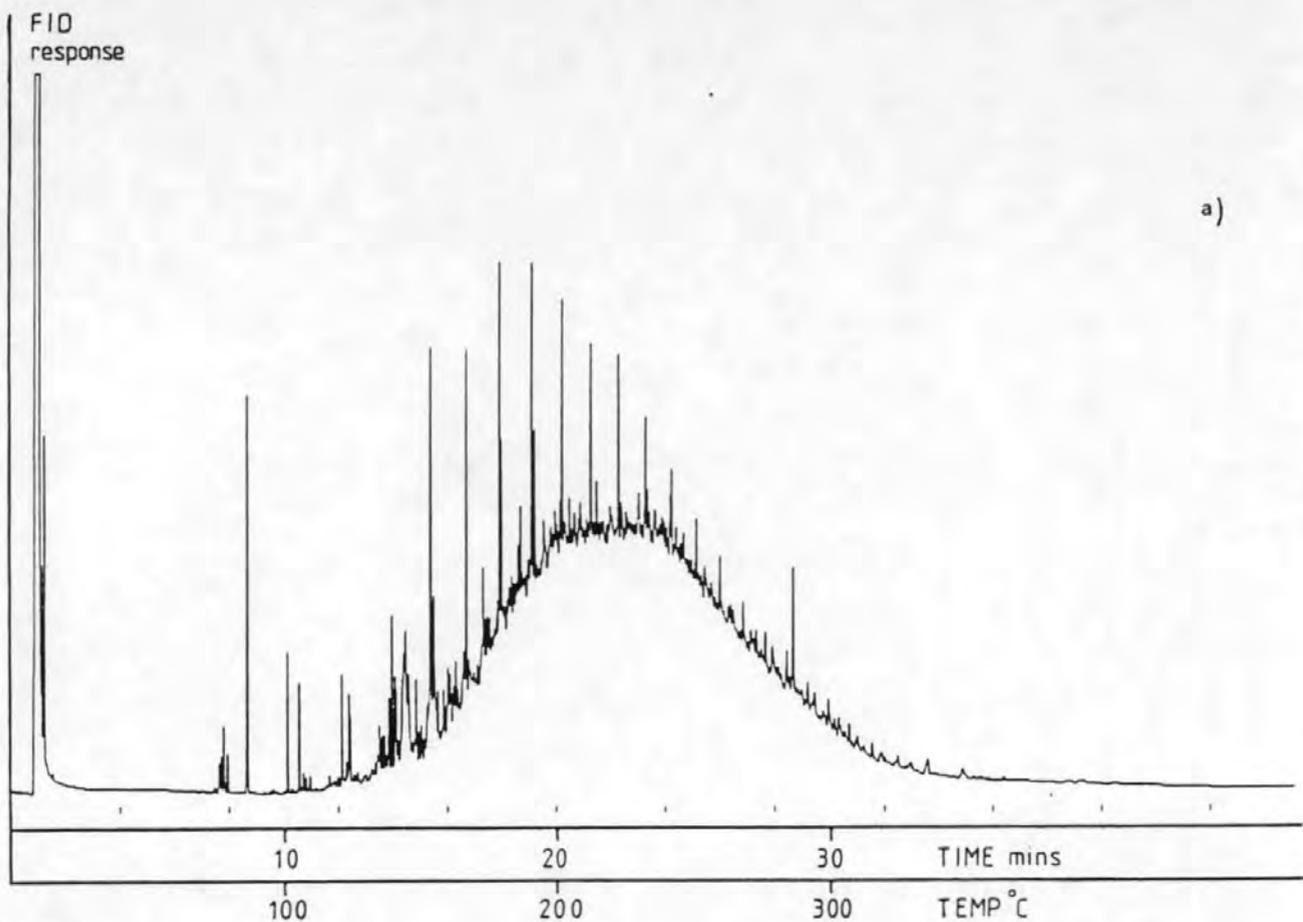


Fig 5.5 Gas Chromatograms for a TES at High Speed and Load, Showing Anomalous Result Due to Contamination. a) Aliphatic Hydrocarbon Fraction. b) Aromatic Fraction.

seems likely this cord had extensively contaminated the samples.

The aromatic fraction also shows an uncharacteristic chromatogram, in this case dominated by compounds with very high retention times not hitherto found in a TES. Close examination of TESSA revealed fragments of epoxy resin from the adhesive used to fix thermocouples inside TESSA, section 4.3.7, and it was concluded that this was the source of the compounds found, at high retention time, in the gas chromatogram.

This experiment has been described to illustrate some of the possible contamination sources. Furthermore, it was felt worth reporting the successful reduction in sampling time and solvent volume, which still yielded more than sufficient material for analysis. The TES from the high load condition yielded aliphatic and aromatic fractions with weights of 17.8 mg and 10.6 mg respectively; this was more than adequate for analysis. The advantage of shorter sampling time in static engine testing is mainly the lower volume of solvent requiring analytical work-up. A shorter sampling time would be essential if TESSA were to be linked to a transient test cycle in the future. It would enable the transitory conditions involved in transient testing e.g. idling, acceleration, motoring, to be sampled individually rather than accumulatively.

It should be noted that some difficulty was experienced in maintaining a steady engine speed (2750 revs/min) during

these runs. On each occasion, a short time after the commencement of sampling with TESSA, the engine speed dropped to 2680 rev/min. This might have suggested that TESSA was adding to the load imposed on the engine by the dynamometer, resulting in a drop in the engine speed. But this was not the case, since manometer readings at the exit of TESSA, taken during similar experiments, measured only a slight backpressure (4.9 cm H₂O). The most likely explanation is that, in this experiment, there was an excess of solvent, which momentarily impeded the upward flow of the exhaust gases, since although the sampling time was reduced by two thirds the solvent volume was only reduced by a half.

5.5 Nitro-PAC in Diesel Exhaust Emissions.

An experiment was undertaken to investigate the presence of nitro-PAC compounds in the TES. The design of TESSA minimises the formation of nitro-PAC from occurring once the diesel exhaust has entered TESSA, i.e artifact formation. Therefore the presence of nitro-PAC in a TES would provide evidence that these compounds can form within the combustion chamber. Alternatively, the lack of nitro-PAC in a TES would reinforce the hypothesis that they are primarily artifacts of sampling by the filter/dilution tunnel method.

The nitration of a PAC is an example of aromatic electrophilic substitution, in which, the electrophile is usually a positive ion, the nitronium ion NO₂⁺, although it

can be a molecule with a dipole. It is a two step reaction: the electrophilic attack results in a highly reactive intermediate, a positively charged arenium ion, then in the second step the molecule loses a proton and stabilises as the nitrated PAC shown in equation 1.

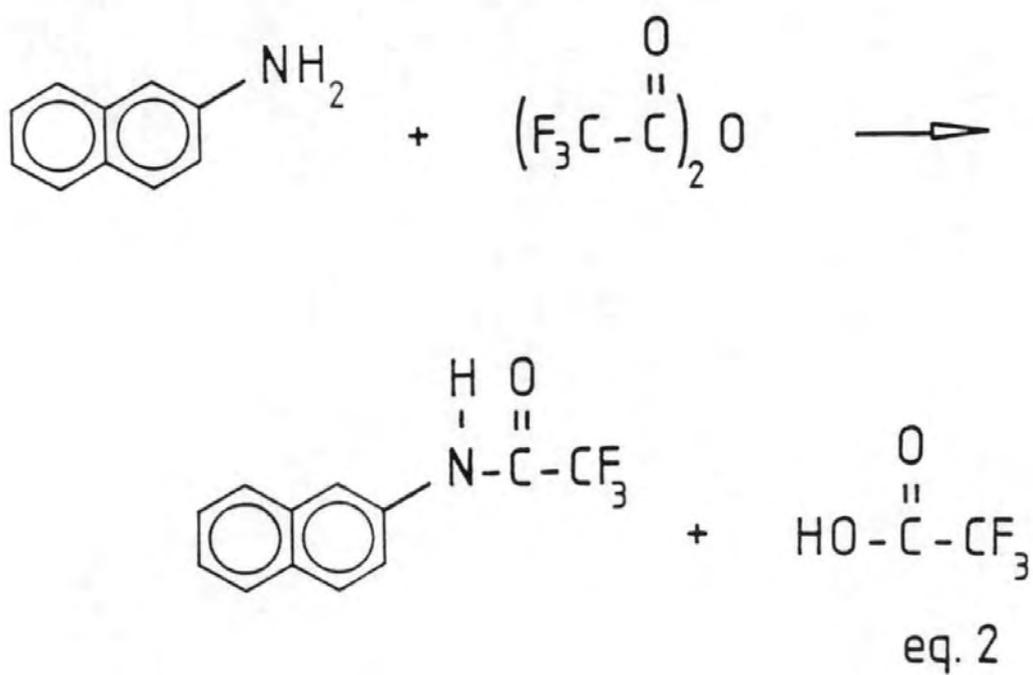
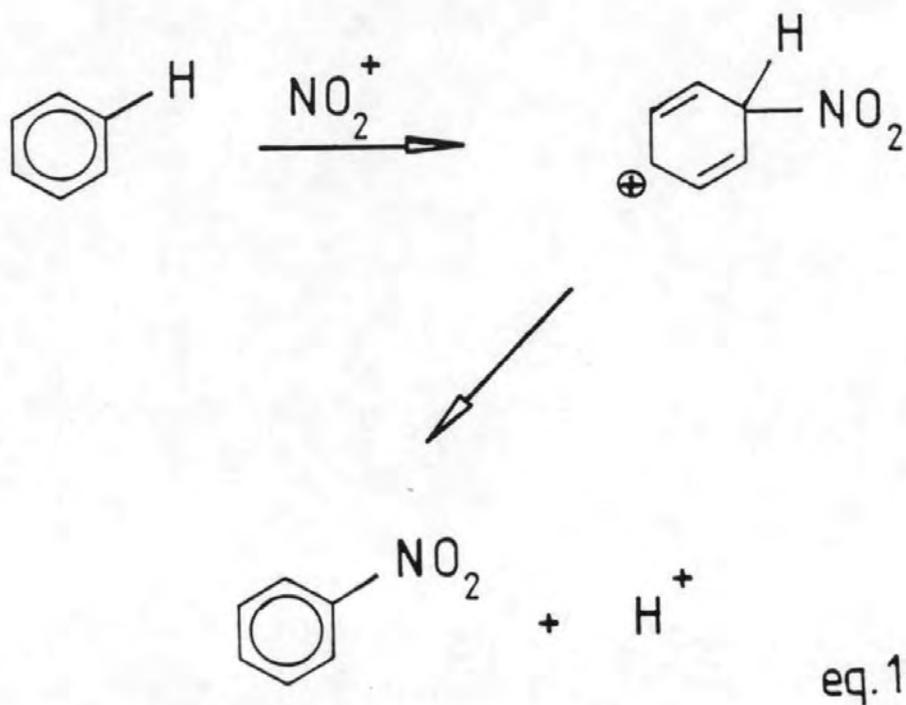
In order to maximise the possibility of nitro-PAC formation, engine conditions were chosen which would result in high NOx levels, using the engine map for NOx emissions, (Fig 3.5), i.e. high speed and full load. This experiment would also enable a comparison to be made with the TES obtained under the similar, high speed and load, operating conditions, described in the previous section (section 5.4), and thereby confirm that the unusual results from that experiment were indeed due to contamination. On this occasion the normal sampling time and solvent volume were used, Table 5.4.

Engine speed (rev/min)	2750
Engine load (kW)	6.6
Fuel consumption (cm ³ /min)	42.3
Sampling time (min)	3
Solvent volume (litre)	2

All other conditions standard,
(Section 5.3).

Table 5.4 Engine and Sampling Conditions Used to Investigate Presence of Nitro-PAC.

A special analytical scheme was used for this particular sample, adapted from work published by Campbell and Lee (1984); it was developed to isolate the nitro-PAC, and then by a process of reduction and derivatization to enable



HRGC and GC/MS analyses with an increased response.

Details are given in the experimental techniques section 3.3.1. As well as the nitro-PAC fraction, aliphatic and aromatic fractions were also obtained.

5.5.1 The Aliphatic and Aromatic Fractions at High Speed and Load.

The gas chromatograms for the aliphatic and aromatic fractions are shown in Fig 5.6(a+b). Familiar features are immediately discernible showing a degree of similarity with the TES from the standard engine conditions (c.f. 2000 rev/min, 3.5 kW, Fig 5.4). The aliphatic fraction has a significant presence from the homologous series of n-alkanes typical of the fuel. The isoprenoids, pristane and phytane are identifiable in close association with n-C17 and n-C18.

There is a distinct UCM hump within a retention time window closely corresponding with that for the UCM hump for lubricating oil. Furthermore a range of resolved peaks on top of the hump can be matched, by retention time and peak height ratios, with similar peaks in the lubricating oil.

There are several distinct features in the aliphatic fraction which are different from typical compounds in either the fuel or the lubricating oil. In particular there is a considerable number of low relative molecular mass compounds, with low retention times, which are not n-alkanes. A second noticeable feature is the

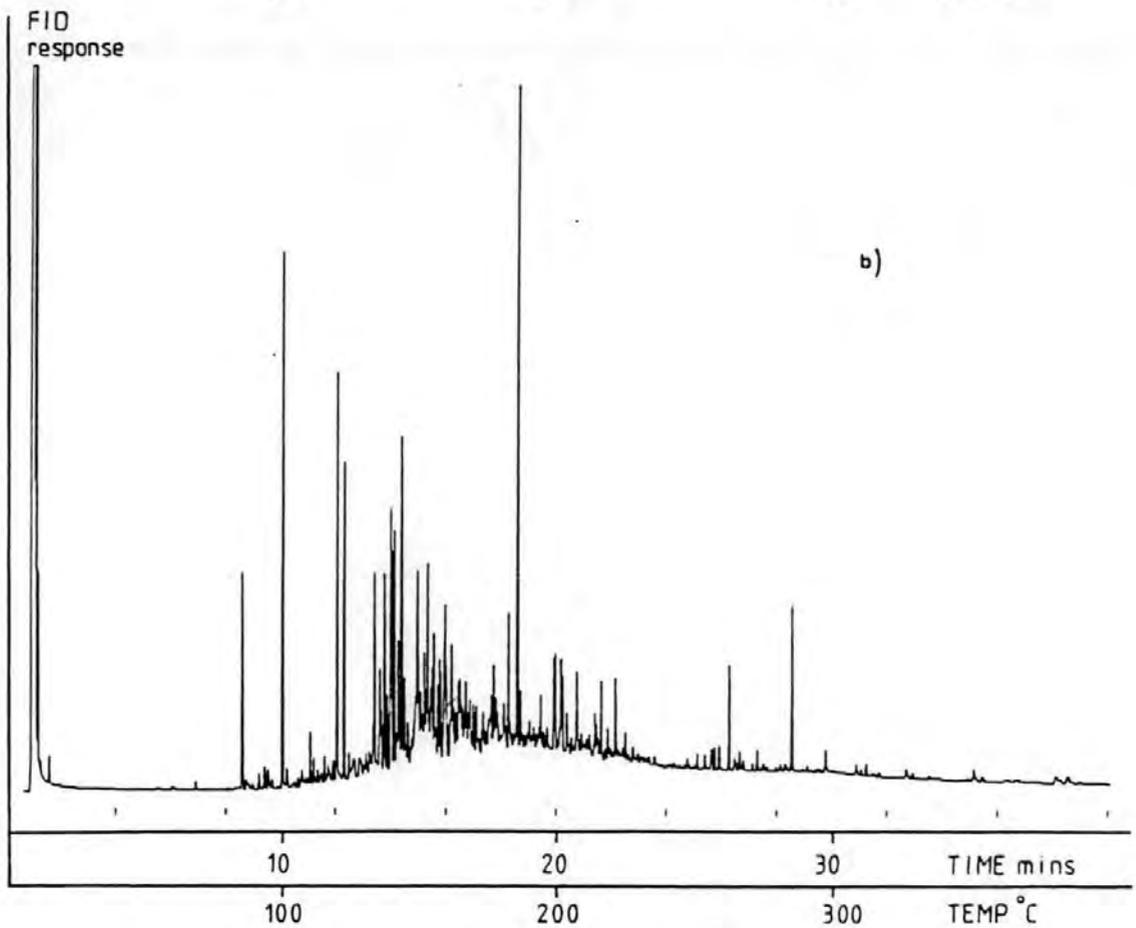
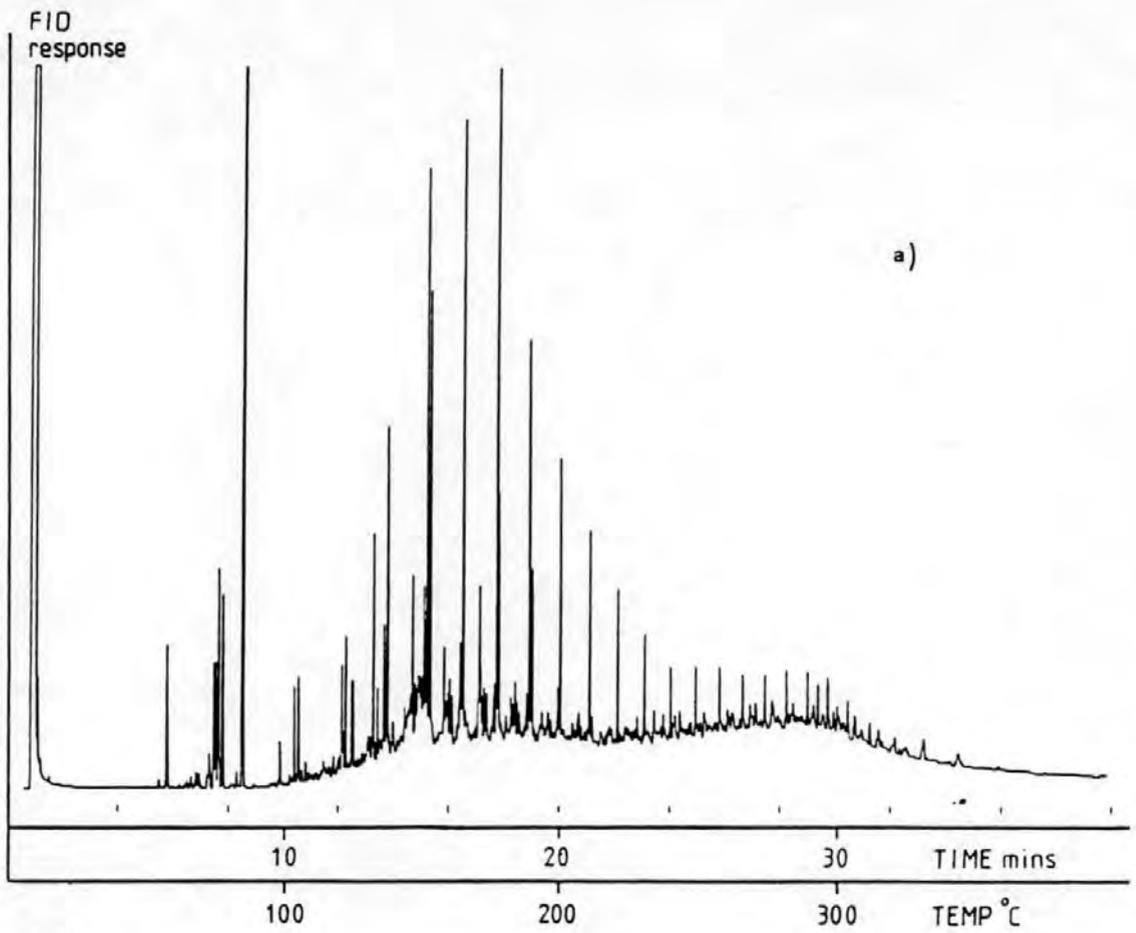


Fig 5.6 Gas Chromatograms for a TES at High Speed and Load: 2750 revs/min and 6.6kW. Normal Result.
 a) Aliphatic Hydrocarbon Fraction. b) Aromatic Fraction.

prolongation of the homologous n-alkane series beyond that associated with the fuel. It is likely that the contribution from n-C26 to n-C32, which are prominently resolved above the lubricating oil hump, have origins other than from the fuel, although it is possible that these compounds have an enhanced presence in the TES due to their poor combustion within the cylinder compared to lower relative molecular mass alkanes. Alternatively, these compounds may indicate the presence of a small amount of contamination from grease.

The aromatic fraction is dominated by parent and alkyl naphthalenes and phenanthrenes, again similar to the fuel distribution. These results lend weight to the conclusion that the TES, obtained in the previous experiment at high speed and load and described in Section 4.5., was anomalous and was the result of extensive contamination.

5.5.2 The Reduced and Derivatized Nitro-PAC Fraction.

The analytical work-up for this sample involved reducing nitro-PAC compounds to their corresponding amino-PAC, and then derivatizing these compounds with a polyfluorinated tag using trifluoroacetic anhydride. This tag also greatly increased the stability of the amino-PAC, which otherwise would have been susceptible to rapid degradation. The derivatization of amino-PAC with trifluoroacetic anhydride (TFA) leads to the formation of trifluoroacetyl amides of the PAC shown in equation 2.

The derivatized sample was analysed by GC/MS. Mass spectral determination of the TFA derivatized amino-PAC is straightforward because the relative molecular mass is increased by 96 mass units, and the derivatized compounds give characteristic mass fragments, described by Later et al. (1982). The molecular ion M^+ fragments to form two major ions: first, the $(M-97)^+$ ion, which corresponds to the loss of the TFA group and gives the relative molecular mass of the underivatized aromatic amine less one mass unit; a second prominent ion then results from the further loss of HCN (27 mass units) from the $(M-97)^+$ fragment. This fragmentation is summarised for several Nitro-PAC in Table 5.5.

Amino PAC (mol wt.)	Relative Molecular Masses of TFA Derivatives		
	(M)	(M-97)	(M-124)
Amino-naphthalene (143)	239	142	115
Amino-fluorene (181)	277	180	153
Amino-phenanthrene (193)	289	192	165
Amino-fluoranthene and Amino-pyrene (217)	313	216	189
Amino-chrysene (243)	339	242	215

Table 5.5 Relative Molecular Masses of TFA Derivatives and their Typical Mass Fragments.

The GC/MS data for the analysis of the TFA derivatized amino-PAC sample were searched for the presence of the specific molecular ions listed in Table 5.5, but no characteristic peaks were identified. It was assumed that the ionising potential (40 eV) had been sufficient to

fragment the molecular ions and the search was extended to the corresponding (M-97)+ ion. Characteristic mass fragments were identified for nitronaphthalenes, nitrofluorenes, and nitropyrenes shown in Fig 5.7, however, this can only be taken as a tentative identification at this time.

Initial results indicate that some nitro-PAC have been isolated and were present in the TES from high load and speed. Nevertheless, the result is in stark contrast with that of Campbell and Lee (1984), who extracted the SOF from 50 mg of diesel particulates, taken from a dilution tunnel with a filter sampling system, and then analysed it for nitro-PAC in the manner described. The gas chromatograms of the diesel particulate SOF in their work revealed a very complex composition of many hundreds of nitrated compounds. Paputa Peck et al. (1982) also detected at least 100 nitro-PAC when they analysed a diesel exhaust particulate extract. In contrast, comparatively few peaks were resolved in the GC/MS TIC, suggesting that far fewer nitrated species were present in the TES compared to the very large number found in the analysis of diesel particulates collected on a filter from a dilution tunnel by these other researchers.

These results represent a preliminary investigation only, and it would be necessary to repeat the analytical technique on a mixture of nitro-PAC standards to enable a more positive identification of peaks. Also it would be helpful to run an analytical blank to find out if any

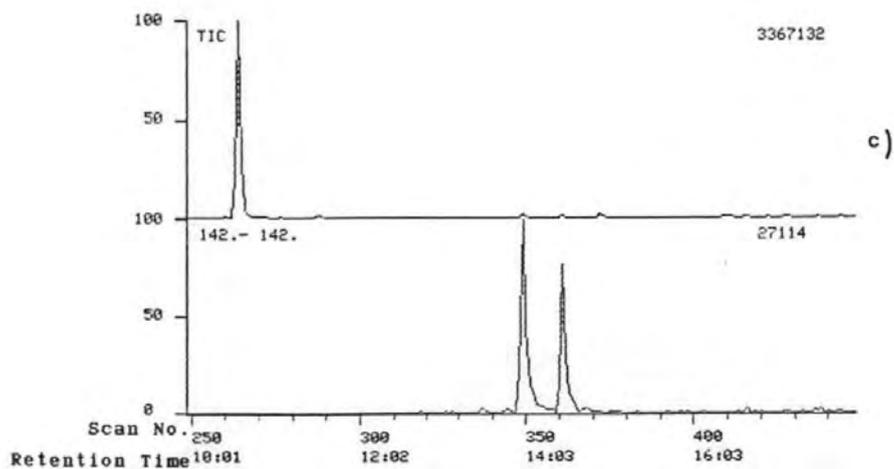
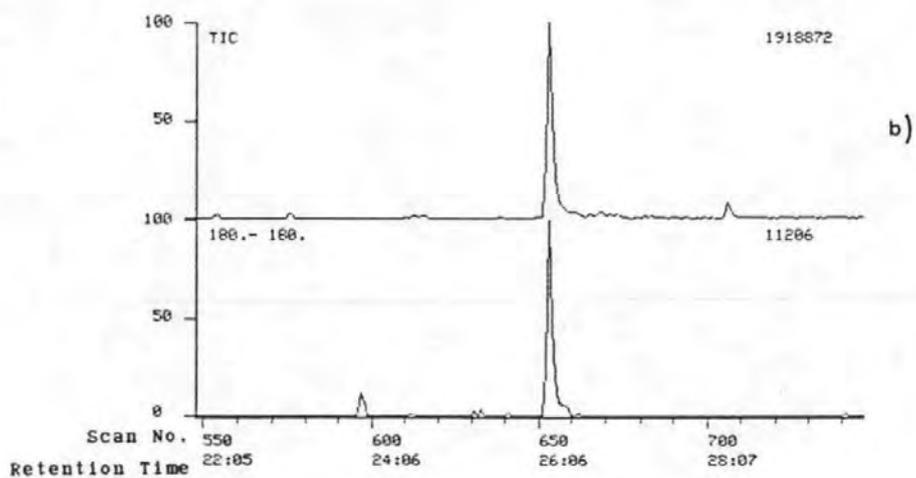
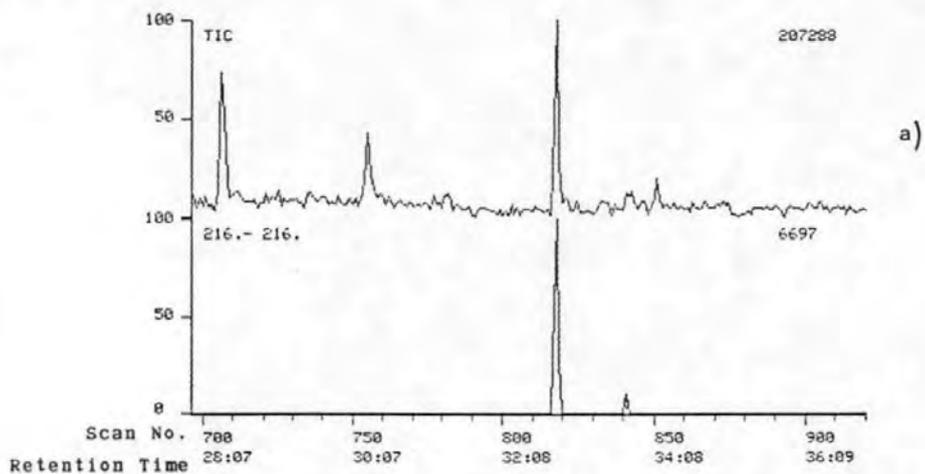


Fig 5.7 GC/MS of Derivatised Nitro-PAC Sample Showing TIC and Characteristic Mass Fragments for:
 a) Nitropyrene. b) Nitrofluorene. c) Nitronaphthalene.

contamination from the reagents was present.

Pentafluoropropionic anhydride (PFP) would be a preferable reagent to TFA in any further experimentation because the PFP derivatized amide gives a very strong response to electron capture detection allowing for greater sensitivity and selectivity in analysis. More recent use of this technique has also used heptafluorobutyric anhydride in place of trifluoroacetic anhydride, (Sellstrom et al.1987).

5.6 Sampling with TESSA at a 3m Distance Down the Tail-pipe.

In this experiment it was intended to compare the TES results obtained close to the engine with a TES taken at the far end of a 3 metre tailpipe, comparable to the typical length of tailpipe used prior to air dilution in a dilution tunnel filter sampling system. The TESSA system was dismantled and rebuilt on a stand at the end of a 3 metre length of exhaust tailpipe. A simple system of valves was used so that the exhaust from the engine could be vented to atmosphere through the tailpipe during the warm-up procedure, then, once the intended operating conditions for sampling had stabilised, the whole exhaust was diverted through TESSA for the 3 minute sampling period.

Engine Speed (rev/min)	2000
Load (kW)	3.5
Fuel Consumption (cm ³ /min)	21.9
Sampling Time (min)	3
Solvent Volume (litre)	2
All other conditions standard, (Section 5.3).	

Table 5.6 Engine and Sampling Conditions Used to Sample at 3m Distance from Engine.

The gas chromatograms for the fractionated TES are shown in Fig 5.8(a+b). The total weight of sample recovered after analytical concentration but before fractionation (41.7 mg) was considerably less than the typical weight of TES recovered from a standard sampling run (70 mg) with TESSA set close to the exhaust port.

In the aliphatic fraction the homologous series of n-alkanes with the associated isoprenoids, pristane and phytane, are dominant and cover the same retention time range as the fuel. The contribution from the compounds eluting within the retention time window of the lubricating oil (24-36 mins) is fairly small. It can be seen more clearly with increased attenuation, Fig 5.9. But again it has some additional high relative molecular mass n-alkanes superimposed on top of the UCM hump of the lubricating oil.

The gas chromatogram of the aromatic fraction is dominated by parent- and alkyl- naphthalenes and phenanthrenes. Both fractions have compounds eluting with very low relative molecular masses.

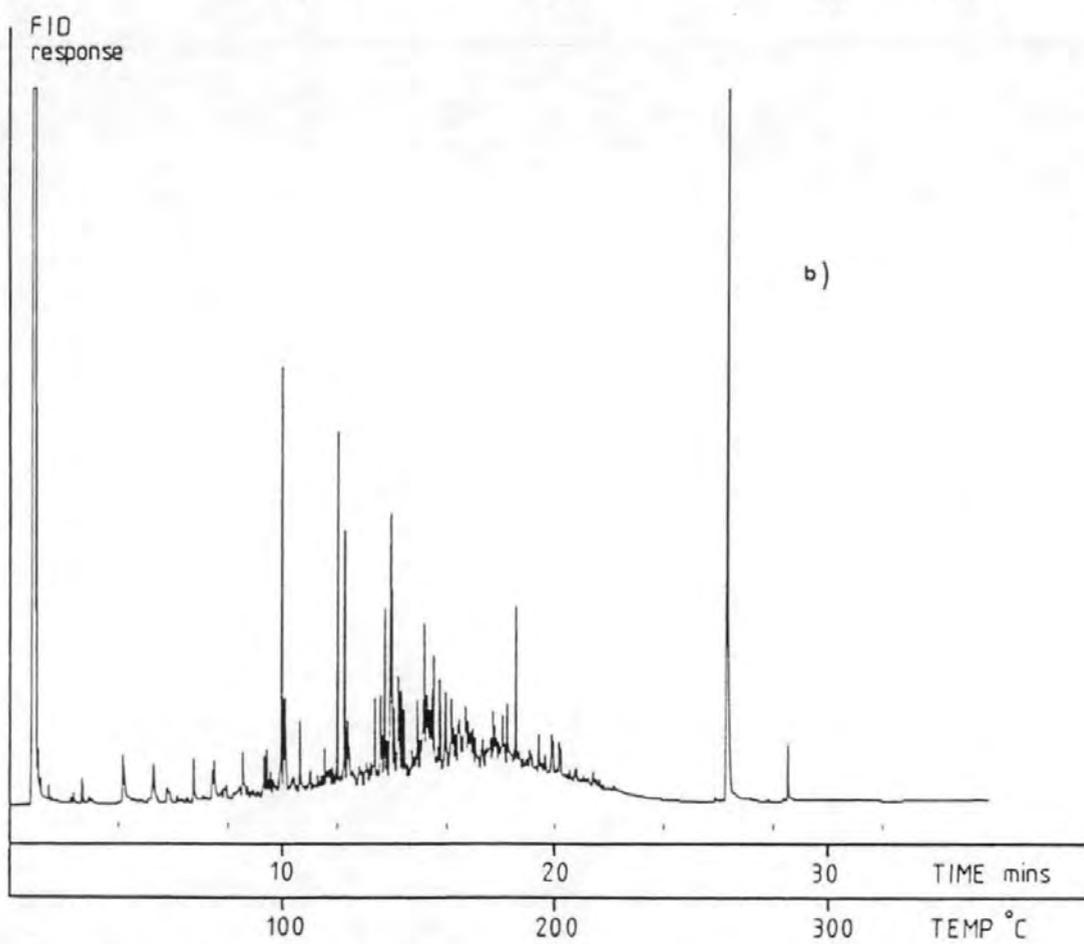
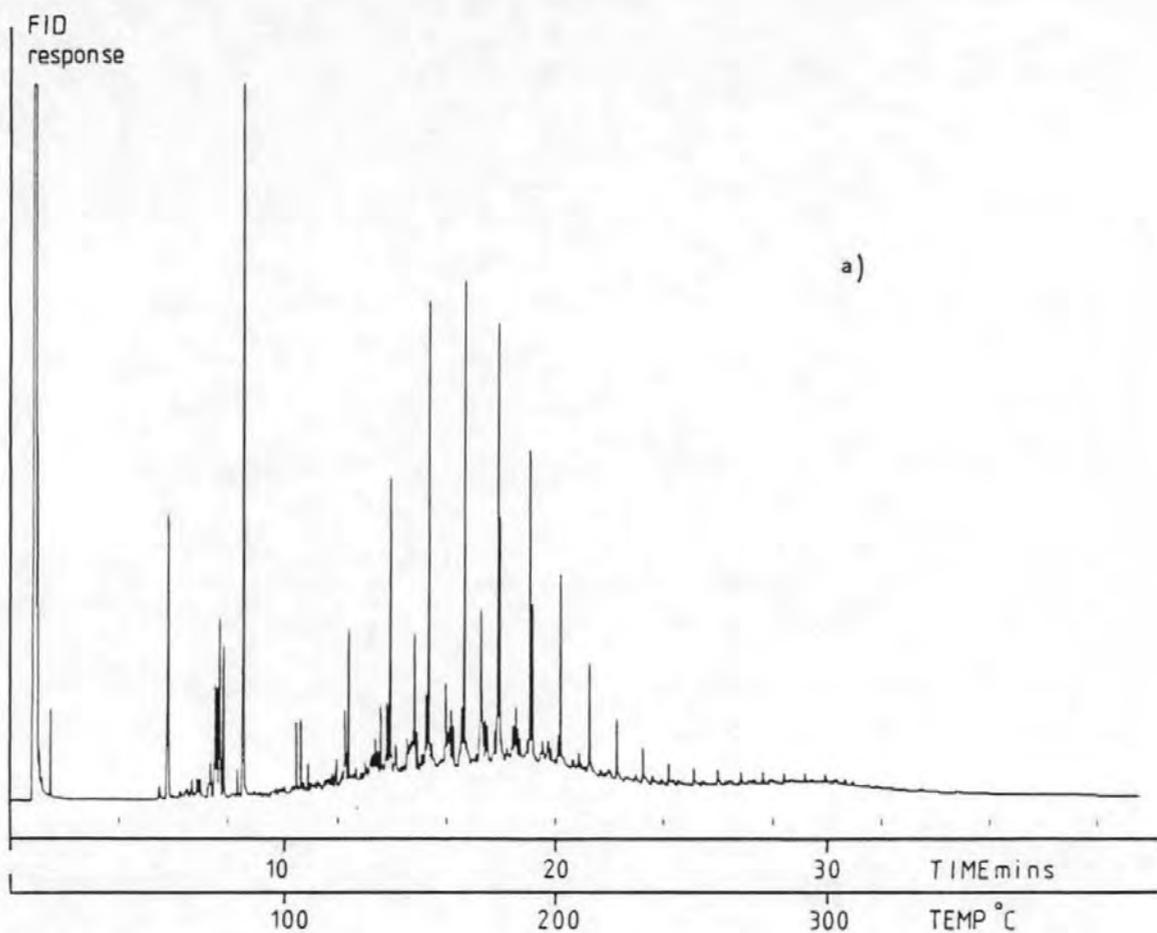


Fig 5.8 Gas Chromatograms for a TES Taken at a 3m Distance Down Exhaust Tailpipe. a) Aliphatic Hydrocarbon Fraction. b) Aromatic Fraction.

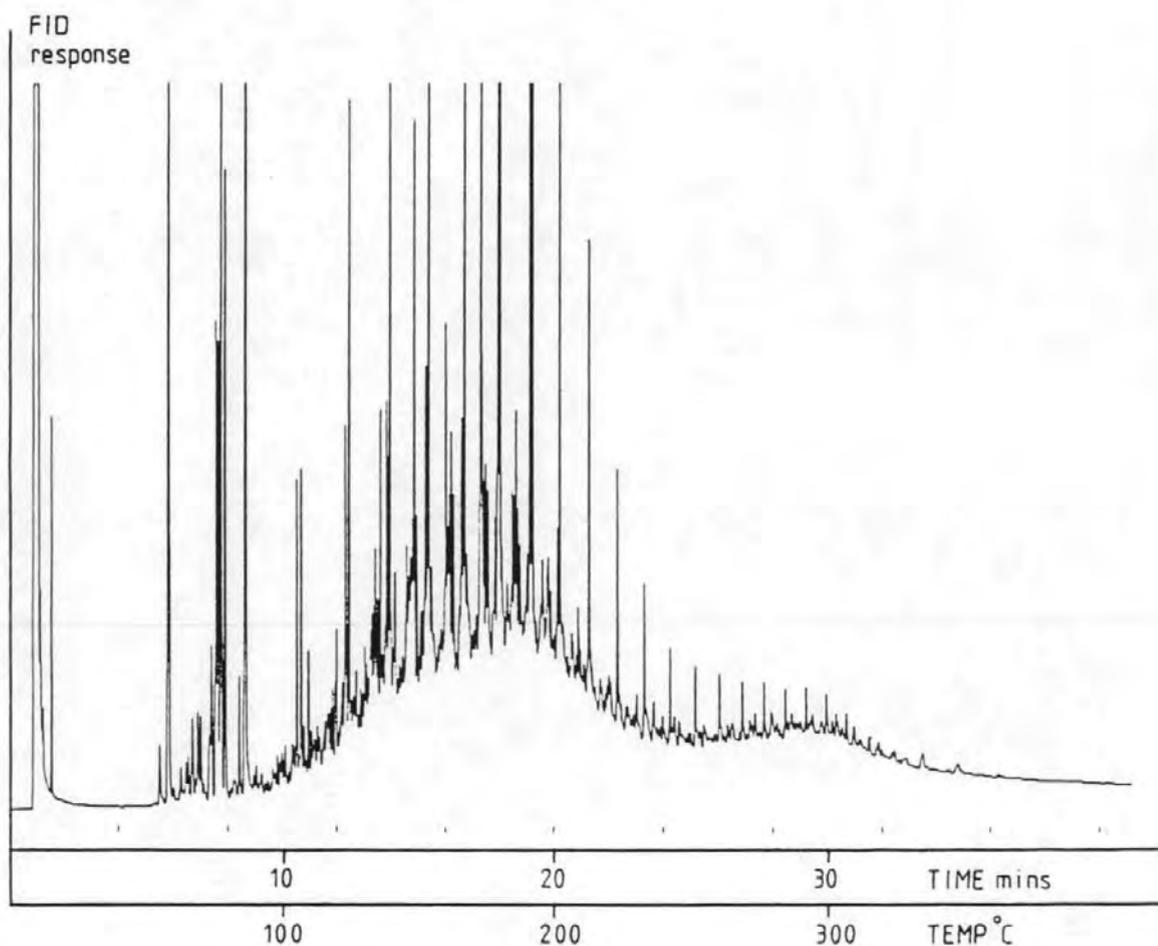


Fig 5.9 Gas Chromatogram for TES Taken 3m Down Exhaust Tailpipe with Decreased Attenuation to Emphasise the Lubricating Oil Contribution.

The decrease in sample weight for this TES can be attributed to two possible causes; either a significant amount of the gaseous organic compounds in the exhaust strongly adsorbed onto the surface of carbon particles during the passage down the tailpipe and were not extracted by TESSA, or, organic compounds continued the process of combustion into the tailpipe and the reduction in sample weight represents a simple process of increased burn-out.

In order to investigate whether the 3 m length of exhaust tailpipe had increased the amount of material that had adsorbed to the carbon particulates, the filters used to filter the solvent mixture from TESSA, immediately after sampling, were transferred to a soxhlet apparatus and extracted with DCM for 12 hours, section 3.1.1. The resulting extract was rotary-evaporated, transferred to a preweighed vial, dried with a stream of nitrogen and then weighed until constant weight was reached. No discernible increase in the weight of the vial was noted.

Notwithstanding the low weight, the vial contents were dissolved in DCM (0.1 cm³) and analysed by HRGC. The resulting gas chromatogram did not resemble the TES but instead was similar to the sort of sample extract obtained from filters, extracted without any sample, although, it is possible that low levels of occluded PAC were also present.

The lack of solvent soluble extractable material from the particulates can be explained if the adsorption of organic species to the carbon particulates did not occur during the

passage through the tailpipe. A thermocouple was mounted inside the transfer pipe, close to TESSA, during this experiment; by the end of sampling, the exhaust temperature in the transfer pipe was 156°C. At a temperature of 150°C, previous research (Kraft et al.1982, Cuthbertson et al.1979), has shown that, although some adsorption of organic compounds to carbon particulates will occur, the bulk of the organic compounds remain in the gas-phase. It is also likely that the action of the solvent system within TESSA stripped into solution any organic compounds weakly adsorbed to the surface of particulates.

In conclusion, the decrease in sample weight is best explained by a continuation of the process of combustion within the tailpipe burning up a significant quantity of residual organic compounds within the exhaust gases.

5.7 Intersample Comparison of Results.

The experiments described in sections 5.3, 5.5, and 5.6, are of interest not only individually but also by comparison with each other in their relation to the fuel and lubricating oil. Two interpretative techniques were used to facilitate comparison. Firstly, the comparison of certain peak ratios in the gas chromatograms, a technique adapted from previous application in organic geochemistry, and also the ratio of aliphatic to aromatic fractions (w/w) in the initial sample fractionation. Secondly, by the use of GC/MS as a specific ion detector, to quantitatively

compare mass fragments, characteristic of a particular compound, between samples.

5.7.1 Comparison of Ratios for Specific Peak Areas and Aliphatic/Aromatic Fractions.

In the aliphatic hydrocarbon fraction of the fuel and TES, the branched alkane isoprenoids, pristane and phytane, (molecular structure represented in Fig 5.10), are in close association with the two straight chain alkanes n-C17 and n-C18. The ratios of pristane/phytane, pristane/n-C17, phytane/n-C18, and n-C17/n-C18 have been widely used in organic geochemistry. They have been used to indicate variation in the temperature and pressure environment experienced by different samples during the processes of geological maturation and diagenesis which are involved in the formation of petroleum oil (e.g. Tameesh and Hanna 1986, ten Haven et al.1987) Small differences in the nature of the oxidation environment were found to make measurable differences in the survivability of each of these four indicator compounds. A similar technique has been used in comparing weathered oil spills with crude oil cargoes, Urdal et al.1986. The same ratios were compared in the present work to see if variations in the engine conditions might be detected and show trends for the survival of the aliphatic fraction of the fuel. Table 5.7 details the ratios for the samples and the fuel.

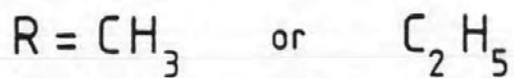
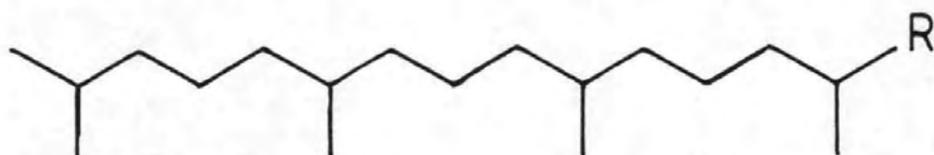


Fig 5.10 Diagram to Illustrate the Molecular Structure of the Isoprenoids, Pristane and Phytane.

	Fuel	Standard TES	High Speed +Load TES	3m Down Tailpipe TES
Ratios of:				
Aliph./Arom.fns.	2.58	1.31	1.14	0.85
Pristane/Phytane	1.17	1.18	1.29	1.34
Pristane/n-C17	0.62	0.67	0.49	0.68
Phytane/n-C18	0.57	0.64	0.59	0.67
n-C17/n-C18	1.07	1.13	1.54	1.32

Table 5.7 Comparison of Various Ratios Between Three TESSA Runs and the Fuel.

Considering the aliphatic/aromatic fraction ratios first, there is a consistent decrease in the ratio between all the samples and the fuel, i.e the TES each show a larger representation from the aromatic fraction than is present in the fuel. This could be explained by the formation of new aromatic compounds, during the process of combustion, from aliphatic hydrocarbons present in the fuel. Petch (1988) demonstrated that ¹⁴C-octadecane produces a significant ¹⁴C aromatic fraction on combustion in the same engine, thus supporting this interpretation.

Alternatively, the aromatic compounds present in the fuel may survive the combustion process marginally better than the aliphatic hydrocarbons. This would be unlikely, since the extremes of temperature and pressure, within the cylinder during combustion, would make such differences negligible. The aliphatic/aromatic ratios for the TES (1.31, 1.14, and 0.85) are much closer to the fuel (2.58) than they are to the used lubricating oil (20.7, see Table 5.1).

The trend of an increased aromatic fraction with respect to the aliphatic fraction develops further for the TES at high speed and load, when compared to the standard TES. This trend must be explained by processes within the cylinder during the combustion since both have been sampled close to the exhaust port. It suggests the possibility that increased temperature at high speed and load increases the transformation of aliphatic hydrocarbons to aromatic compounds by pyrosynthesis.

The TES at 3m distance from the engine is the only sample with a larger aromatic than aliphatic fraction. In this case, the explanation is different because the sample reflects not only the processes within the engine, but also, further reactions within the exhaust tailpipe. In the tailpipe, reasonably high temperatures (150-300°C) but a much lower pressure could be expected to favour the further combustion of any trace levels of aliphatic hydrocarbons, rather than the aromatic compounds, which have a greater chemical stability (see section 2.1.2). In other words the aliphatic hydrocarbons carry on burning, during their passage through the hot exhaust system, to a greater extent than do the aromatic compounds.

The four ratios for pristane, phytane, and their corresponding n-alkanes, are very similar for the fuel and TES taken at standard conditions. The mean of the differences for each of the four ratios between the fuel and the standard TES is only 0.048; all the values for the

standard TES are higher than for the fuel but only by a very small amount. The result offers further strong evidence that a significant contribution is made to the TES from fuel, which must pass through the engine unchanged. In fact for the specific compounds in question the fuel must actually be very dominant in the TES, if this were not so, then the closeness of the ratios, for several compounds, would be very unlikely to be maintained. For instance, any formation, within the combustion chamber, of pristane or phytane would, if it occurred, be unlikely to result in exactly the same ratio for the compounds as that found in the fuel.

Recent research by Eglinton (1988) has simulated the maturation process for a series of isoprenoids including pristane and phytane. He found that over a prolonged period (200 hours+) at elevated temperature and pressure the pristane/phytane ratio increased, whilst the pristane/n-C17 and phytane/n-C18 ratios lowered. This same trend is reflected in the TES at high speed and load.

A current theory in the field of geochemistry, which may well be applicable to the diesel engine results in some circumstances, has been put forward by Rowland (1988). He suggests that the phytane and n-C18 lose a CH₂ fragment to form pristane and n-C17 more readily than the pristane and n-C17 react to form the next lower isoprenoid and n-alkane; in a diesel combustion chamber this would be a process of pyrosynthesis. The result is a slight increase in the respective ratios.

Thus, an increase in the pristane/phytane and n-C17/n-C18 ratios may be a useful indicator for the process of pyrosynthesis. Applying this to the samples, the TES at standard conditions appears to be made up predominantly from fuel which has survived combustion. Whereas the TES at high speed and load has a significant contribution from pyrosynthesised products of partial combustion. Furthermore, since the ratios for the TES at 3m down the exhaust tailpipe should differ from the TES at standard conditions only through the reactions that have occurred in the exhaust system, the increase in the pristane and n-C17 ratios, in this sample, indicates that pyrosynthesis occurs in the exhaust tailpipe as well as in the combustion chamber.

5.7.2 Single Ion Detection by GC/MS.

In the second interpretative technique, GC/MS was used as a specific ion detector to make intrasample and intersample comparisons for certain groups of compounds in the aromatic fraction.

The GC/MS can be used as a specific ion detector by retrieving from the TIC selected data relating to specific ion masses. Operating the GC/MS at a low ionising potential of 40 eV, it is possible to detect molecular ions which have been ionised but not fragmented. Selecting an ion mass corresponding to the molecular mass, for a compound of interest, enables the molecular ion for this

compound to be highlighted, in spite of the compound being part of a complex mixture.

For example, the molecular mass of naphthalene is 128 mass units, the TIC can be searched and only the ions with 128 mass units retrieved for display. Although ions with this mass may be spread throughout the TIC, by using retention times, it is possible to identify the molecular ion for naphthalene and be reasonably confident that there is very little interference by ions from other compounds, which would not only have to be co-eluting, but also to have the same mass. The peak area for the molecular ion can then be quantified.

In order to illustrate the technique, Figs 5.11 and 5.12 show the molecular ion peaks for naphthalene, methyl naphthalenes, and dimethylnaphthalenes from the fuel and TES at high speed and load, respectively. The retention times are printed at the apex of the relevant peak, and integration marks are included at the base of peaks, indicating the area that the computer has integrated for quantification. Table 5.8 lists the groups of compounds which were identified by single ion detection in the same manner:

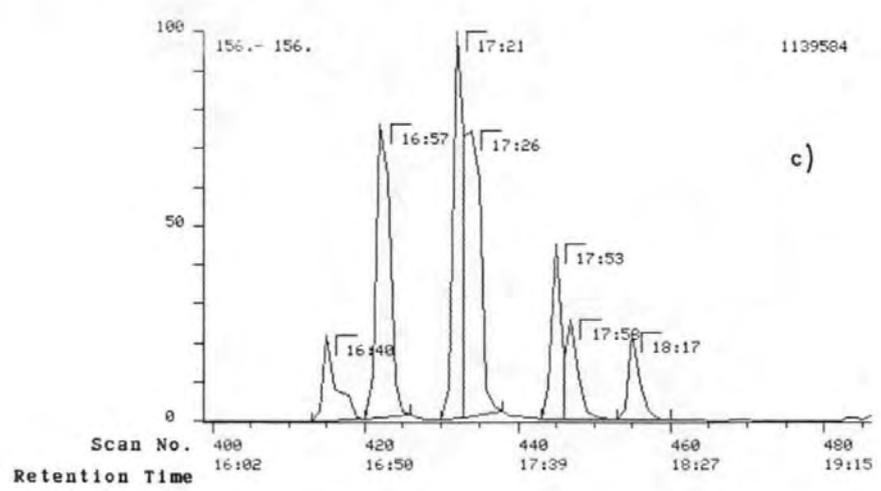
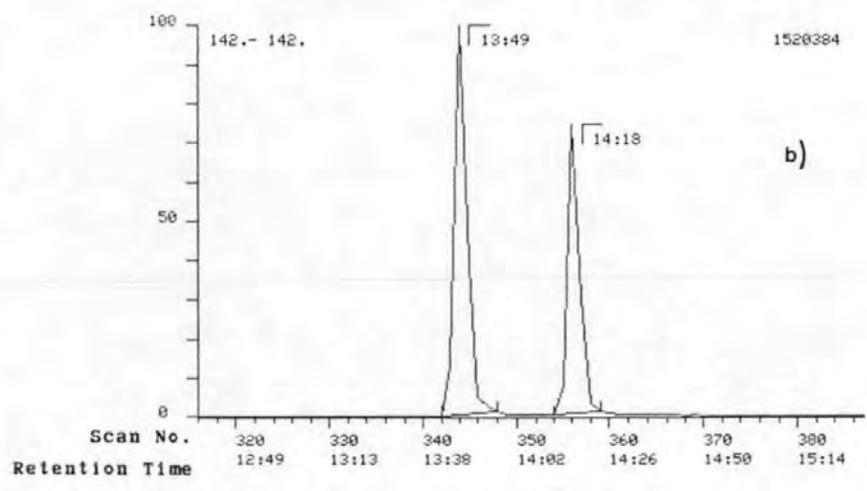
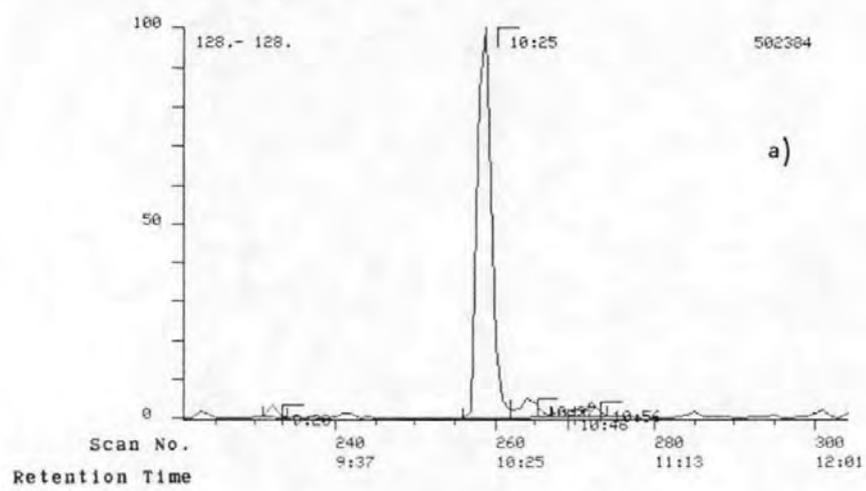
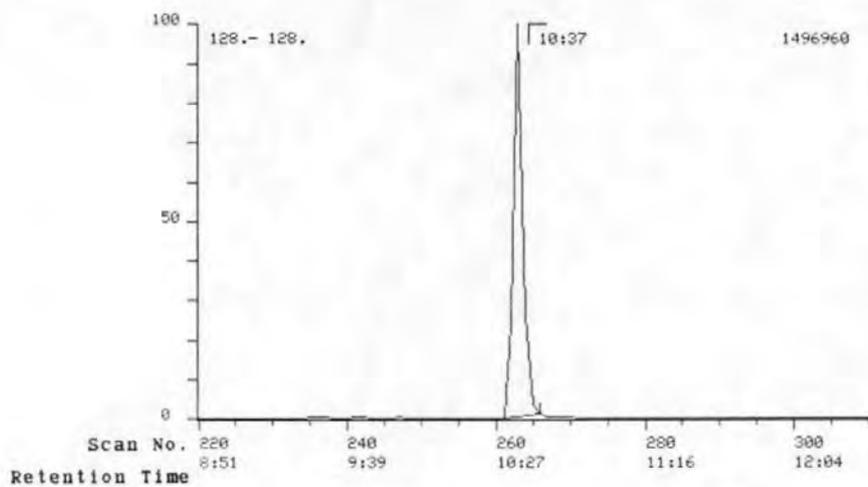
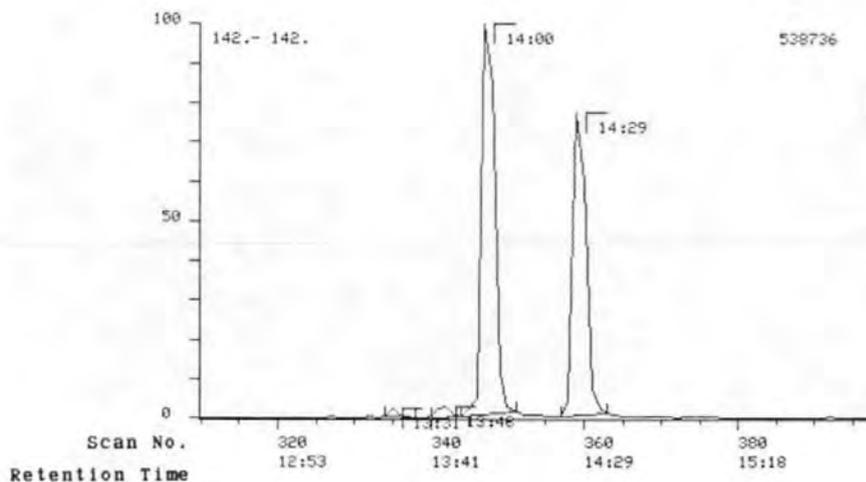


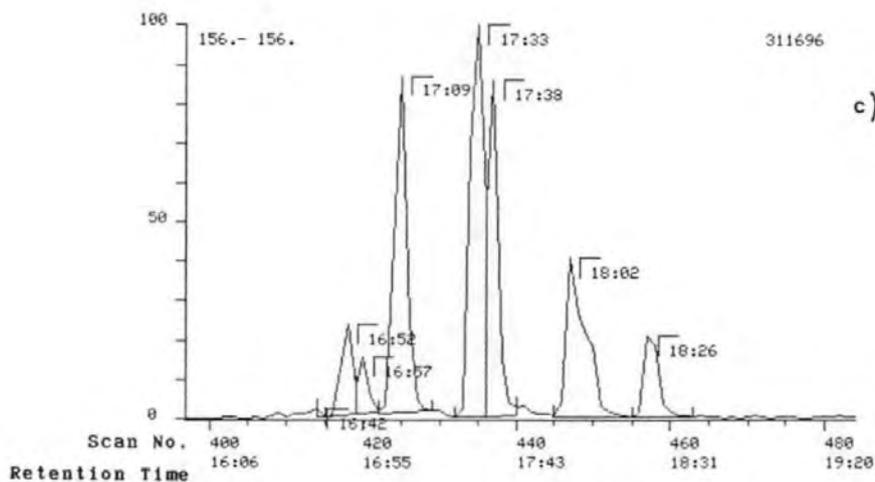
Fig 5.11 Selective Ion Detection Showing Molecular Ions in Fuel for: a) Naphthalene. b) Methyl naphthalenes. c) Dimethyl naphthalenes.



a)



b)



c)

Fig 5.12 Selective Ion Detection Showing Molecular Ions in TES at High Speed and Load for: a) Naphthalene b) Methylnaphthalenes. c) Dimethylnaphthalenes.

	Mol wt.	No of isomers	No of peaks quantified	Abbreviations used in figures
Naphthalene	128	1	1	NP
Methylnaphthalenes	142	2	2	C1-NPs
Dimethylnaphthalenes	156	10	7	C2-NPs
Fluorene	166	1	1	FR
Methylfluorenes	180	4	4	C1-FRs
Phenanthrene	178	1	1	PA
Methylphenanthrenes	192	5	4	C1-PAs
Dibenzothiophene	184	1	1	DBT
Methyl-dibenzothiophenes	198	4	3	C1-DBTs
Dimethyl-dibenzothiophenes	212	16	6	C2-DBTs

Table 5.8 List of Compounds Analysed by Single Ion Detection.

High purity analytical standards were not available for the external quantification of most of these compounds and although the response factors for different compounds varies in GC/MS analysis, nevertheless the quantification of the peak areas for the specific molecular ions enabled interesting comparison within, and between samples, as well as with the fuel, where the same compound is involved.

An internal standard of n-C11 was added to each of the samples, during the final dilution step prior to GC/MS analysis; this internal standard was quantified easily by monitoring the molecular ion at 156 mass units. In this way variations in the weight of sample injected onto the capillary column could be compensated for in any intersample comparison of molecular ions.

Whereas, in the GC/MS data for the fuel, only trace levels of the heavier PAC were detectable, in all the TES the

presence of fluoranthene (RMM 202), pyrene (RMM 202), and chrysene (RMM 228), were immediately identifiable by their molecular ions and relative retention times. The single ion detection display, from the TES for high speed and load, is shown, along with the corresponding mass spectra, in Figs 5.13 and 5.14. The molecular ion for the internal standard, n-undecane (RMM 156), is also shown.

The mass spectral data for fluoranthene, pyrene, and chrysene shown in Fig 5.14 have characteristic features common to most PAC: the most prominent are an intense molecular ion, with the $(M+1)^+$ ion due to the ^{13}C isotope next to it on one side, and the $(M-1)^+$, $(M-2)^+$, $(M-3)^+$, and $(M-4)^+$ ions on the other side, (Lee et al.1981). A doubly charged molecular ion is common for PAH (Karcher et al.1985), and the $m/2z$ ions for both fluoranthene and pyrene, at a mass number of half that of the molecular ion i.e. 101, are clearly observable.

The presence of these higher relative molecular mass PAH, fluoranthene, pyrene, and chrysene, within the TES exhaust extracts, when they were not present at detectable levels in the GC/MS data for the fuel, is most easily explained by their formation through pyrosynthesis within the combustion chamber, and this conclusion follows similar results by other researchers, Williams et al.1987.

A very large peak was visible in the TIC from the aromatic fraction of the fuel, with a retention time higher than the bulk of the other compounds making up the fuel. Mass

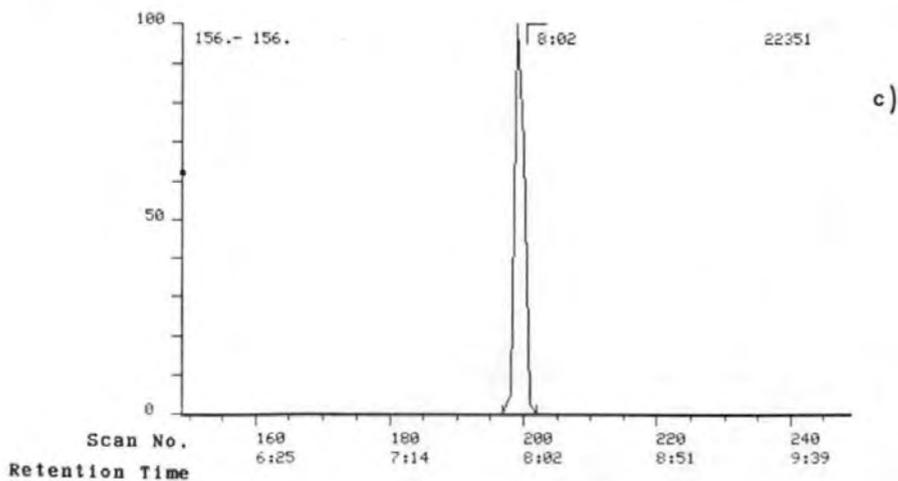
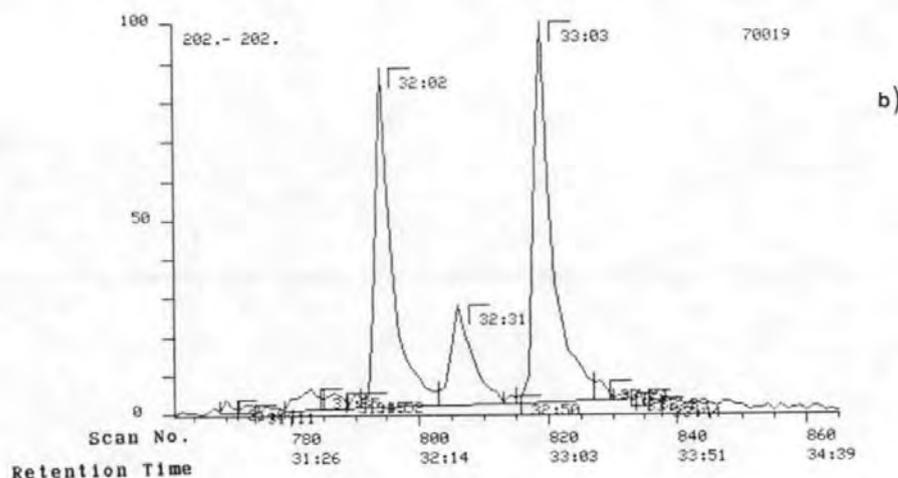
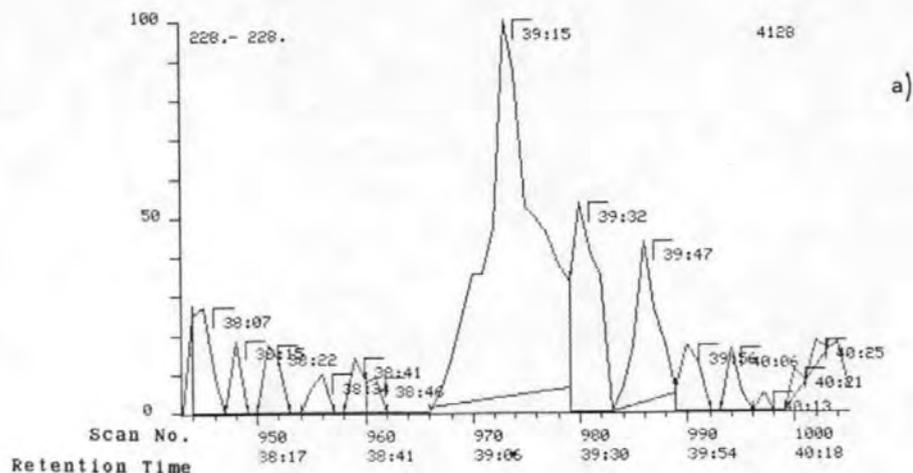


Fig 5.13 Selective Ion Detection Showing Molecular Ions in the TES at High Speed and Load for: a) Chrysene. b) Fluoranthene and Pyrene. c) Undecane, (Internal Std).

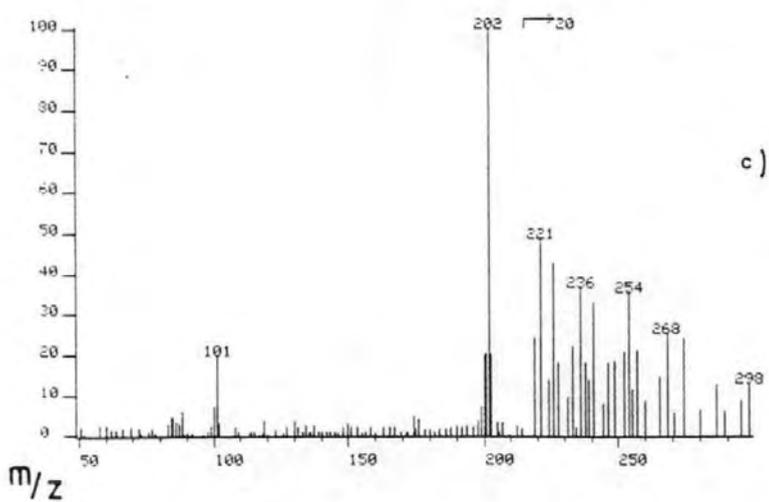
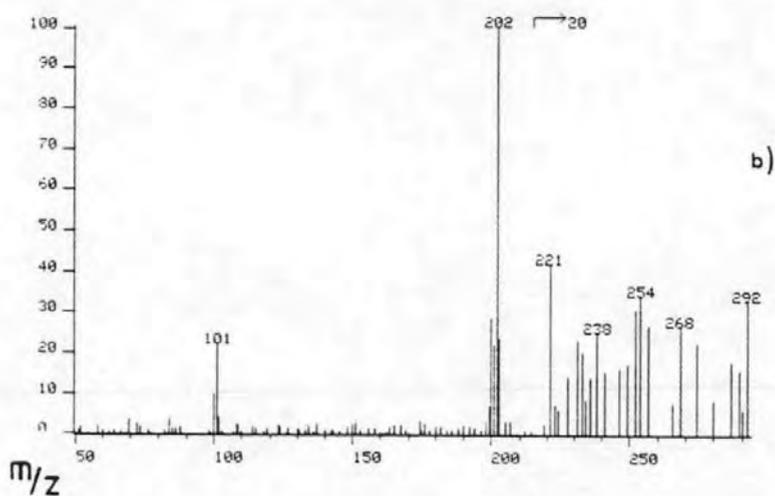
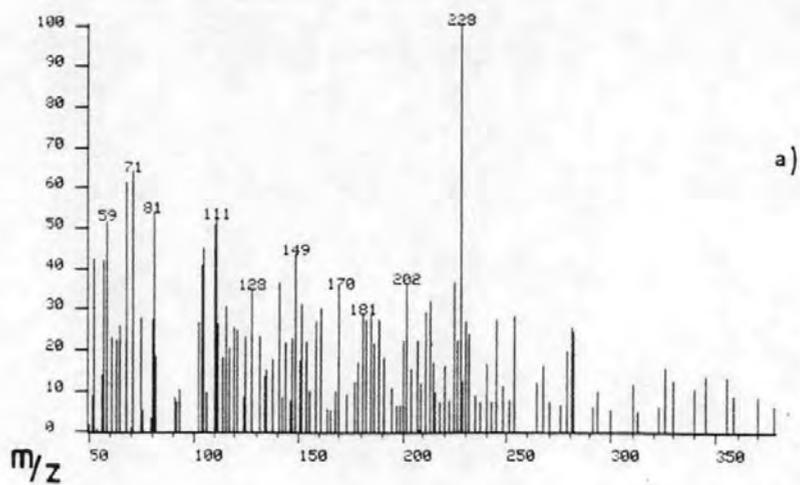


Fig 5.14 Mass Spectra from TES at High Speed and Load for: a) Chrysene. b) Pyrene. c) Fluoranthene.

spectral data indicated that it was a phthalate ester, Fig 5.15(a). This compound is a contaminant present within the fuel at a considerable concentration; it elutes at a high enough retention time not to interfere with the analysis. The bulk of this compound elutes in the polar fraction.

The aromatic fraction of the used lubricating oil was further analysed by GC/MS; the trace for the TIC showed very few peaks resolved above the UCM except for one very dominant peak. A spectrum of this peak proved to be identical to that of the phthalate ester contaminant found in the fuel, (see section 4.3.7), with respect to retention time and fragmentation ion masses, Fig 5.15(b) This comparison gives a good indication of the accumulation of fuel in the lubricating oil. A specific molecular ion search for both the light and heavier PAC's, that might also have been expected to have accumulated in the lubricating oil from the fuel, revealed only trace levels for any of them.

5.7.3 Results of Selective Ion Quantification.

Once the specific molecular ions had been quantified, a list of each ion, and the corresponding integrated peak area, was printed out, Table 5.9 shows the peak area listing for the specific ions in the TES at high speed and load.

For intrasample comparison, a ratio was then calculated for

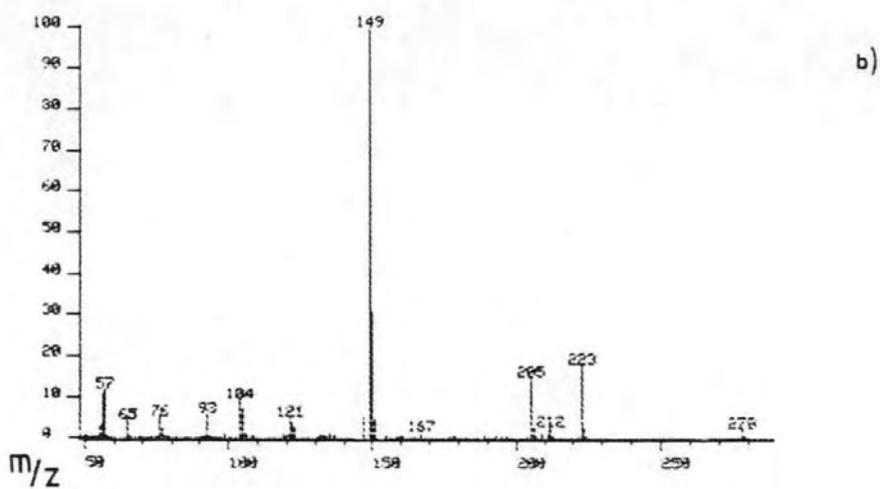
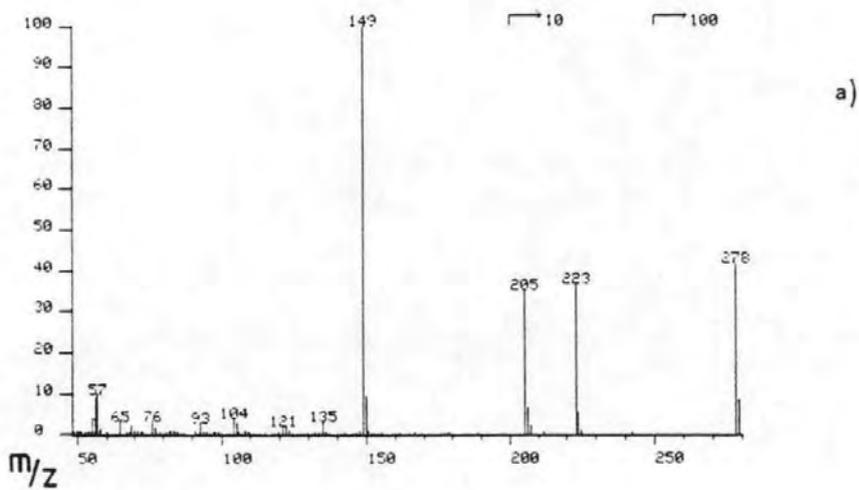


Fig 5.15 Mass Spectra of Phthalate Ester Contaminant in: a) Aromatic Fraction of Lubricating Oil. b) Aromatic Fraction of Fuel.

Relative Molecular Mass	Retention Time	Area Count	Relative Molecular Mass	Retention Time	Area Count
			202.0000 - .0000	31:04	3669
128.0000 - .0000	10:37	2261539		31:11	3782
142.0000 - .0000	13:31	15932		31:35	15532
	13:48	30663		31:45	9810
	14:00	1079870		31:52	4899
	14:29	793992		32:02	188886
156.0000 - .0000	8:02	39544		32:31	70459
	16:42	6276		32:50	2463
	16:52	130323		33:03	223348
	16:57	81041		33:24	8565
	17:09	492971		33:34	1707
	17:33	693782		33:39	4039
	17:38	495445	212.0000 - .0000	33:44	1594
	18:02	351814		29:46	11363
	18:26	138992		29:56	50071
166.0000 - .0000	20:20	4712		30:16	17562
	20:27	6418		30:25	75406
	20:44	5798		30:40	34710
	20:54	9638		30:52	69685
	21:13	57430		31:11	20364
	21:33	68356		31:16	12206
	21:42	269557		31:26	6018
	21:59	23421		31:33	6534
	22:12	59041		31:40	1546
	22:33	29387		31:47	4299
	22:43	51776		32:02	3278
	22:50	7348	226.0000 - .0000	30:57	688
178.0000 - .0000	26:14	2007055		31:02	953
	26:26	163497		31:09	2513
180.0000 - .0000	24:03	14637		31:26	1762
	24:17	16579		31:35	3225
	24:27	82512		31:40	2508
	24:37	111407		31:47	10941
	24:51	58716		32:00	4628
	25:03	1625		32:17	19717
	25:08	3033		32:31	6104
	25:23	21155		32:43	8006
	25:30	3395		32:48	6964
	25:35	643		32:55	11399
184.0000 - .0000	25:15	22627		33:03	6291
	25:37	377378		33:15	16062
	26:14	20479		33:22	6638
192.0000 - .0000	27:48	23218		33:32	11076
	28:44	148843		33:44	3429
	28:51	316069		33:48	1648
	29:15	235625		33:53	1062
	29:20	260135	228.0000 - .0000	34:01	1613
	29:51	692		34:05	2608
	29:56	1579		34:15	1649
	30:01	0		34:20	1721
198.0000 - .0000	26:50	3254		38:07	2554
	27:50	142016		38:15	780
	28:05	9830		38:22	1317
	28:17	74095		38:34	677
	28:29	11571		38:41	917
	28:34	6435		38:46	724
	28:39	6200		39:15	21222
	28:46	43012		39:32	6738
				39:47	4176
				39:56	1489
				40:06	882
				40:13	200
				40:21	294
				40:25	275

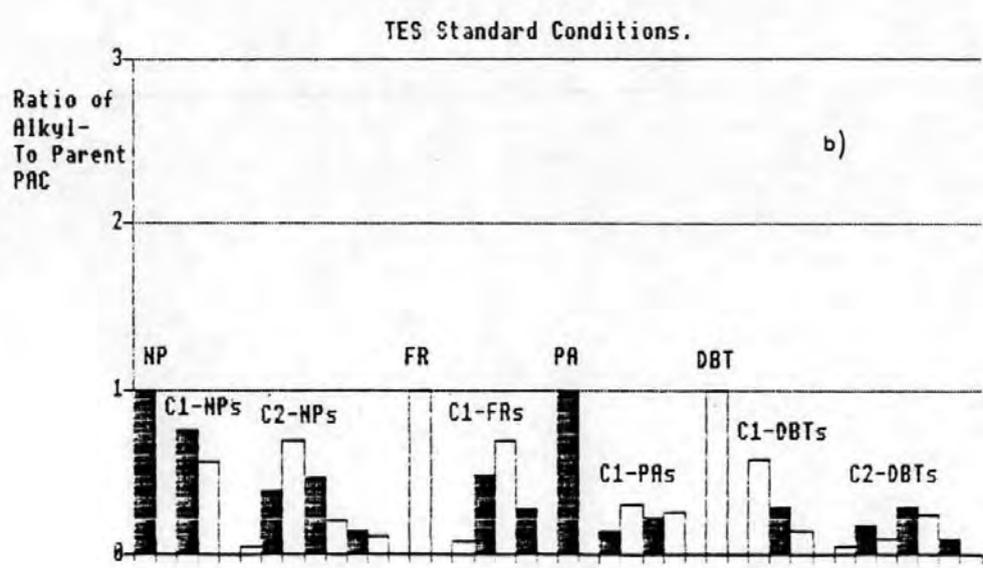
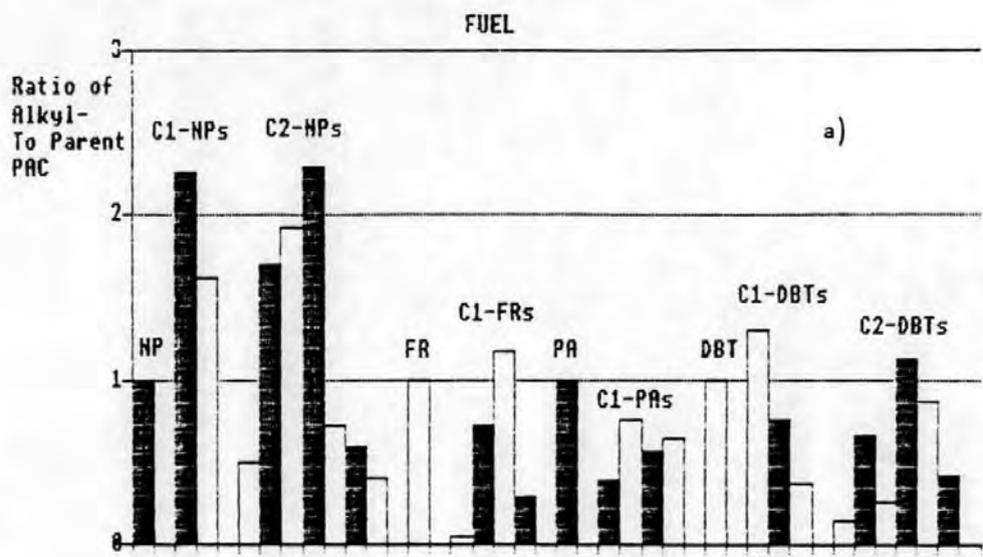
Table 5.9 Peak area listing for the specific ions in the TES at high speed and load.

the peak area from each of the alkylated derivatives relating it to the respective parent compound; the peak area for the parent compound was divided into all the corresponding alkyl-PAC peak areas, e.g. the peak area for naphthalene was divided into those for the methyl- and dimethyl- naphthalenes . The resulting sets of ratios, from each of the samples and the fuel, were plotted as histograms, to facilitate interpretation. The histograms are shown in Figs 5.16 and 5.17.

The histogram for the fuel shows that many of the alkylated PACs have a ratio greater than 1, and, in the case of several of the methyl- and dimethyl- naphthalenes, it is greater than 2. If a similarity in GC/MS response factors is assumed, for the parent and corresponding alkyl PACs, then, this means that some alkyl naphthalenes are more than twice as abundant as naphthalene, in the fuel.

There is a dramatic contrast in the histograms for the TES, when compared to that for the fuel. In these, the ratios of the alkyl PACs have changed so that they are always less than one, and, in the case of the TES at high speed and load, they are less than 0.5, i.e. in this TES, the parent PACs are at least twice as abundant as the alkyl PACs.

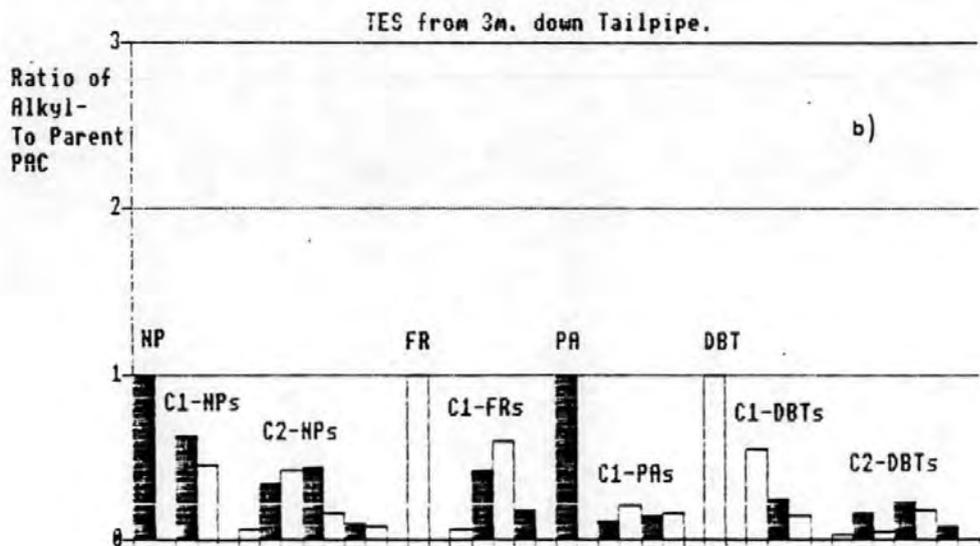
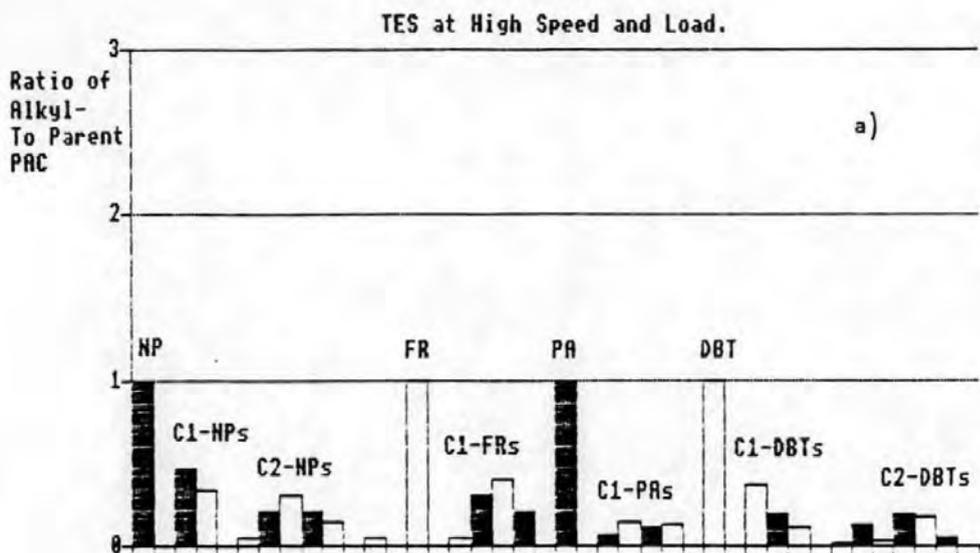
Whereas the overall increase in the relative concentration of parent PAC, with respect to the corresponding alkyl PAC, could be explained by a difference in combustibility, this is unlikely, since the extreme temperature and pressure regime within the cylinder, during combustion, would tend



Key to Abbreviations:

- | | | | |
|--------|------------------------|---------|------------------------------|
| NP | = Naphthalene | PA | = Phenanthrene |
| C1-NPs | = Methylnaphthalenes | C1-PAs | = Methylphenanthrenes |
| C2-NPs | = Dimethylnaphthalenes | DBT | = Dibenzothiophene |
| FR | = Fluorene | C1-DBTs | = Methyl dibenzothiophenes |
| C1-FRs | = Methylfluorenes | C2-DBTs | = Dimethyl dibenzothiophenes |

Fig 5.16 Histograms Showing Ratio of Parent- to Alkyl- PAC in: a) Fuel. b) TES at Standard Conditions.



Key to Abbreviations:

NP	= Naphthalene	PA	= Phenanthrene
C1-NPs	= Methylnaphthalenes	C1-PAs	= Methylphenanthrenes
C2-NPs	= Dimethylnaphthalenes	DBT	= Dibenzothiophene
FR	= Fluorene	C1-DBTs	= Methyl dibenzothiophenes
C1-FRs	= Methylfluorenes	C2-DBTs	= Dimethyl dibenzothiophenes

Fig 5.17 Histograms Showing Ratio of Parent- to Alkyl- PAC in: a) TES at High Speed and Load. b) TES Taken 3m Down Exhaust Tailpipe.

to minimise such differences. A more plausible explanation is that the concentration of the parent compounds surviving combustion, is enhanced by the formation of these compounds by pyrosynthesis during combustion. If this is correct, then the TES at high speed and load, which involves a higher temperature during combustion and also a lower AFR, includes a greater amount of parent PAC formed by pyrosynthesis.

To look at the relationship between the fuel and TES more closely a further series of ratios were calculated to facilitate intersample comparison. For this, the peak area for every one of the PAC in a TES (listed in Table 5.8), was divided by the peak area for the corresponding compound in the fuel. The series of ratios are presented in the form of a histogram for each of the TES in Fig 5.18.

These histograms again reveal an increasing relative concentration of parent PACs in the TES, when compared to the fuel, whilst at the same time, showing a decreasing relative concentration for the alkyl PAC. The difference in the ratios, between parent and alkyl PAC, is strongest in the TES at high speed and load. In so far as these histograms represent the survivability of alkyl PAC in the fuel, passing through the combustion process, (this assumes that alkyl PAC are not formed by pyrosynthesis in any significant amount) then the very similar ratios, within each group of alkyl PAC, means that these have survived to a similar extent; e.g. the methyl phenanthrenes, in each of the TES, all have very similar ratios, and therefore

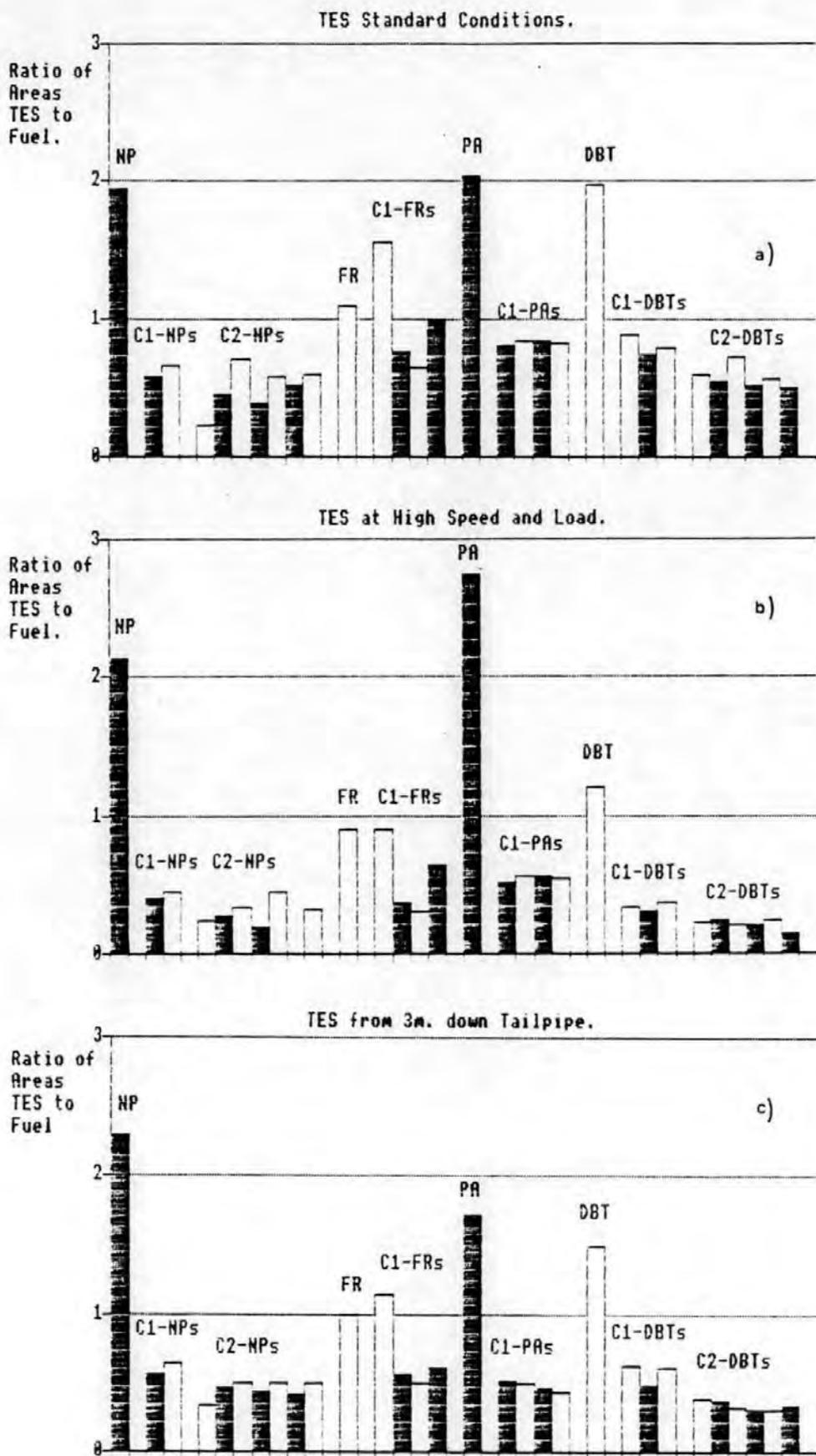


Fig 5.18 Histograms Showing Ratio of Peak Area Between TES and Fuel for Specific PAC in: a) TES at Standard Conditions. b) TES at High Speed and Load. c) TES Taken 3m Down Exhaust Tailpipe. (For key to abbreviations see Fig 5.17.)

their survivability does not vary with the position to which the methyl group is attached on the polycyclic structure.

The parent PACs generally have ratios greater than 1. This supports the hypothesis that there is a significant formation of these compounds, through pyrosynthesis within the engine. There is a considerable variation in ratio between the different parent compounds within a sample, which might be explained by a greater or lesser propensity to being formed within the engine, perhaps, based on the individual molecular structures of the compounds. For example, the ratios for fluorene, within the three samples remain around 1, whereas for naphthalene they are all close to 2. The formation of phenanthrene appears to be strongly favoured in the TES at high speed and load.

Concurrent research by Petch (1988) has shown that combustion of a fuel containing radiolabelled benz(a)pyrene resulted in many compounds in the exhaust, including naphthalene, which must therefore have been formed through pyrosynthesis. Another interesting outcome of the experiments by Petch was that radiolabelled methyl-anthracene did not appear to produce anthracene; demethylation has always been assumed to be an important pathway in pyrosynthesis but this result raises some doubt whether this is true. If molecular structure determines the likelihood of a compound being formed through the partial combustion of a larger PAC molecule like benz(a)pyrene then it may be possible to find a correlation

between molecular structure and pyrosynthesised exhaust products.

CHAPTER 6.

Comparison Between TESSA and a Dilution Tunnel/Filter Sampling System.

This chapter describes an experiment in which the exhaust from a light duty diesel engine was sampled by TESSA, connected close to the exhaust manifold, whilst further down the exhaust tailpipe, a standard dilution tunnel system was connected, enabling filter samples to be taken in the manner recommended by the United States Environmental Protection Agency (EPA). Thus, the TESSA sample gave an indication of the type and concentration of organic material leaving the engine, whereas the filter sample was indicative of the organic species, associated with exhaust particulates, which would have entered the atmosphere. In other words, the particulate sample reflected further chemical reactions that occurred in the exhaust tailpipe or on the filter in the dilution tunnel (Risby 1983).

It is acknowledged that filtering of low relative molecular mass volatile organic compounds, which may remain in part within the gaseous phase, such as 2 and 3 ringed aromatics, is not completely effective (Williams et al. 1985). Therefore, a normal procedure is to monitor the total unburnt hydrocarbon (UHC) levels in the exhaust, by the means of a flame ionisation detector (FID), to give an indication of those compounds not trapped by the filter; the TESSA system offers additional information on these

compounds because it traps gas-phase as well as particulate bound organics, which, with their subsequent analysis by HRGC, can be studied in detail. In a recent review, Schuetzle and Frazier (1986) emphasised the significance of the contribution that gas phase pollutants from diesel and petrol engines can make to air pollution.

6.1 Facilities Available.

TESSA is a reasonably mobile system, and for this experiment it was transported to Ricardo Consulting Engineers plc (Shoreham by Sea), where a testbed was made available with a modern passenger car IDI ca. 2-litre, 4 cylinder, naturally aspirated diesel engine mounted on it, and a mini-dilution tunnel and filter system attached to the exhaust. The engine was fully controlled and monitored by computer, to include analysis of the exhaust gases: NO_x, CO/CO₂, UHC, and O₂, along with Air/Fuel Ratio (AFR) and Bosch smoke.

In order to enable the TESSA system to be connected to the main exhaust pipe, a short (60 cm) transfer pipe was added very close (15 cm) to the exhaust manifold. Appendix A includes plates G and H illustrating the set-up employed for this experiment. The maximum temperature of the transfer pipe, as measured by a thermocouple inserted into the gas stream during the experiments described here, did not exceed 480°C.

From earlier measurements taken with the single-cylinder

test engine, (Ricardo E.6/T), reported in section 3.6, the maximum capacity of TESSA was estimated to be 500 l/min, when using a solvent volume of 2 l and a sampling time of 3 minutes. The back-pressure exerted by TESSA on the exhaust system was measured with a manometer during sampling and gave a reading of only 4.9cm of water. Since TESSA could not handle the total exhaust flow from this engine, it was necessary to split the exhaust. The minimal backpressure from TESSA made it possible to distribute the exhaust gases, between the transfer pipe and main exhaust, approximately in the ratio of the cross-sectional areas of the respective pipes, (approximately 1:4 was achieved). Thus, TESSA was receiving an optimal flow of ca. 500 l/min. A measurement by manometer at the top exit from TESSA, during the sampling, gave a reading of 5.7 cm of water, which was similar to that measured in previous tests.

Previous research has indicated that the load on the engine is the most significant engine operating parameter affecting the emission of PAH and PAC, (Schuetzle and Frazier, 1986). Therefore, it was decided that the experiment to be carried out would be done at a constant engine speed of 2500 rev/min, whilst varying the load.

6.2 Test Procedure.

The engine was conditioned by running at full-load and speed for one hour, before selecting 2500 rev/min and the chosen load, and further conditioning the system for 15

minutes. The valve in the transfer pipe was kept fully closed until the end of the conditioning period, when it was opened fully and a TESSA sample taken in the manner described in section 4.4. Only static engine conditions can be sampled with the present design of TESSA, and a range of typical operating conditions was selected to give a comprehensive picture of the changes in emissions from full to low load i.e. 20, 40, 55, and 100 Nm load.

6.2.1 Filter Sampling.

Filter samples were taken at a temperature maintained below 52°C, after air dilution. Only a part of the exhaust was drawn off into the dilution tunnel, and exact dilution was monitored and adjusted by comparing the concentration of NO_x in the exhaust before and after dilution. A volume of diluted exhaust was drawn through each filter for a sufficient sampling time to ensure a particulate loading per filter of around 10 mg; the exhaust volume sampled was accurately recorded for each sample. The exhaust emissions were routinely monitored for hydrocarbons during the sampling procedure using a probe in the exhaust and a heated transfer line, kept above 190°C to prevent condensation of material, before reaching the FID.

6.3 Analytical Techniques.

The sample from TESSA was filtered under reduced pressure immediately after sampling. The DCM fraction was then extracted by liquid/liquid partition. The sample was

concentrated by rotary evaporation under reduced pressure at 35°C, transferred to a preweighed vial where any remaining solvent was removed by blowdown with nitrogen gas, the TES was then ready for fractionation prior to analysis, (section 3.1.2).

The filter samples were extracted with a soxhlet apparatus for 12 hours using DCM as the solvent. The resulting extract, soluble organic fraction (SOF), was then rotary evaporated in a similar manner to the TES sample. Both samples were fractionated by column chromatography, (section 3.1.4).

6.4 Results and Discussion.

The SOF and TES results can be compared with the UHC measurements taken during sampling in Figs 6.1 and 6.2. The general picture is one of increasing hydrocarbon emissions as load decreases. This is the expected result from a modern engine, in which the high air-fuel ratios at low load lead to localised over-lean conditions preventing complete combustion from being effected, whereas the problem of over-fuelling prevalent in older engines at high load is well under control (Lily 1984). The variations in the TES are not very different for the four load conditions. The data for the TES represents the results for only one experiment and need to be repeated to confirm the trends, in particular the low reading for the 20 Nm load.

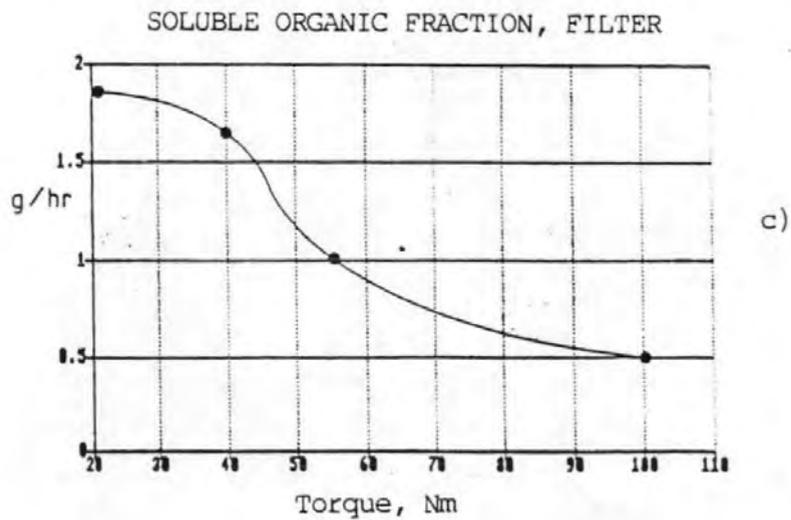
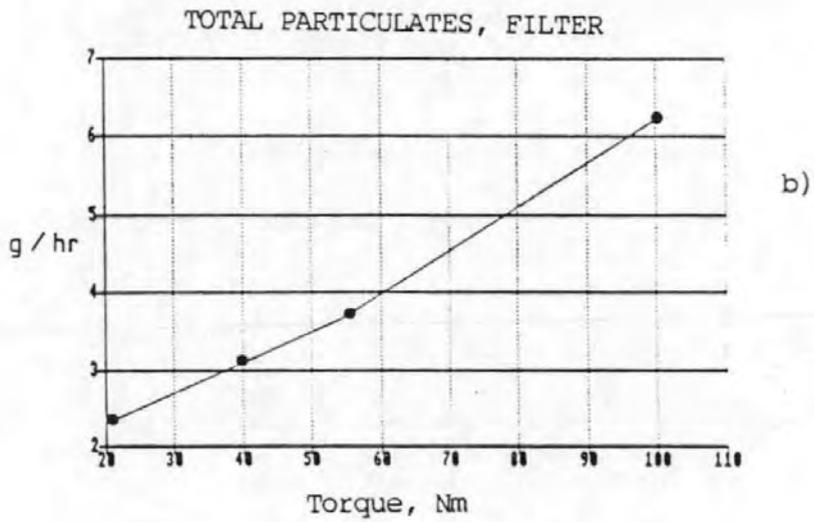
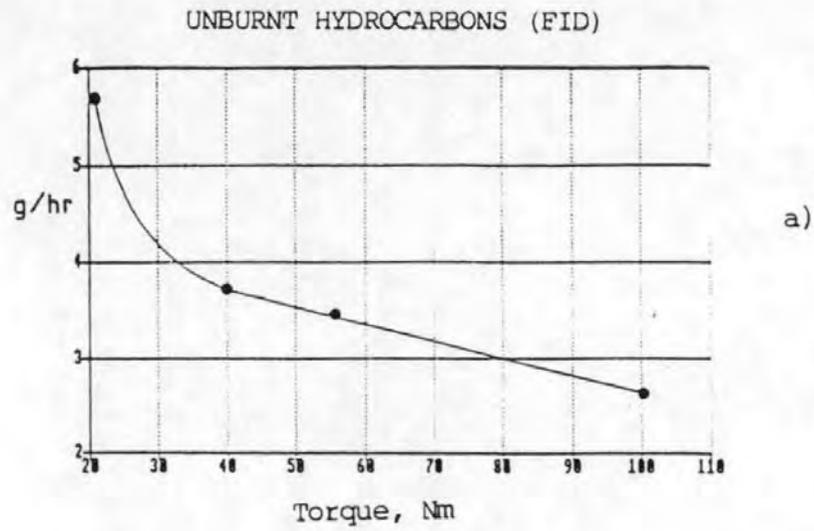


Fig 6.1 Graphs Showing the Variation in Emissions at Different Loads: a) Unburnt Hydrocarbons. b) Total Particulates from Filter. c) Soluble Organic Fraction from Filter.

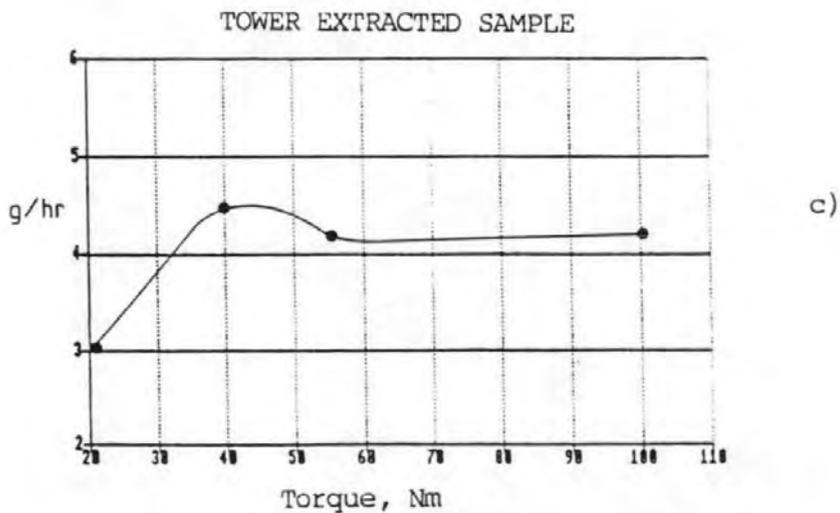
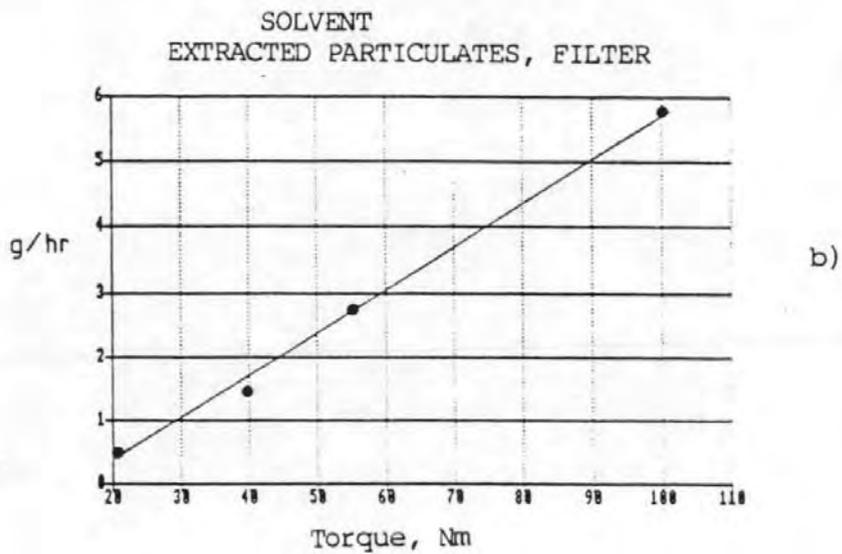
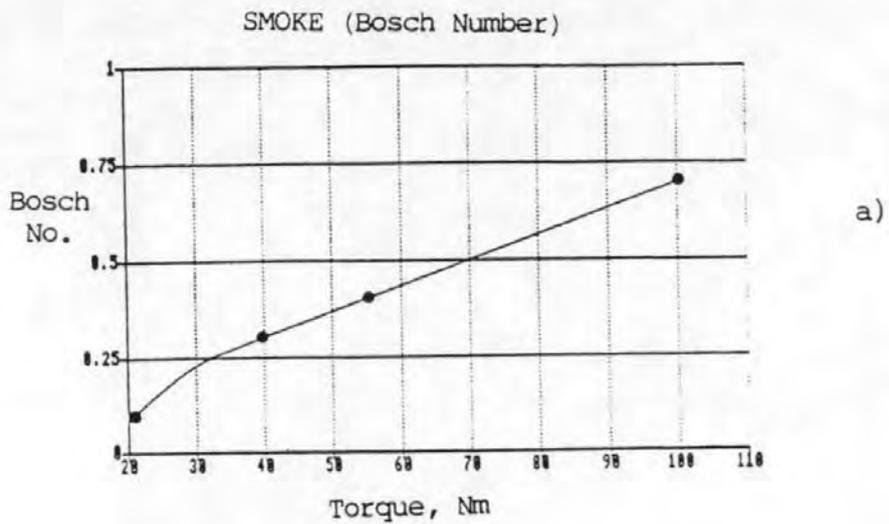


Fig 6.2 Graphs Showing the Variation in Emissions at Different Loads: a) Bosch Smoke Number. b) Solvent Extracted Particulates from Filter. c) TESSA Extracted Sample.

The results from this experiment can be compared with published data for an on-the-road, 1.8 l IDI diesel, tested under similar steady state conditions, (Cartellieri and Tritthart 1984). The results for the UHC and total particulates are of the same order of magnitude for both sets of data, but the Bosch smoke figures are much lower for the engine used in the present test, shown in Fig 6.3. Alkidas (1984) correlated Bosch smoke, total particulates and extracted particulate (carbon) for an IDI diesel engine, and described similar trends to those shown in Fig 6.1.

Examination of the gas chromatograms for the aliphatic fractions of the fuel and lubricating oil used in the engine test, shows a prominent representation from a homologous series of n-alkanes with an approximately normal distribution around the carbon numbers C14-C15 for the fuel, whilst the used lubricating oil has a characteristic UCM hump with well resolved peaks superimposed on top, again normally distributed but this time positioned around a boiling point range corresponding to that for the n-C26 and n-C27 alkanes, Fig 6.4. It can be seen in the GC trace of a corresponding TESSA sample (aliphatic fraction), Fig 6.6a, that the homologous n-alkane series, although still prominent, has shifted in its distribution towards n-C17, and is less normal in its distribution.

The compounds of lower GC retention time than the n-C14 peak comprise mainly light aromatics, such as alkyl naphthalenes, which have unintentionally been eluted with the

Comparison of Smoke Levels from Two IDI Diesel Engines

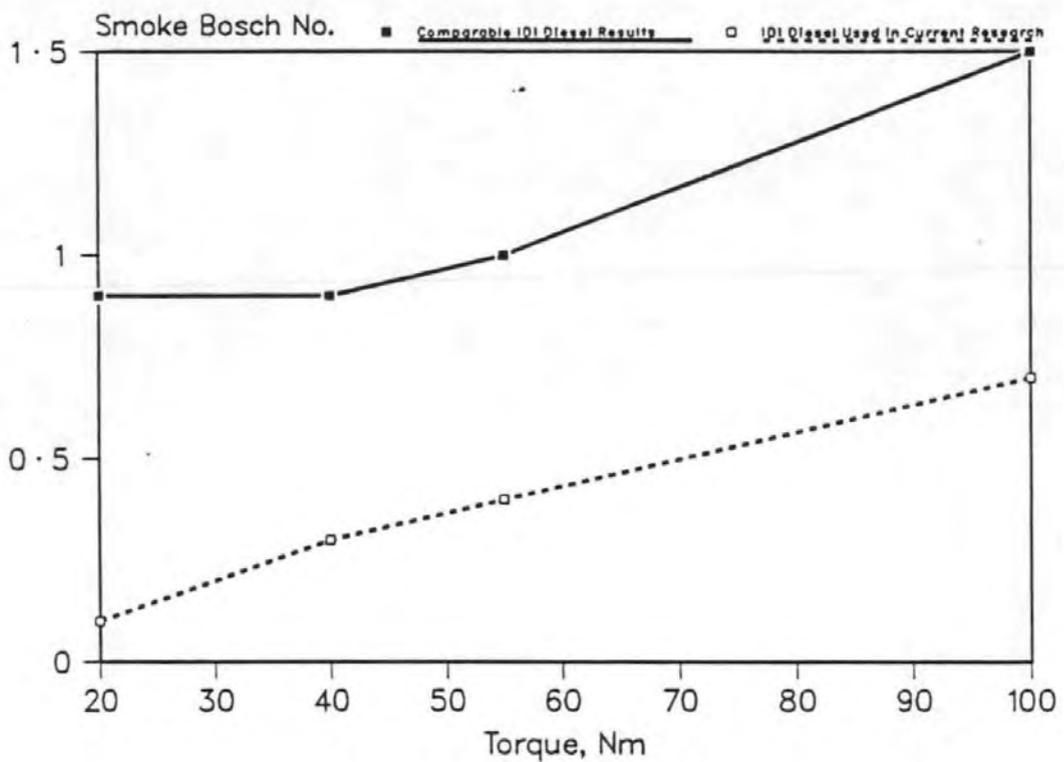


Fig 6.3 Comparison of Smoke Bosch Number, between engine used in present work and a similar engine reported in literature, (Cartellieri and Tritthart 1984).

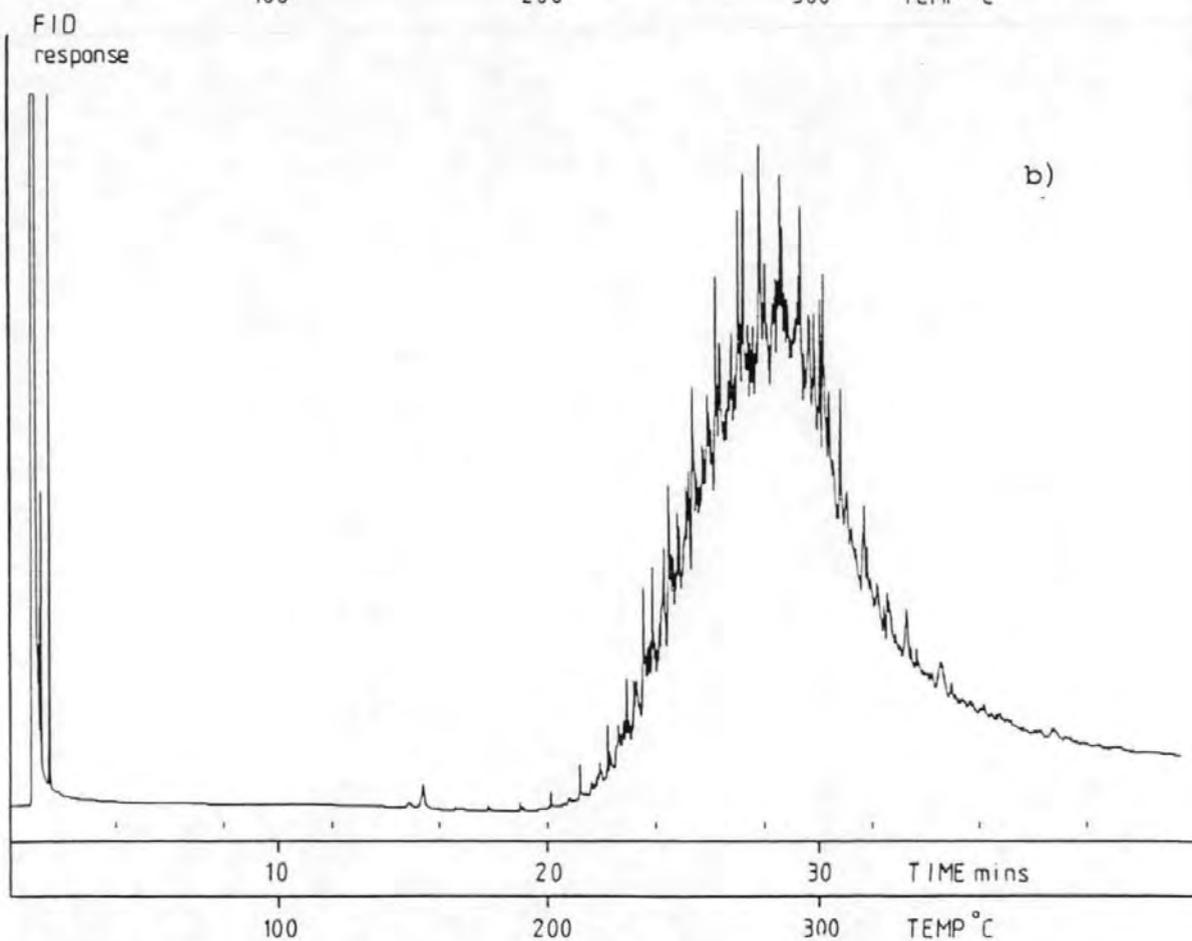
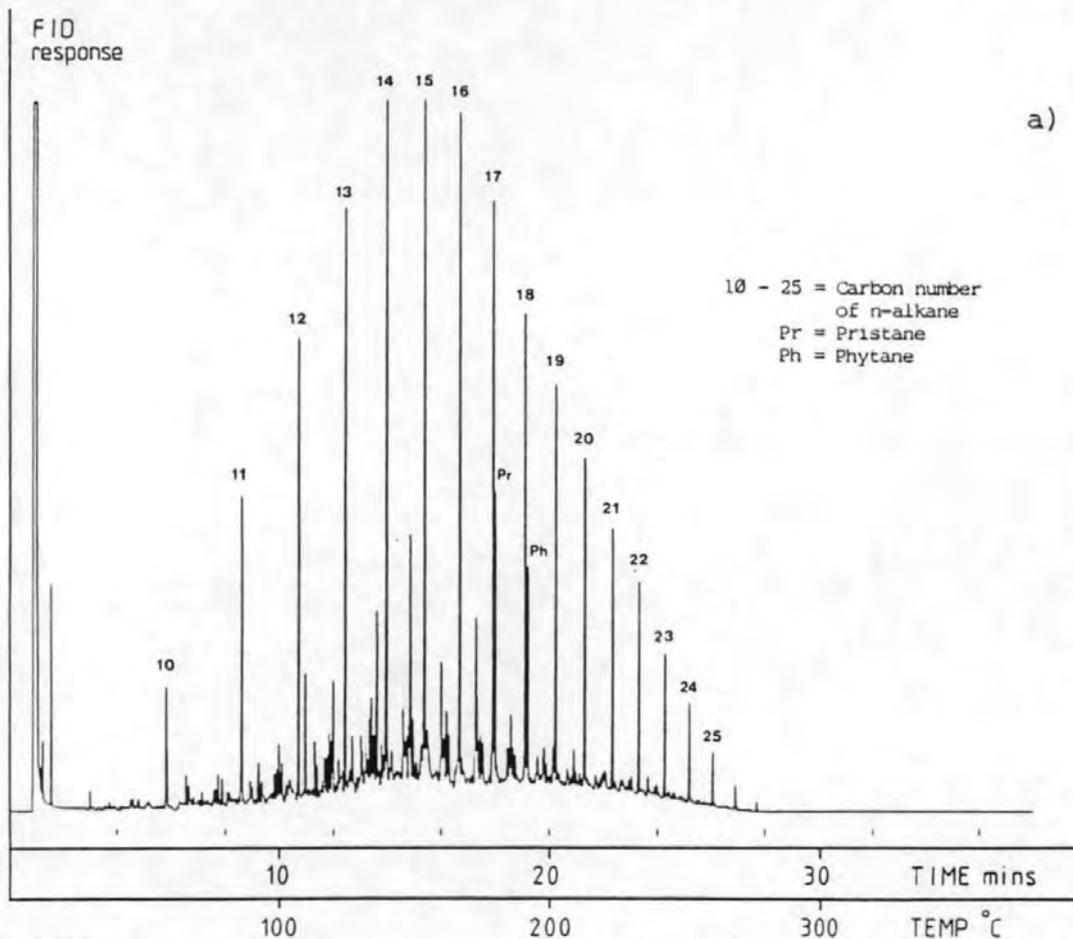


Fig 6.4 Gas Chromatograms for the Aliphatic Fractions of: a) Diesel Fuel. b) Lubricating Oil.

Exhaust Emissions from Four Different Load Conditions

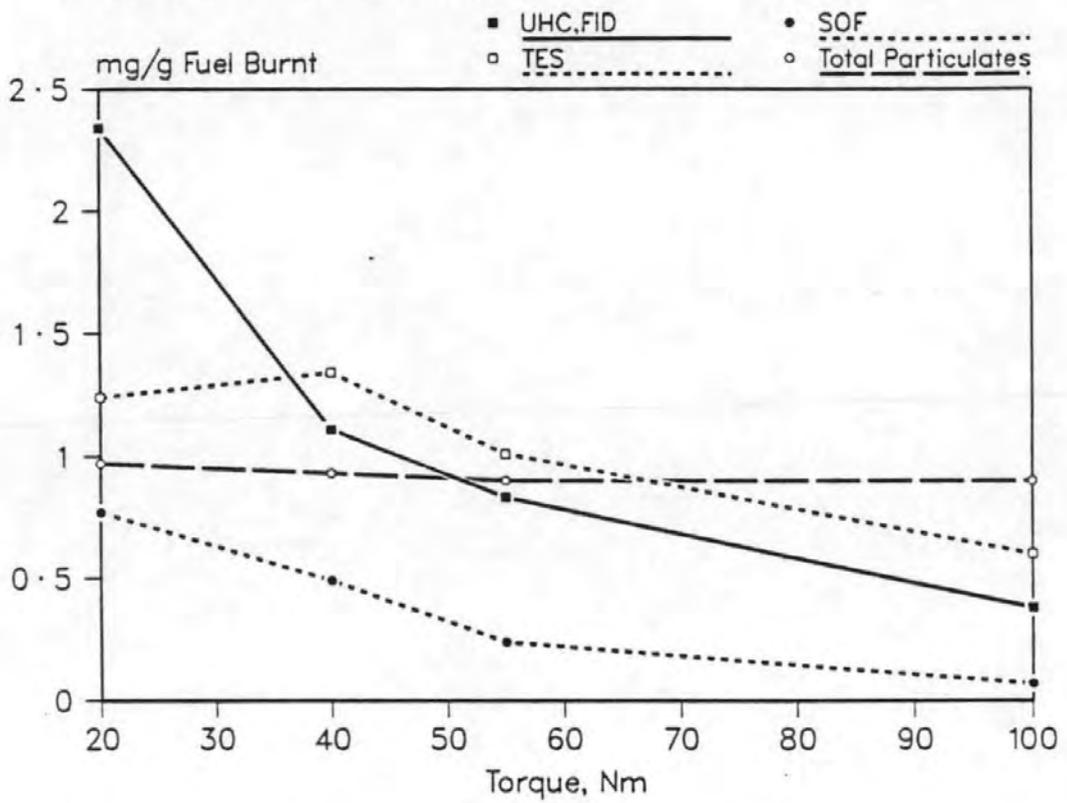


Fig 6.5 Exhaust emissions expressed as mg. per gram of fuel burnt, from four different load conditions.

aliphatic fraction in the column chromatography fractionation. The percentage survival from the fuel of these alkyl naphthalenes is calculated in Table 6.1, and an increasing trend with lower load can be seen.

	Torque, Nm			
	20	40	55	100
Naphthalene	0.209	0.070	0.088	0.020
Methyl-Naphthalenes				
2-methyl	0.096	0.030	0.027	0.008
1-methyl	0.121	0.034	0.046	0.012
Dimethyl Naphthalenes (Dmn)				
2,6- and 2,7- Dmn	0.082	0.034	0.023	0.010
1,3- and 1,7- Dmn	0.074	0.028	0.014	0.007
1,6- Dmn	0.065	0.023	0.014	0.006
1,5- Dmn	0.070	0.029	0.012	0.005
2,3- Dmn	0.073	0.028	0.012	0.005
1,2- Dmn	0.077	0.036	0.022	0.008

Table 6.1. Percentage survival of lower relative molecular mass PAC in the TESSA samples.

For these calculations, the assumption has been made that all the alkyl naphthalenes originate from the fuel, which is supported by the very similar distribution and relative peak heights for these compounds in both the fuel and TESSA samples; although, as has been shown in the last chapter, section 5.7, this is not likely to be a good assumption for naphthalene which, as a parent PAH, is likely to have been formed by pyrosynthesis as well as surviving from the fuel. The survival of the alkyl-naphthalenes shows similar trends to the overall increase of UHC and SOF, when the data is considered in terms of weight of emissions (mg) per gram of fuel burnt, Fig 6.5: an overall increase as the load

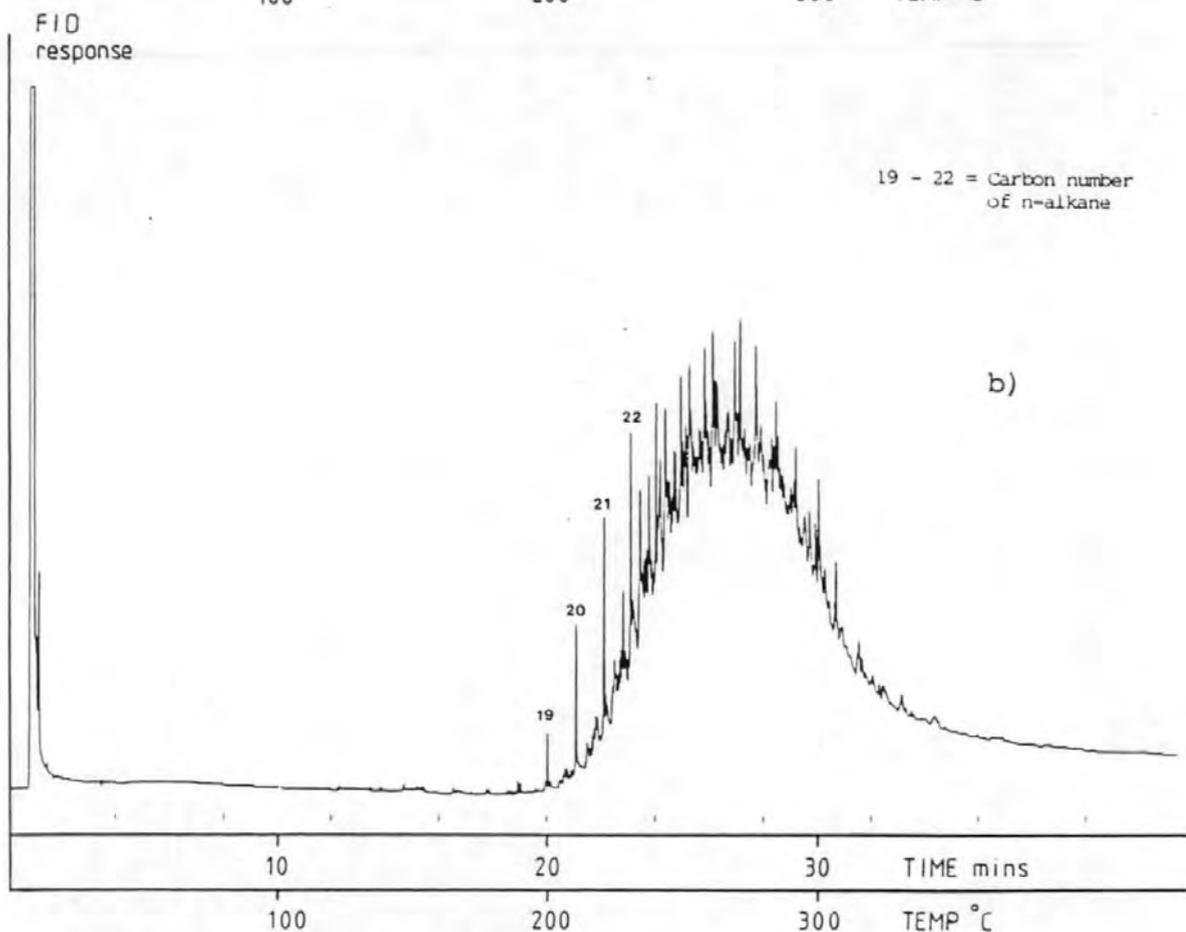
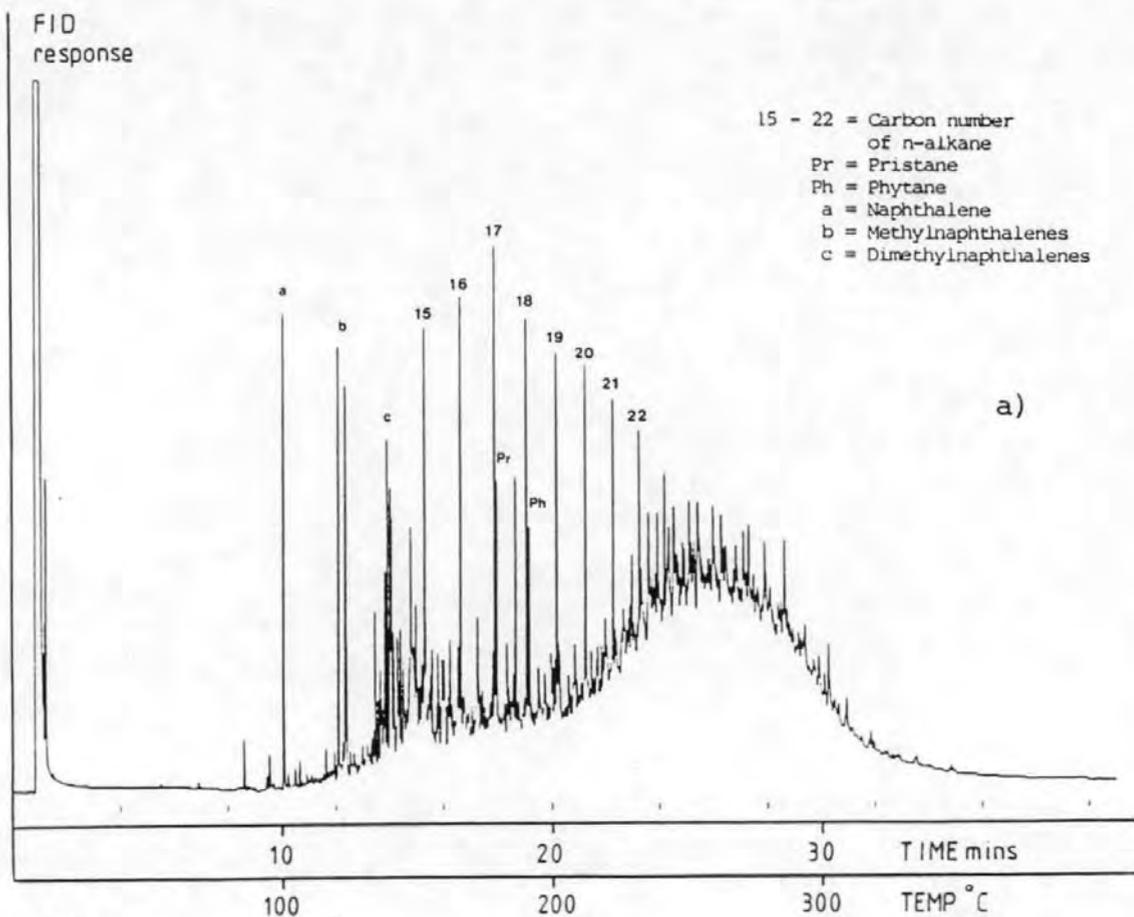


Fig 6.6 Gas Chromatograms for the Aliphatic Fraction of: a) TES at 40 Nm Load. b) SOF from Filter at 40 Nm Load.

decreases . It is interesting to note that the total particulates remains roughly the same at all loads, but the contribution from the SOF, which includes a contribution from both the particulates and the lubricating oil, is much more load-dependent.

The gas chromatogram for the aliphatic fraction of the TES taken at 40 Nm load is shown in Fig 6.6a. It has two prominent regions of peaks, the first is made up by low relative molecular mass material up to n-C20, which mainly originates from the fuel; the similar n-C17/pristane, n-C18/phytane ratios between the TESSA and fuel chromatograms support this conclusion that the lighter, more volatile, material in the exhaust sample is in fact unburnt fuel. In the second area, beyond n-C20, a series of peaks protrude from a broad hump of unresolved complex material (UCM). Although this material, in large part, corresponds with the relative molecular mass range of lubricating oil, it is broader and also includes a wide range of compounds in the lower relative molecular mass region at the beginning of the UCM, which have probably formed in the engine through partial combustion and pyrolysis of fuel and oil.

Close inspection of the corresponding aliphatic fraction of the filter sample taken at 40Nm load, Fig 6.6b, shows a far heavier dominance from material in the boiling range of the lubricating oil. By expanding the chromatogram, many of these peaks can be matched between the lubricating oil and the filter sample, in terms of corresponding retention

times and relative peak areas; the similarity between the lubricating oil and the area of matching retention time in the TES is investigated with greater rigour, using statistics, in the next chapter, section 7.3.2.

Only a very few of the n-alkanes typical of the fuel are present. These are the less volatile compounds above n-C19 which are only present in low concentrations barely rising above the outline of the UCM hump. In contrast to the TESSA sample, none of the lighter aromatic compounds such as alkyl-naphthalenes are present in the filter sample. The lower boiling point area of the UCM hump exhibits the same broadening which results from compounds not present in the lubricating oil. Once again, this indicates that chemical processes within the cylinder transform some of the fuel and lubricating oil, without completing the combustion of these products.

These results confirm a significant contribution of lubricating oil to the filter samples and to a less extent the TESSA samples. Previous work (Cuthbertson et al.1987) has shown that filter samples can trap more of the low relative molecular mass material than was apparent in this experiment. One explanation for this difference can be found in the very low Bosch smoke readings. In other words, the present engine on test produces very little carbonaceous soot but appreciable amounts of lubricating oil in its exhaust emissions. Soot with its very high surface area is known to be highly effective in scavenging the light organic material from the gaseous phase.

Organic compounds adsorb strongly onto the carbon particulates and are trapped with the particulates on the dilution tunnel filter. In such a dilution tunnel sampling system it is suggested that there is insufficient soot to scavenge the gaseous phase organics, which therefore pass through the filter. These gas phase organics are included in the measurement of the total unburnt hydrocarbons by FID and, of course, are trapped by the TESSA system.

The situation described highlights a limitation of the tunnel dilution and filter method, which depends for the efficiency of collection of vapour phase organics from the engine on the presence of sufficient particulate matter with a large surface area of contact to scavenge the organics. In modern engines, in which particulates are at low levels in the exhaust, much of the vapour phase organic compounds may not be trapped by a filter. Nevertheless, Amann and Sieglä (1982) do suggest that in considering the processes of adsorption and condensation the bulk of extractable material is acquired by the particulates after the exhaust gas is mixed with dilution air. If the level of dilution in this experiment was too low, it may also in part explain why the particulates did not effectively scavenge the gas-phase organic compounds.

The ratios of the TES to SOF and TES to UHC in Fig 6.7 are of interest. At high load, the TES is eight times higher than the SOF, the lighter relative molecular mass material has not been trapped on the filter. At low load the

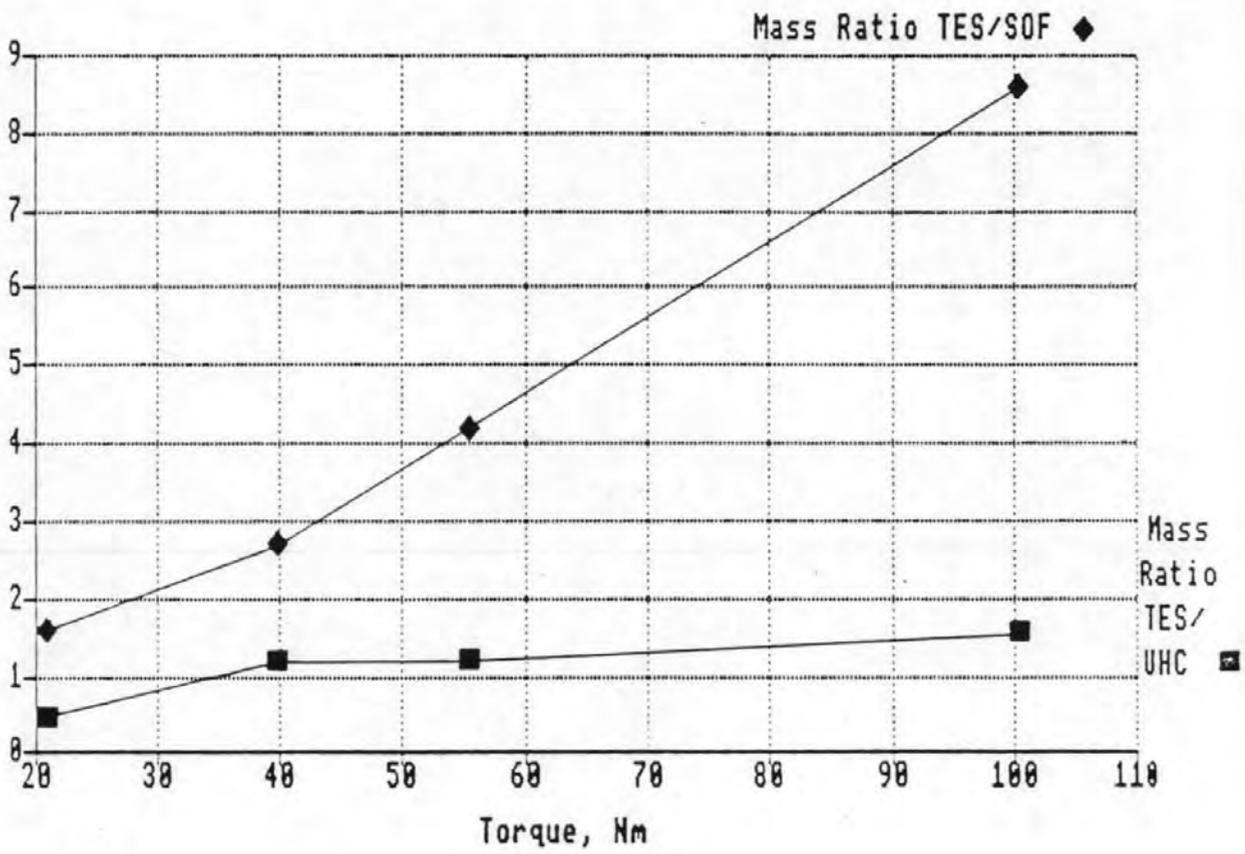


Fig 6.7 Graph Showing Ratios of TES to SOF and TES to UHC for Four Different Loads.

lubricating oil contribution becomes more significant, in relation to the total particulates, and the ratio is closer to unity. The TES/UHC ratio remains fairly constant just over 1:1. The TESSA system thus compares reasonably well with the UHC's. Some very low relative molecular mass gaseous hydrocarbons are detected as part of the UHC but which are not registered in either the TES or SOF. On the other hand, some losses occur, for the UHC, through the condensation of high relative molecular mass material in the heated line to the FID (Tritthart 1984); most of the compounds that make up the lubricating oil, for instance, have boiling points which are much higher than 190°C; whereas this material is effectively collected by TESSA.

6.5 Conclusions.

The TESSA system has been shown to be a capable sampling device for organic species in diesel exhaust emissions, particularly those species that remain in the gaseous phase, allowing a more complete characterisation.

Some degree of bias has been confirmed in the way that the dilution tunnel filter sampling system discriminates against low relative molecular mass volatile organic material. This bias can distort the apparent influence of lubricating oil to exhaust emissions. This work has also shown that, at low load especially, lubricating oil can make a significant contribution to total particulates.

Modern diesel engines, with very low elemental carbon

particulate emissions, may produce significant concentrations of gaseous phase organics which are not scavenged by particulates and therefore are not effectively sampled by a filter system.

CHAPTER 7.

The Contribution of Lubricating Oil to Diesel Exhaust Emissions.

With the availability of HRGC, based on capillary columns which give very high resolution, it was decided to develop new methods to aid the interpretation of the complex gas chromatograms associated with diesel exhaust analysis, thereby giving more detailed information on the lubricating oil contribution to SOF samples from diesel exhaust particulates. In this chapter the development of two methods of assessing the lubricating oil contribution to samples is described; both use HRGC. The first method relies on specific marker compounds, present in only the lubricating oil, whilst the second uses the increased information available from a computerised peak integrator.

7.1 A New Method To Assess the Lubricating Oil Contribution.

HRGC gives an order of magnitude more information from a sample than do chromatograms from packed column GC. At the same time, a more sophisticated interpretation is required to actually make use of the additional information. In the case of diesel exhaust emissions, analyses were first undertaken on a range of seven different fuels and five different lubricating oils, to aid the interpretation of both filter/dilution tunnel and TESSA samples, details are given in Table 7.1.

A. Oil Samples

- Ref. 1 - SX40 grade
- 2 - X30 grade
- 3 - 10W/30 grade
- 4 - 15W/40 grade
- 5 - 20W/20 grade

B. Fuel Samples

- Ref. 1 - U.K. Derv
- 2 - Phillip's D-2 (standard U.S. fuel)
- 3 - Low quality middle distillate
- 4 - Upgraded shale oil
- 5 - U.K. Derv-type fuel
- 6 - High end boiling point diesel
- 7 - Highly aromatic diesel

Each of the fuels except ref. 2 has had the fraction boiling below 325°C removed. For ref. 2 this was not possible since its end boiling point is about 325°C.

Table 7.1 List of 7 Diesel Fuels and 5 Lubricating Oils Used for Tests.

7.1.1 HRGC Response Factors from Fuel and Oils.

Initially, the range of diesel fuels and lubricating oils were diluted with DCM, and individually analysed by GC/FID; each sample had a slightly different boiling point range. In the next stage of analysis, different mixtures of each fuel and a lubricating oil were made up and analysed. Some of the fuel and oil mixtures showed almost complete baseline separation, e.g. Fig 7.1a, whereas other mixtures showed considerable overlap, e.g. Fig 7.1b.

Any assessment of lubricating oil contribution to diesel exhaust particulates is aided by a good chromatographic separation between the bulk of the fuel and the bulk of the lubricating oil components. In this work, described below, the UK Derv diesel fuel and the SX40 lubricating oil were used because a mixture of these two showed good separation.

Using a standard FID detector, and a temperature programme ramp to a final temperature of 300°C, the response factor for lubricating oil was found to be much lower for a given concentration than it was for fuel. The response factor was assessed by analysing a series of standard mixtures of fuel and lubricating oil, at a range of concentrations from 90% fuel and 10% lubricating oil (by weight) to 10% fuel and 90% lubricating oil. The 50/50 mixture indicated that the fuel had a considerably enhanced response compared to the lubricating oil, Fig 7.2a, in fact equal response was

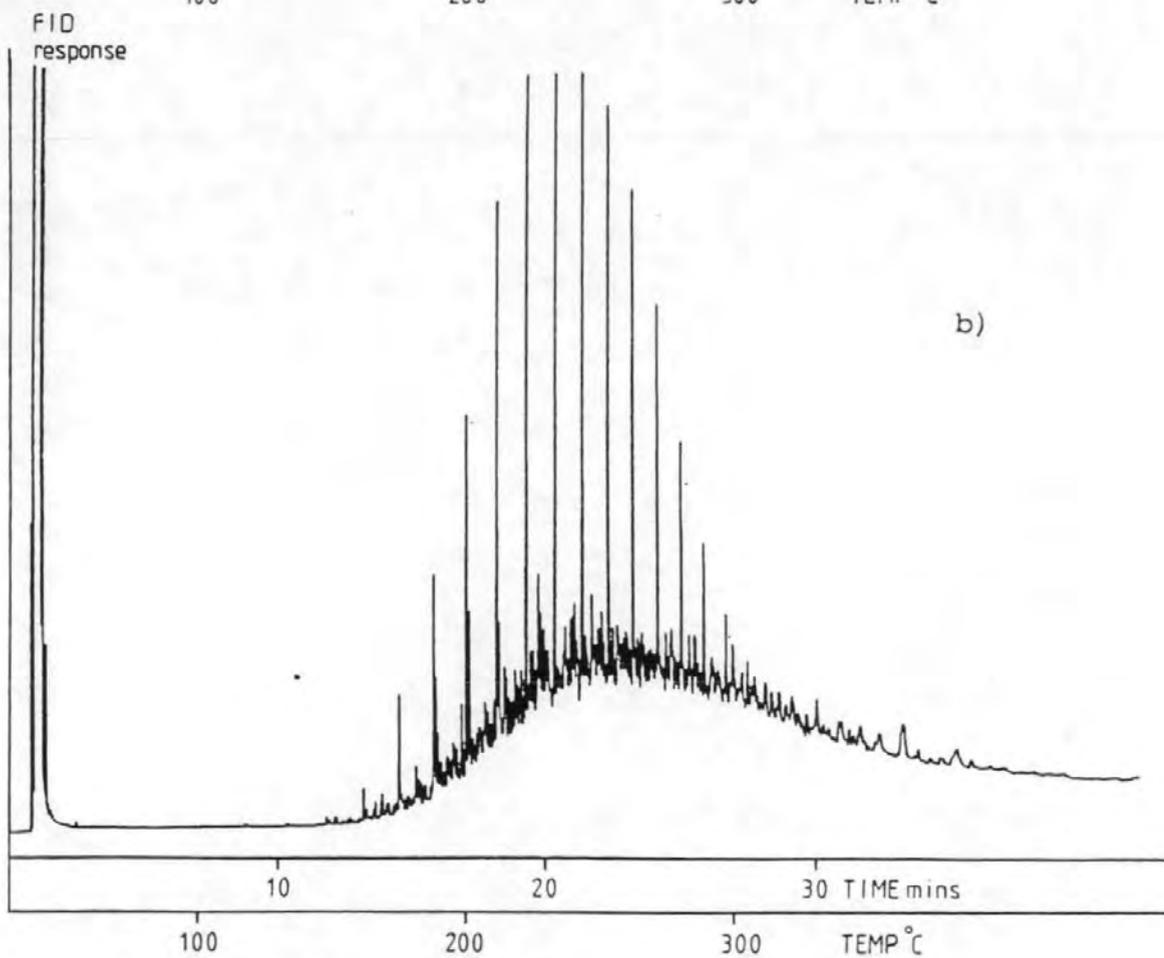
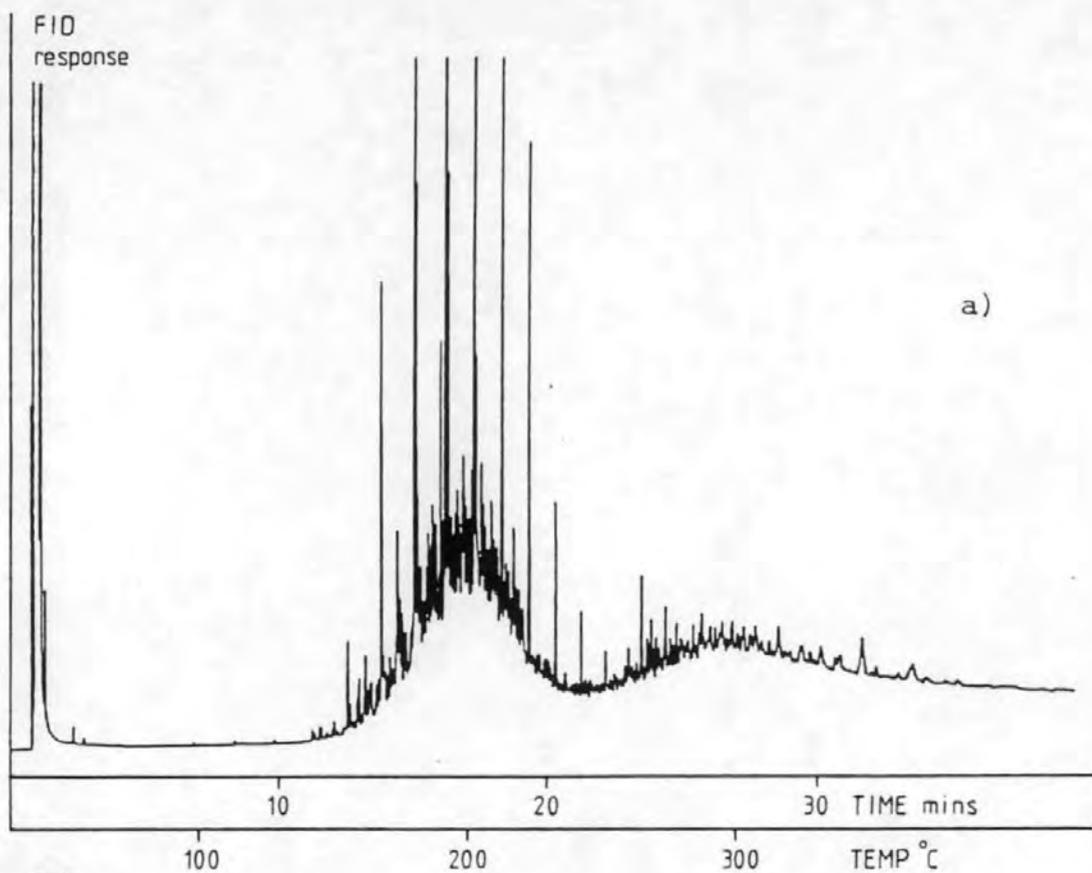


Fig 7.1 Gas Chromatograms of Fuel and Oil Mixtures
 Showing: a) a Mixture with Baseline Separation, Fuel 2 and
 Oil 2. b) a Mixture with Considerable Overlap, Fuel 6 and
 Oil 2.

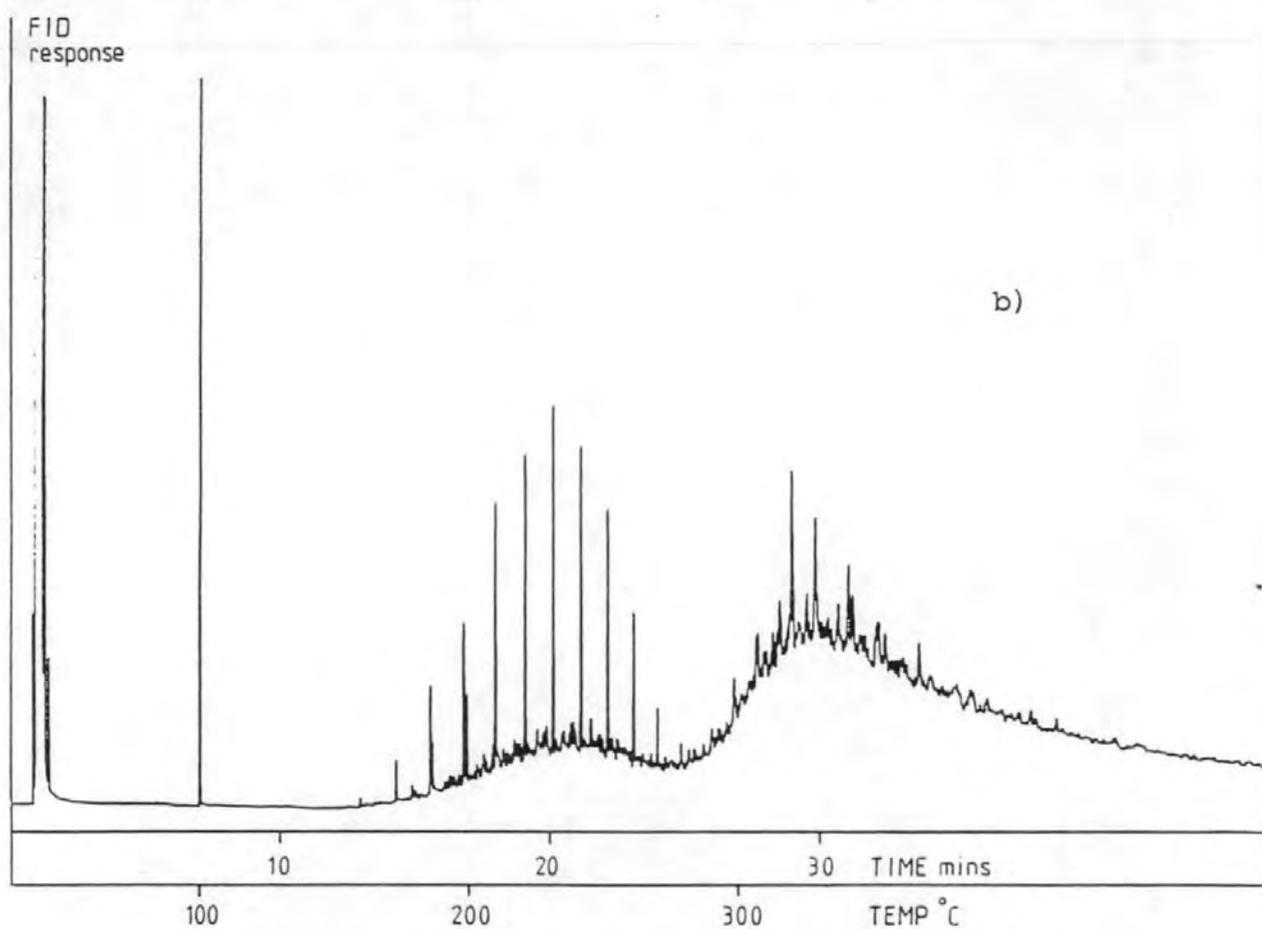
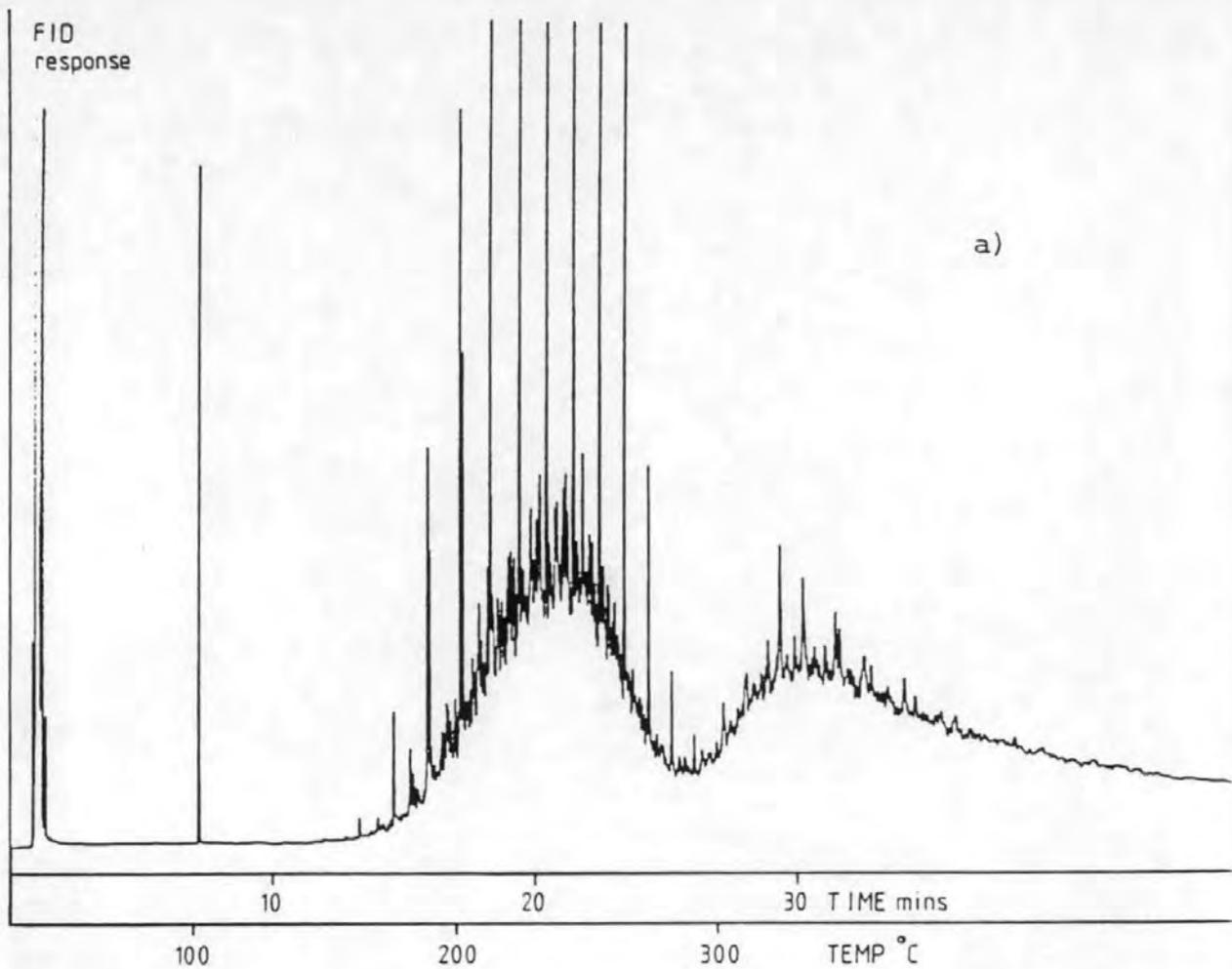


Fig 7.2 Gas Chromatograms Showing Difference in FID Response Between Fuel and Oil: a) 50/50 (w/w) Mixture. b) 10/90 (w/w) Mixture.

only achieved from the 10/90 mixture, Fig 7.2b. It is interesting to note that previous work on packed column GC reports a 20% reduction in response from lubricating oil compared to fuel (Cuthbertson et al.1987), the comparative response is much less with capillary GC.

The increased response by diesel fuel can be misleading when interpreting diesel exhaust SOF chromatograms, and can lead to an under estimate of the contribution by weight that the lubricating oil makes to the sample. Another important feature, shown in both gas chromatograms of Fig 7.2, is the UCM hump, associated with the lubricating oil, which remains even with high resolution capillary GC. The fuel also has a hump containing unresolved naphthenic compounds, but to a far lesser extent than the lubricating oil.

The gas chromatogram for a diesel exhaust SOF sample 1, extracted from a dilution tunnel filter, is shown in Fig 7.3. It is immediately apparent that the lubricating oil component is readily identifiable by retention time, and that its contribution by weight is dominant, compared to the unburnt fuel components, when the previously mentioned response factors are taken into account. Nevertheless, there is no clear baseline separation between the unburnt fuel and lubricating oil, indicating the presence of a considerable amount of pyrolysed and partially burnt hydrocarbons, which complicates the assessment of the lubricating oil contribution.

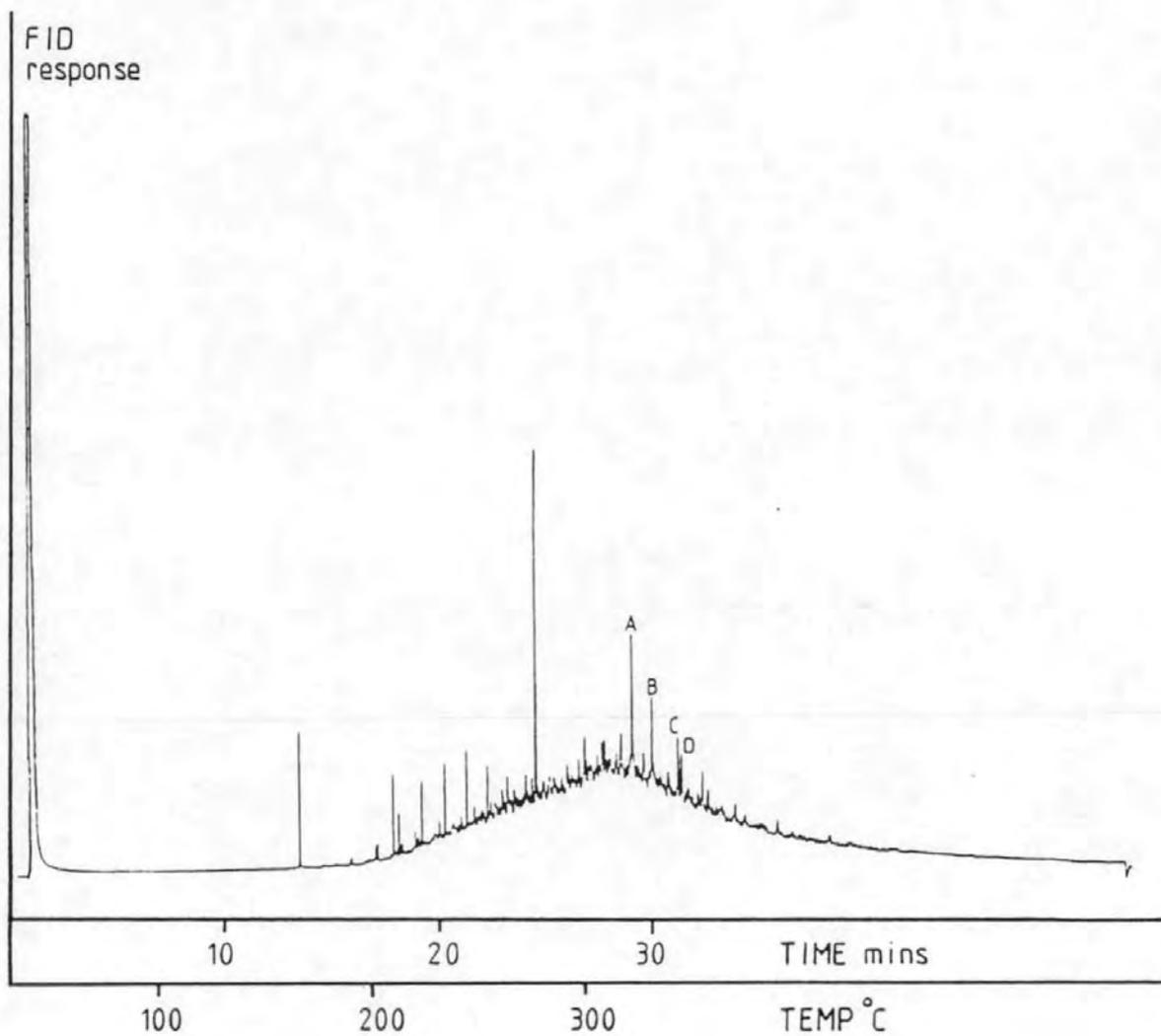


Fig 7.3 Gas Chromatograms from an IDI Diesel Exhaust SOF, Sample 1, Showing the Hopane Peaks: A = C₂₉-Hopane; B = C₃₀-Hopane; C = C_{31S}-Hopane; D = C_{31R}-Hopane. (S and R are stereoisomeric forms of the same structure)

7.1.2 Use of Specific Marker Compounds Found Only in the Lubricating Oil.

In developing a method, it was decided to investigate the prominent peaks, matched in both lubricating oil and corresponding SOF, which are superimposed on top of the UCM hump. If a linear increase in either peak height or area, with increasing lubricating oil concentration, could be shown for these peaks, then a semi-quantitative comparison between known concentrations of lubricating oil in the calibration blends could be made with lubricating oil concentration in an SOF.

Initially, four prominent peaks (marked A, B, C and D in Fig 7.3), readily identifiable in both the lubricating oil and SOF chromatograms, were chosen. These peaks were identified by GC/MS as members of the ab - hopane series of pentacyclic triterpenoids. The precursors of these hopanes were produced in ancient sediments by the activities of bacteria, (Simoneit 1984a). Subsequent geological maturation processes have modified the series of geochemical precursors to form the complex cyclic alkanes, represented in the lubricating oil, and whose complexity and uniqueness of structure precludes the possibility of in-cylinder formation during combustion. Since these hopanes are not present in diesel fuel, their presence in an SOF sample unequivocally points to the lubricating oil within the engine as source. Hopanes have previously been used as marker compounds in tropospheric studies by

Simoneit (1984b).

The structure of a typical hopane is presented in Fig 7.4. The hopane is easily identifiable using GC/MS by the diagnostic m/z mass fragment of 191 mass units, (Simoneit 1984). Authentic standards for the hopanes, to corroborate the identification, were not commercially available. Instead the saturated fraction of a Kuwait crude oil sample was used, which has a prominent representation by the hopane series and can be matched with the other samples. The GC/MS data for the Kuwait crude is presented in Fig 7.5 including a TIC chromatogram for the total sample, an expanded section comparing the specific part of the TIC with the m/z mass fragment of 191 mass units, and the mass spectrum from the C - 30 hopane peak (peak B). The comparable data for Rotella SX40 lubricating oil, and the SOF sample 1 (Fig 7.3), are shown in Figs 7.6 and 7.7 respectively. The similarity between the spectra for the C - 30 hopane, for all three samples, confirms the identity of the hopane peaks.

The hopane series was used to achieve a quantitative indication of the contribution of lubricating oil to the SOF. For each of the four peaks, the distance from the peak apex perpendicular to the baseline was measured (Fig 7.8). The baseline was obtained from the zero-response line for a temperature programmed HRGC analysis, without injected material. These measurements were first made on a series of lubricating oil calibration standards made up at different concentrations, Table 7.2. For each

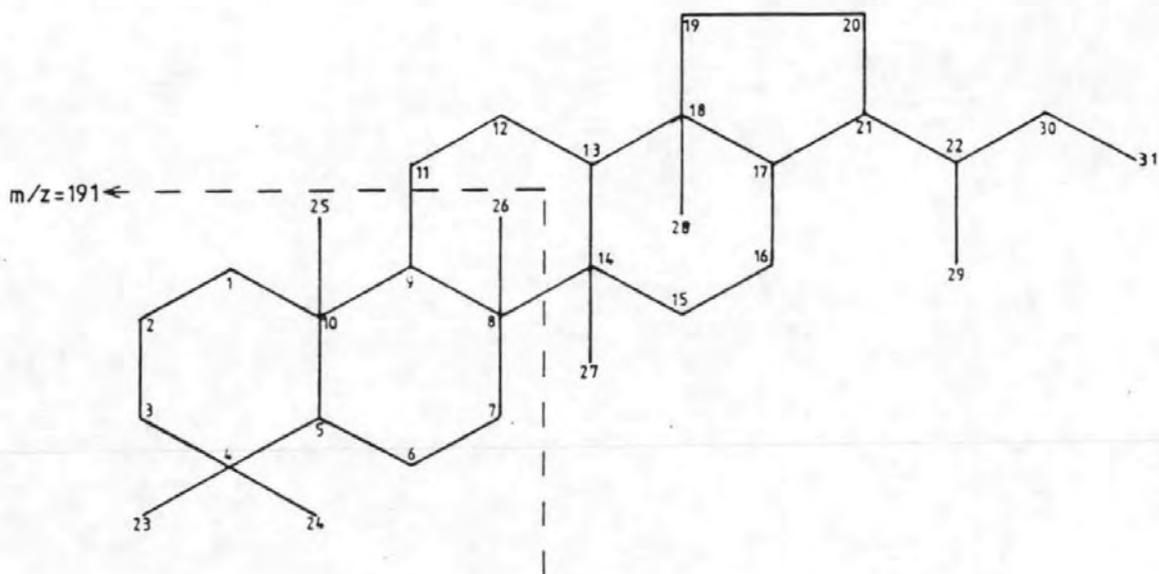
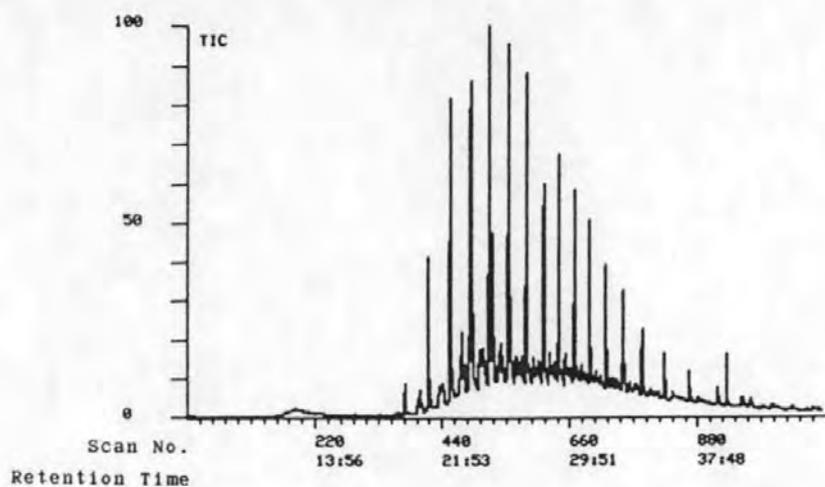
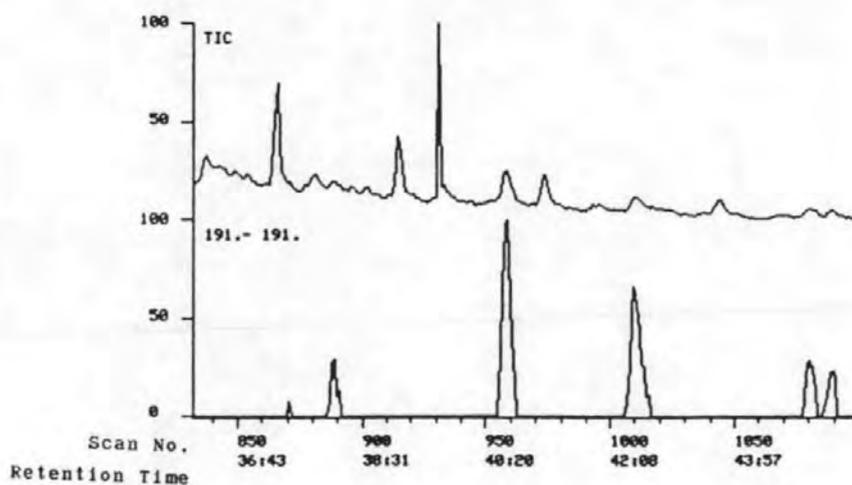


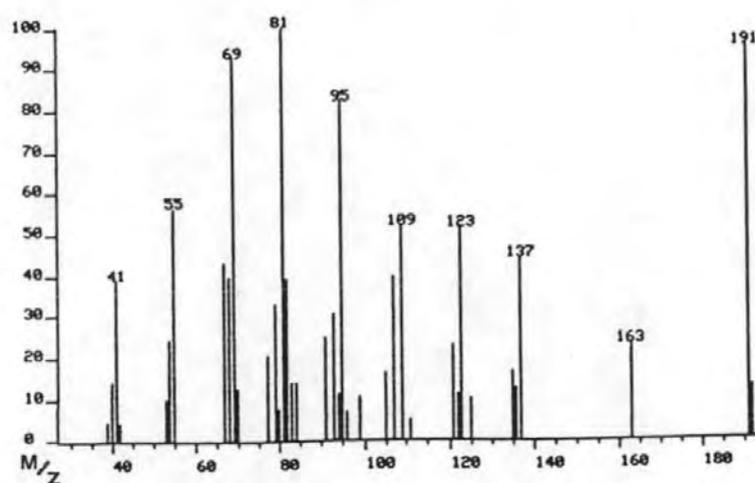
Fig 7.4 Diagram to Show the General Structure of a C₃₁-Hopane with the Mass Fragment Indicated for $m/z = 191$.



a)

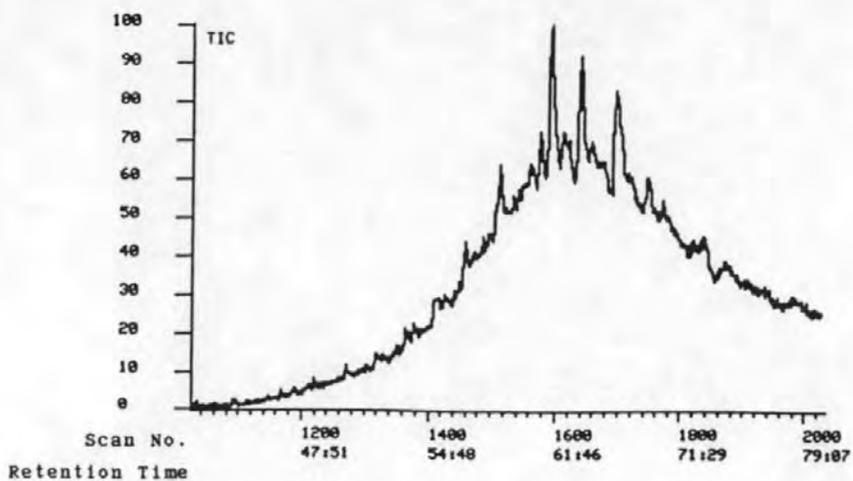


b)

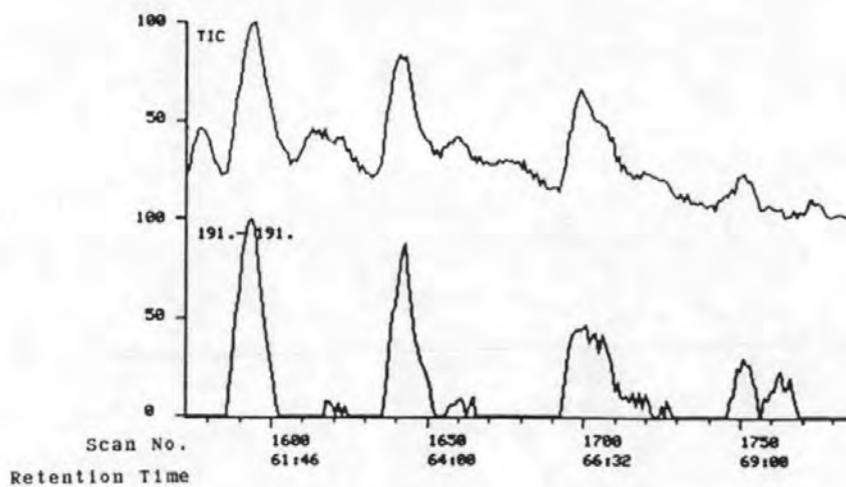


c)

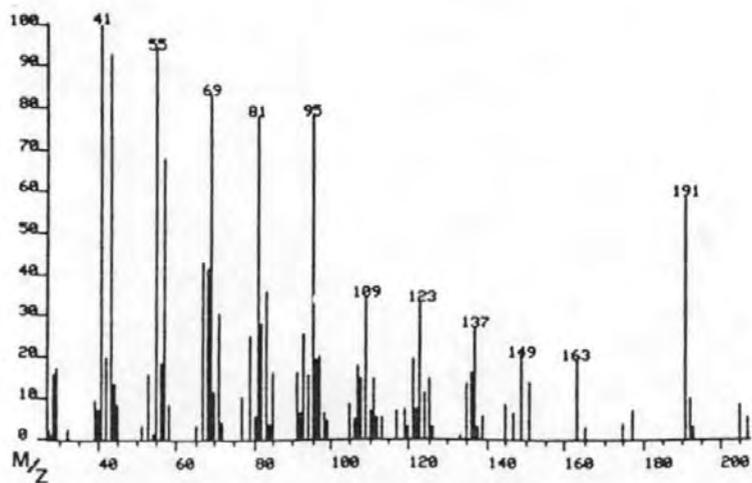
Fig 7.5 GC/MS Data for a Kuwait Crude Oil Showing:
 a) the TIC. b) Expanded Section of TIC and Mass Fragment $m/z = 191$. c) Mass Spectrum for the C₃₀-Hopane peak, (peak B).



a)

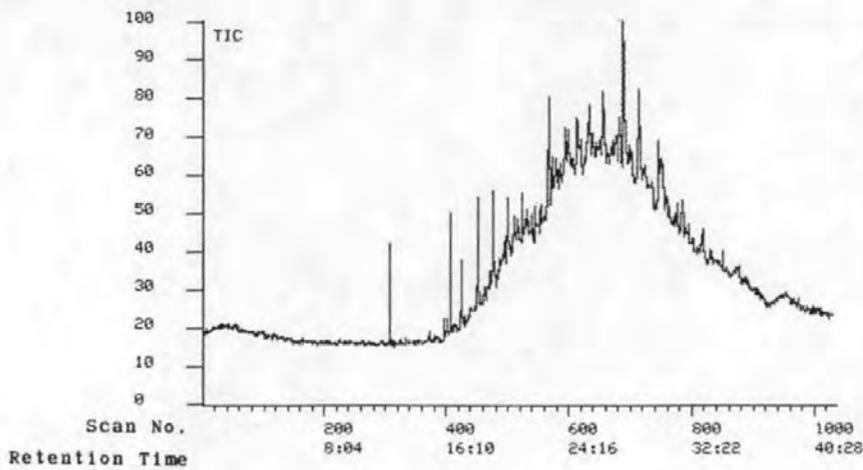


b)

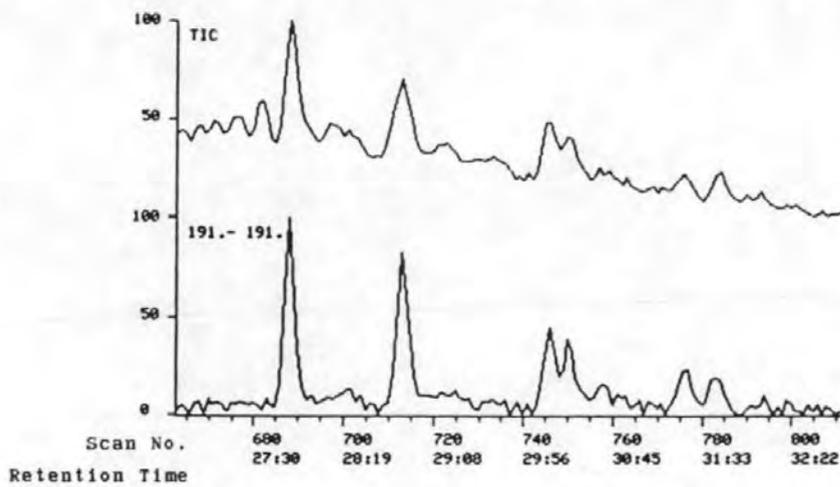


c)

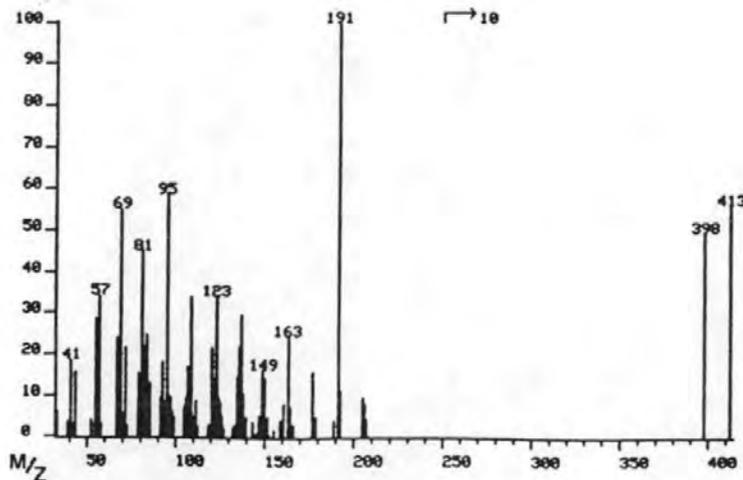
Fig 7.6 GC/MS Data for Rotella SX40 Lubricating Oil:
a) the TIC. b) Expanded Section of TIC and Mass Fragment $m/z = 191$. c) Mass Spectrum for the C₃₀-Hopane peak, (peak B).



a)



b)



c)

Fig 7.7 GC/MS Data for SOF Sample 1: a) the TIC.
 b) Expanded Section of TIC and Mass Fragment $m/z = 191$.
 c) Mass Spectrum for the C₃₀-Hopane peak, (peak B).

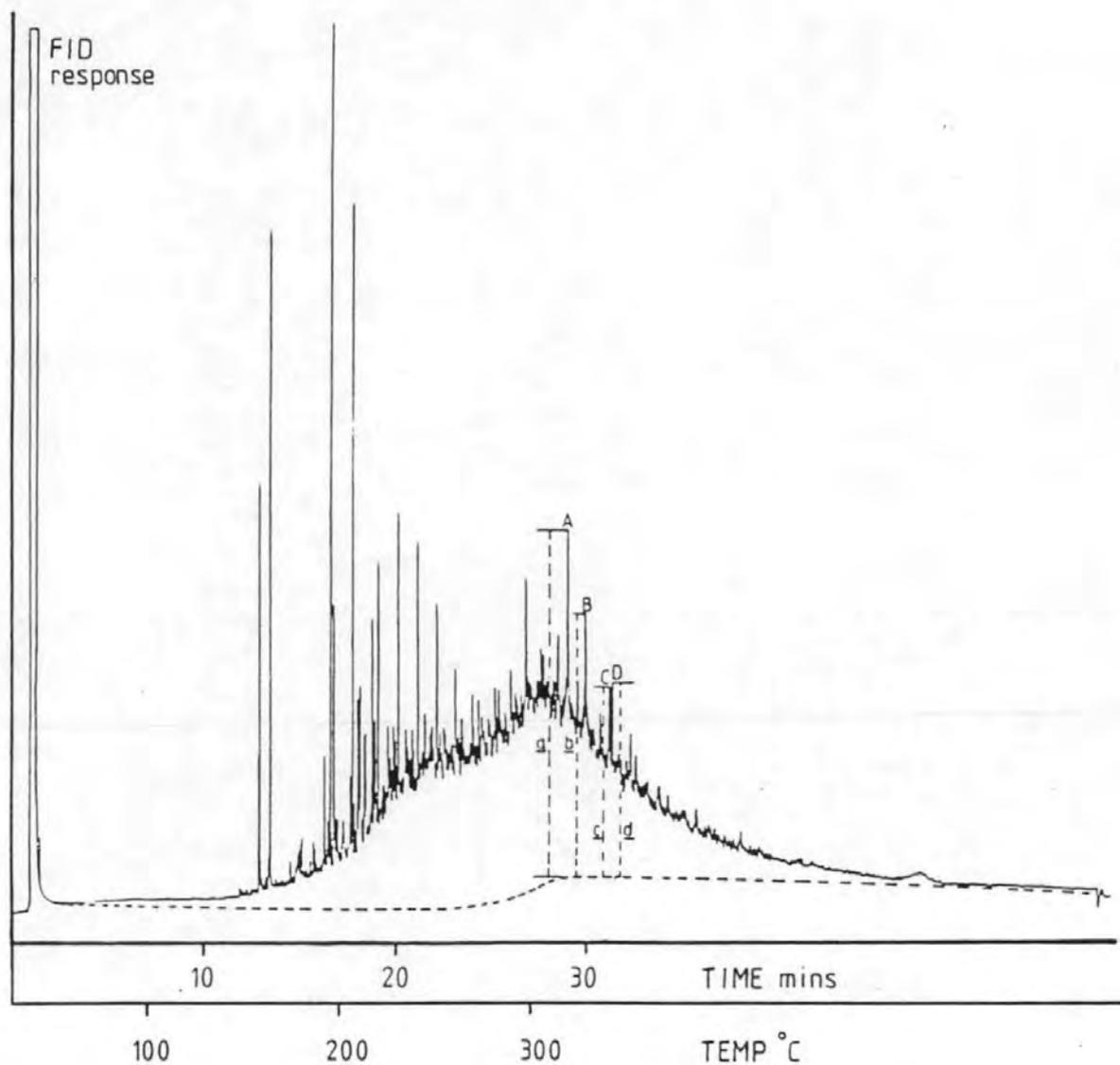
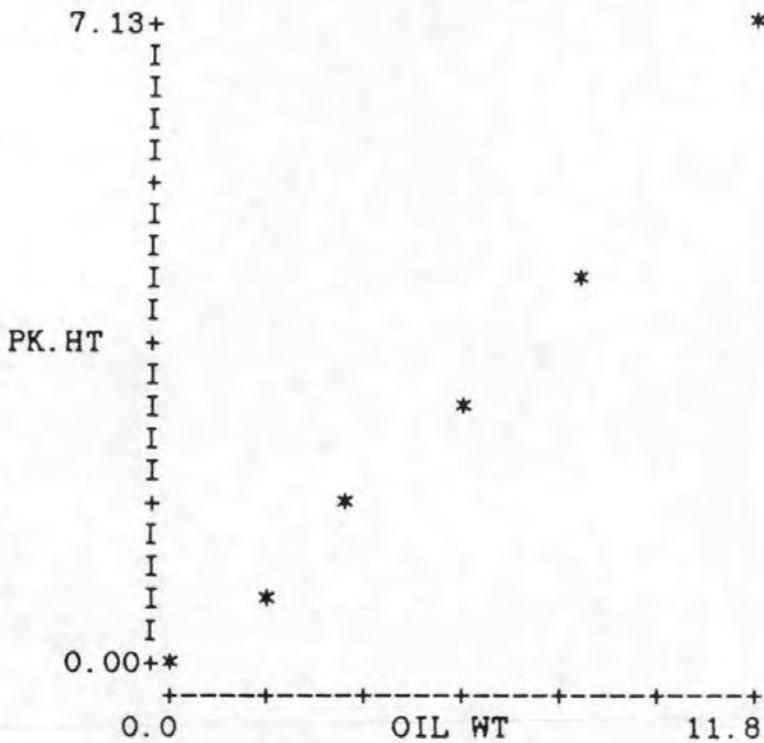


Fig 7.8 Gas Chromatogram for an SOF from a Light Duty Diesel Exhaust, Sample 2, with the Gas Chromatogram for the Solvent Only Injection (Dotted Line) Superimposed to Show How the Heights of the Hopane Peaks a, b, c, and d were calculated. A = C29-Hopane; B = C30-Hopane; C = C31S-Hopane; D = C31R-Hopane.

concentration of the lubricating oil standard, the ratio of the various peak heights with respect to the C - 31R (peak D) peak heights were calculated, Table 7.3. Thus, for each peak used, there was a set of ratios to the C - 31R peak, one for each of the different concentrations. For each peak 95% confidence limits were calculated using these ratios, Table 7.4. The calibration line based on the hopane peak C - 31R is shown in Fig 7.9 with the corresponding regression equation and coefficient of correlation (R-squared). As long as the peak ratios, for each of the four peaks identified in an SOF sample, fall within the relevant confidence limits, then, the various calibration curves can be used to calculate the lubricating oil contribution, based on each peak.

The following examples serve to demonstrate the method. Samples 1 and 2 are diesel exhaust SOF extracts from dilution tunnel filters, Figs 7.3 and 7.8 respectively. The relevant peak heights and corresponding peak ratios derived from the GC analyses of these samples are shown in Tables 7.5 and 7.6. For the peak heights to be acceptable for use in the quantification the confidence limits in Table 7.4 apply. Thus, for Sample 1, peak heights A and B are unacceptable, whilst for Sample 2, all the peaks can be used. By fitting the acceptable values into the calibration data from the oil standard, a good estimation of the oil contribution for each of the two samples can be made, Table 7.7. Once the dilution of the samples, made prior to the GC analysis, is taken into account, the percentage contribution of lubricating oil to the SOF can

Calibration curve for the response of various concentrations of OIL 1 based on the measurement of the height of the hopane peak C31-R from a superimposed baseline.



$$\text{OIL WT} = 0.47325 + 1.64007 * \text{PK. HT}$$

COLUMN	COEFFICIENT	STDEV	T
	0.47325	0.24616	1.923
PK. HT	1.64007	0.06467	25.360

$$S = 0.378 \quad \text{DF} = 4$$

$$R\text{-SQUARED} = 99.382\%$$

Fig 7.9 Calibration Line for the Response from Solutions of OIL 1, of Varying Concentrations, Based on the Measurement of the Height of the C31R-Hopane Peak from a Superimposed Baseline.

Oil concentration (mg/cm ³)	Peak heights (cm)			
	<u>C₂₉ (A)</u>	<u>C₃₀ (B)</u>	<u>C₃₁-S (C)</u>	<u>C₃₁-R (D)</u>
0.0	-	-	-	-
2.0	1.52	1.20	1.09	0.82
4.0	3.09	2.58	2.20	2.05
6.0	5.42	4.32	3.58	3.20
8.0	7.16	6.29	5.32	4.58
10.0	9.90	8.77	7.72	7.13

Table 7.2 Measured Peak Heights (peak apex to base-line) of the Hopanes for a Variety of Lubricating Oil Concentrations.

Oil concentration (mg/cm ³)	Peak height ratios		
	<u>C₂₉ (A)</u>	<u>C₃₀ (B)</u>	<u>C₃₁-S (C)</u>
2.0	1.85	1.46	1.33
4.0	1.51	1.26	1.07
6.0	1.69	1.35	1.12
8.0	1.56	1.37	1.16
10.0	1.39	1.23	1.08

Table 7.3 The Ratio of the Hopane Peak Heights to the C₃₁-R Hopane Peak Height for the Lubricating Oil Standards.

<u>Hopane peak</u>	<u>Mean</u>	<u>Standard Deviation</u>	<u>95% Confidence Limits</u>
C ₂₉ (A)	1.60	0.18	1.60 ± 0.35
C ₃₀ (B)	1.33	0.09	1.33 ± 0.18
C ₃₁ -S (C)	1.15	0.11	1.15 ± 0.21
C ₃₁ -R (D)	-	-	

Table 7.4 Statistical Data for the Peak Ratios Obtained from the Standard Solutions of Lubricating Oil.

<u>Sample</u>	<u>Peak heights (cm)</u>			
	<u>C₂₉ (A)</u>	<u>C₃₀ (B)</u>	<u>C₃₁-S (C)</u>	<u>C₃₁-R (D)</u>
1	3.38	2.37	1.73	1.48
2	6.08	4.60	3.32	3.39

Table 7.5 The Measured Peak Heights of the Hopanes for the Sample SOF's.

<u>Sample</u>	<u>Peak Ratios</u>		
	<u>C₂₉ (A)</u>	<u>C₃₀ (B)</u>	<u>C₃₁-S (C)</u>
1	2.28	1.60	1.17
2	1.79	1.36	0.98

Table 7.6 The Ratio of the Hopane Peak Heights to the C₃₁-R Hopane Peak Height for the Samples.

<u>Sample</u>	<u>Total lubricating oil weights (mg) in SOF from peak height data</u>			
	<u>C₂₉ (A)</u>	<u>C₃₀ (B)</u>	<u>C₃₁-S (C)</u>	<u>C₃₁-R (D)</u>
1	* 5.78	*4.97	4.42	4.79
2	1.97	1.75	1.50	1.71

* These values are outside the 95% confidence limits set out in Table 7.4 and are therefore excluded from the quoted range of lubricating oil contributions to SOF.

Table 7.7 Calculated Lubricating Oil Weights for Total SOF (from data in previous Tables).

be calculated

Sample 1	40% lubricating oil in SOF
Sample 2	55% lubricating oil in SOF

In this way, a method has been developed enabling a rapid, semi-quantitative assessment of the contribution of lubricating oil to the SOF of diesel particulates. The technique uses a simple analysis of the peak ratios of a small number of selected peaks in a high resolution gas chromatogram. The method has been applied to a further 4 SOF samples from dilution tunnel filters. The chromatograms are presented in Figs 7.10 and 7.11. The calculations of lubricating oil contribution are based on the peak height data for the C - 31S and C - 31R peaks for each sample and presented below.

Test 1	40%
Test 2	50%
Test 3	40%
Test 4	20%

7.2 Further Development of the Methodology.

The method so far described was limited to giving a semi-quantitative result based on the survival from the lubricating oil of hopanes in the SOF. Other possibilities have been investigated in order to improve the accuracy of the technique.

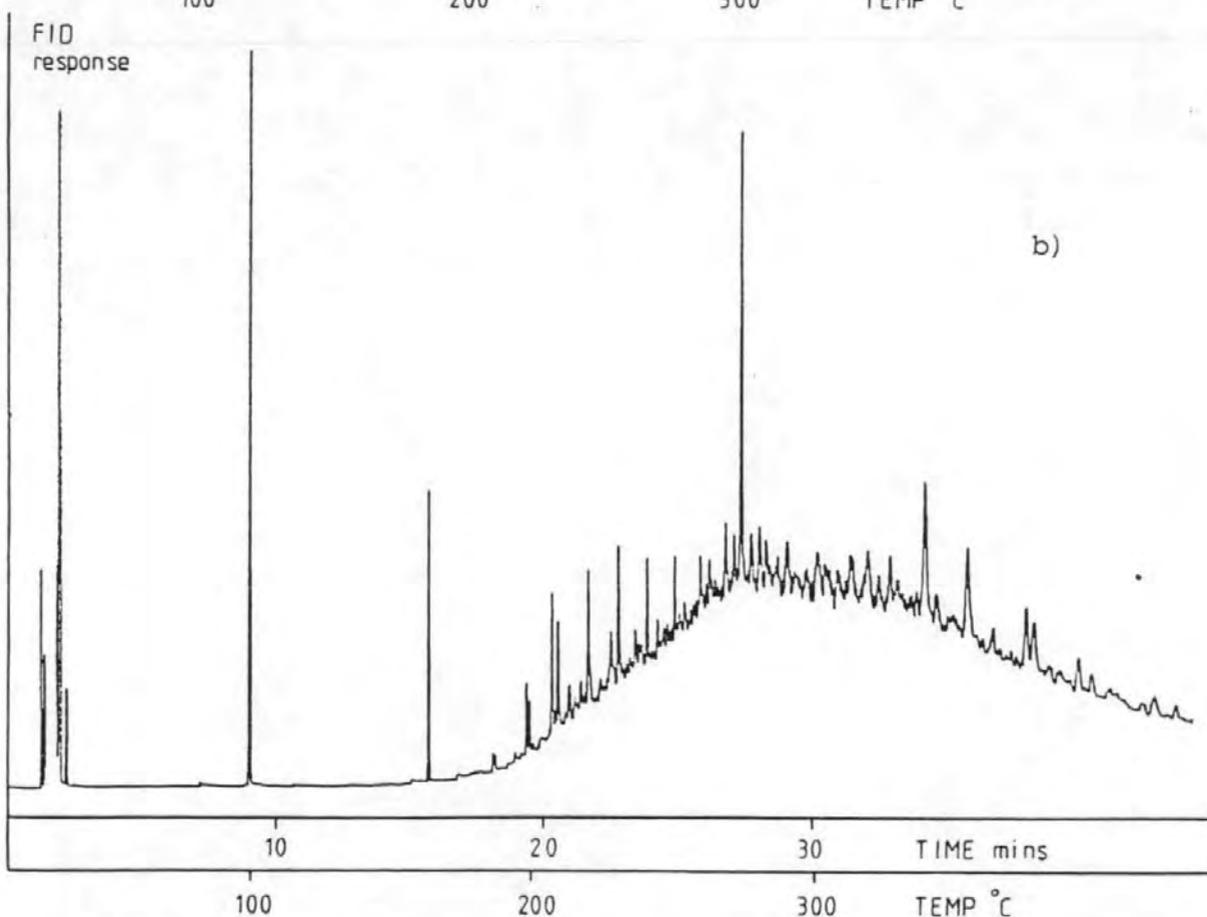
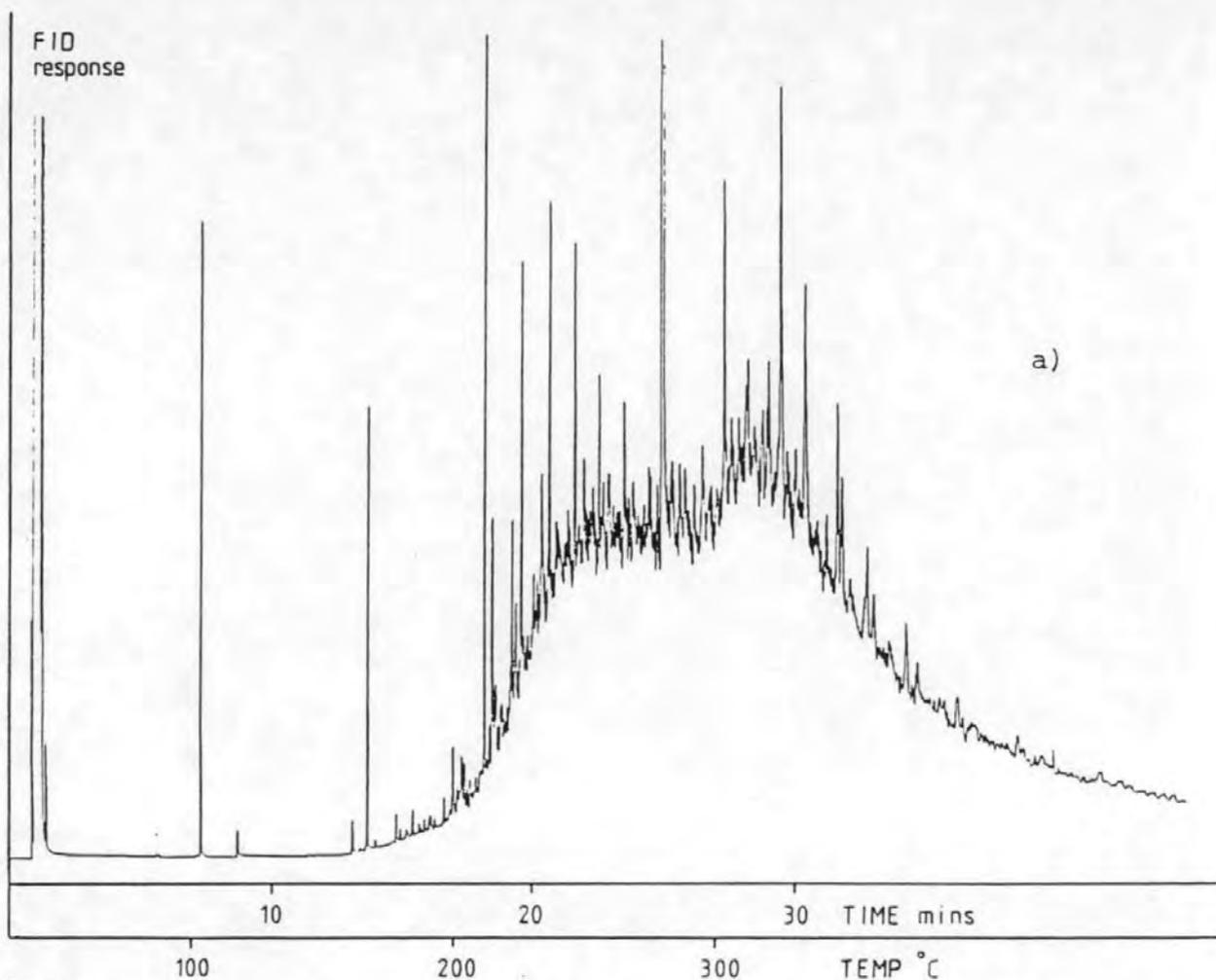


Fig 7.10 Gas Chromatograms for Two Diesel Exhaust SOF Samples: a) Test 1. b) Test 2.

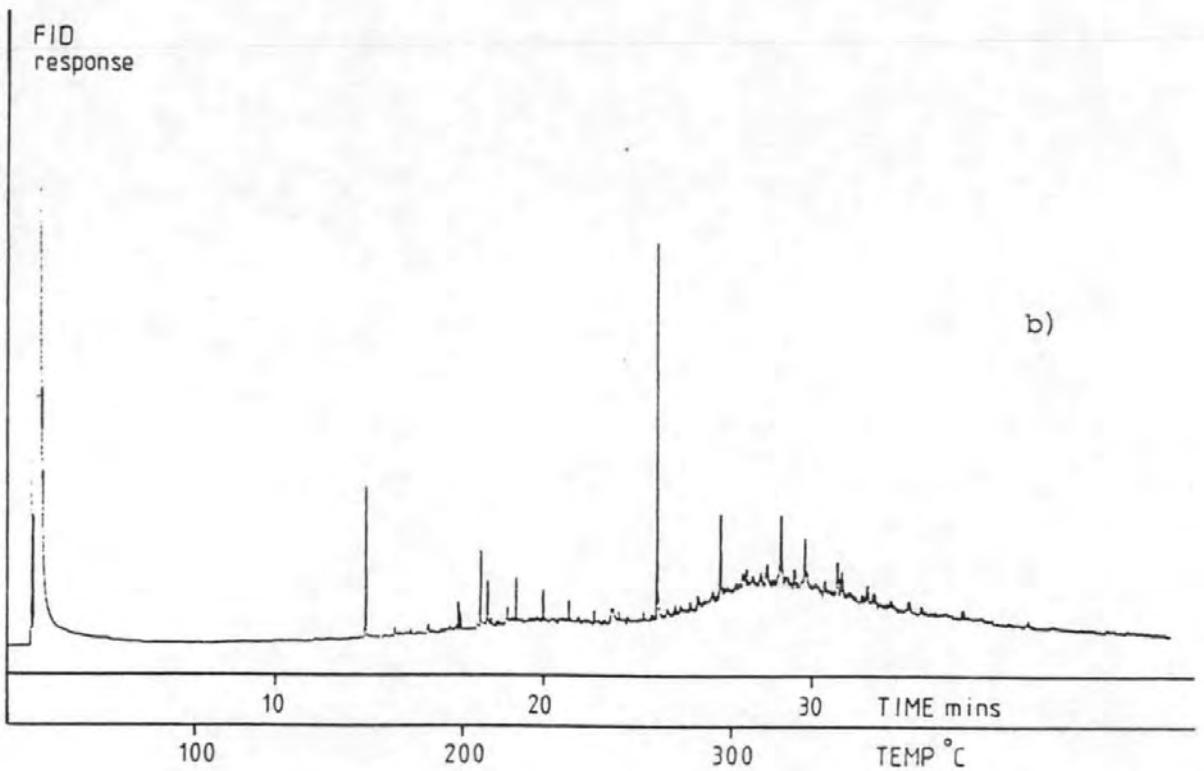
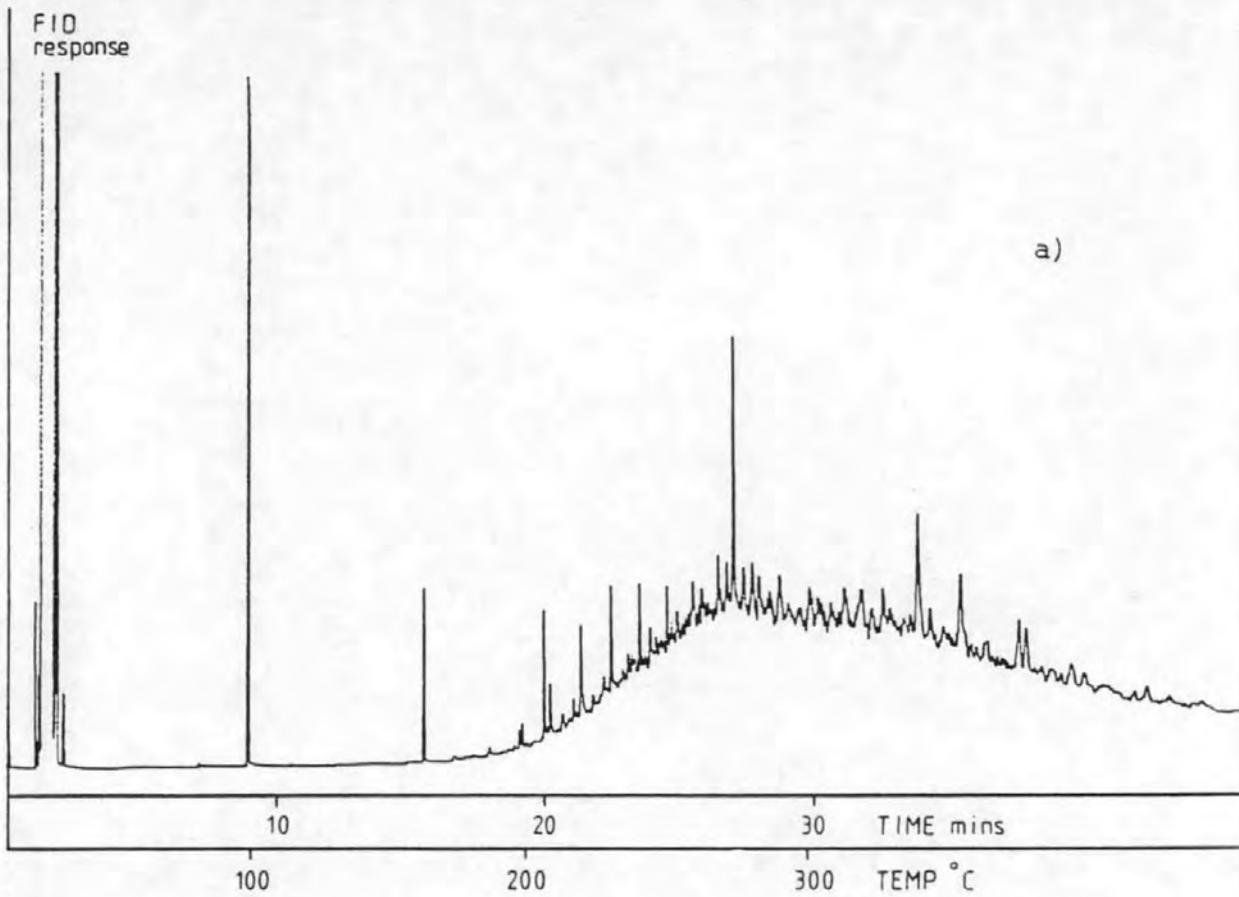


Fig 7.11 Gas Chromatograms for Two Diesel Exhaust SOF Samples: a) Test 3. b) Test 4.

7.2.1 Limitations of the Method Using Hopane Marker Compounds.

There are several problems associated with the use of the triterpenoid hopanes, as marker compounds, to assess the lubricating oil contribution to diesel exhaust particulates. Most lubricating oils do not contain the hopanes at sufficient concentrations to present prominent peaks above the UCM hump and thereby allow accurate measurement manually; only a few crude oils have prominent hopane peaks.

Lubricating oils are classified by various criteria such as viscosity (discussed earlier) and may be made up from a variety of different crude oils, so that the exact composition changes over a period of time. In addition, even when the four hopane peaks are present, and measurable on the GC chromatogram, a direct measurement of height from the experimentally established baseline, for an oil standard and a sample, will not yield directly comparable results if the exhaust sample contains significant levels of pyrolysis and partial combustion products enhancing the UCM hump in the sample. The measurement of the hopane peak heights from the baseline may be affected by this unquantifiable enhancement of the UCM, and could result in the lubricating oil contribution to a sample being overestimated.

Furthermore, even if a reasonably accurate measurement

could be made of the four peaks in the exhaust sample, the hopane compounds may behave differently to the bulk of the oil, which is made up from many other compound classes. Their relative molecular masses are at the higher end of their distribution for the total lubricating oil and they may, for this reason alone, preferentially survive combustion, if it can be assumed that these higher relative molecular mass compounds do not ignite so readily, (Dale 1984b).

Modern GC systems, incorporating an integrator, should allow the use of many more peaks than simply the four hopane peaks. A method based on the output from the integrator would avoid some of the problems listed above; particularly if, with data from more than four peaks, it would be possible to estimate the effect of the combustion products on the UCM. Finally using an integrator would remove the need for the laborious identification of specific peaks and the manual measurement of peak heights.

7.2.2 Criteria for Refinement of the Method.

In the light of the above limitations in the use of hopanes as marker compounds to assess the lubricating oil contribution, a refined method has been developed which uses the output from an integrator and does not depend on

the presence of the hopane peaks. The following criteria were used:

a) The refined method should use a large number of prominent peaks from the lubricating oil, spanning the full range of boiling points represented by the bulk of the oil components. A larger number of peaks would allow a more rigorous statistical analysis.

b) Peaks identified by the integrator would be accepted as data. Previously published work (Davis and Giddings 1985), has shown that the majority of peaks above a UCM hump are in fact multicomponent peaks. It was not considered necessary or possible to identify every peak. Indeed, lubricating oil is such a complex mixture that it has so far eluded complete characterisation (IARC 1981).

c) The limitations of the relatively cheap Shimadzu integrator would be accepted since it is fairly typical of integrator systems currently in use. The main shortcoming of the Shimadzu integrator is that it is not possible to identify the precise position of the baseline which the integrator has used. This problem is discussed further below, section 7.3.2.

d) Data should be easily transferable from the integrator output to a computer so that it could be analysed statistically with ease.

7.2.3 Improvements in Analytical Technique.

In the experimental work described in section 7.1, calibration standards were prepared from fresh oil, equivalent to that in the test engine sump. In the work described here, a sample of the used lubricating oil was drawn from the sump, cleaned up to remove the particulates (see analytical section 3.1.3 for details), and fractionated on silica gel, before being used as the calibration standard. Furthermore, since the bulk of lubricating oil elutes in the aliphatic fraction, from silica gel column chromatography fractionation, it was considered sufficient to restrict the analyses to the aliphatic fractions for all the samples; the results from these analyses could then be extrapolated in the final calculations to include the total sample weights.

7.3 Data Acquisition by Computer Integrator.

Before the results from a computer integrator could be used they had first to be assessed in terms of reproducibility, and accuracy. This was the first of three steps involved in developing a more refined method for estimating lubricating oil concentration in a gas chromatogram.

7.3.1 Assessment of Integrator Response for Different Concentrations of Lubricating Oil.

Five solutions of a lubricating oil were prepared in DCM at

concentrations of: 1, 3, 5, 7, and 10 mg/cm³. The analysis of each solution, by capillary column GC, and integrator was repeated three times to test reproducibility. Reproducibility of chromatographic data was found to be very good, the correlation coefficient of the peak heights, for 3 repeat injections of the same concentration of lubricating oil standard, in every case was greater than 0.99.

The result of this experiment was to show that a linear response for peak heights could be expected for the lubricating oil, up to the 5 mg/cm³ concentration. At higher concentrations, the linearity of response was lost and was most likely a function of the capillary column capacity being exceeded, resulting in a deterioration of resolution. It was also found that the integrator results for peak heights were more consistent than those for peak area. Whereas the ratio of the peak heights for the 1 mg/cm³ and 5 mg/cm³ was 1 : 5, for peak areas the ratio was 0.6 : 5. Other results also highlighted the inaccuracy of area measurements, particularly in real samples, where peak area was far more influenced by closely eluting compounds from sources other than the lubricating oil.

7.3.2 Integrator Baseline.

The baseline of the Shimadzu integrator used in this work can be altered by changing the setting of the Drift control. Using an arbitrarily high value (eg 10000) causes the baseline to be drawn so that it closely follows

the top of the UCM hump. The peak heights obtained are then (approximately) the height of that part of the peak which is resolved above the UCM hump. When a high value for Drift was used, it was found that the linearity and correlation between different concentrations of the lubricating oil standard deteriorated considerably. Therefore, the Drift setting was kept at 0, the automatic setting allowing the machine to determine its own baseline using specific algorithms.

7.3.3 Experiment to Determine Influence of Co-Eluting Compounds on Integrator Baseline.

In the light of some of the points raised above, an experiment was carried out to find whether inter-sample comparability of the baseline would be adversely effected for a complex environmental sample, if the area of interest in the chromatogram corresponding to the lubricating oil had additional non-lubricating oil components. The experiment also enabled direct comparison between the results from the integrator and those obtained manually.

A compound not present in lubricating oil, the four-ring PAH chrysene, was co-injected with the lubricating oil. Chrysene has a retention time of 25.5 minutes which is within the range of the retention time for compounds within the lubricating oil. The chromatogram obtained was then compared with those for chrysene and the lubricating oil, individually, to determine how the addition of a non-lubricating oil component might effect the integrator

response. An internal standard of naphthalene, which has a retention time much less than 24 minutes, was also included to monitor any variability of injection technique. For this work, a 5 mm³ on-column syringe was used, which is less reproducible than the 0.5 mm³ syringe, but does allow co-injection.

The gas chromatogram of chrysene, in Fig 7.12, shows that although the compound elutes as a sharply defined peak, there is some tailing, which might be expected to influence any peak which immediately follows it. The concentration of chrysene used was chosen so that the peak would be similar in size to the lubricating oil peaks above the UCM hump.

By comparing the two chromatograms in Fig 7.13, which have been extended over the retention time period of interest, it can be seen that the chrysene peak emerges immediately after the small peak at 25.525 minutes, and has a retention time of 25.595 minutes, as expected. The small peak at 25.635 minutes, present in the chromatogram of the lubricating oil on its own, is completely swamped by the chrysene peak and is not separately resolved. As anticipated, the peak at 25.675 minutes on the chromatogram of lubricating oil with chrysene is higher than would otherwise have been expected.

Table 7.8 shows the ratios of heights for peaks close to chrysene in the two chromatograms and the effect of the tailing can be seen again clearly. From these ratios there is no evidence to suggest that the baseline used by

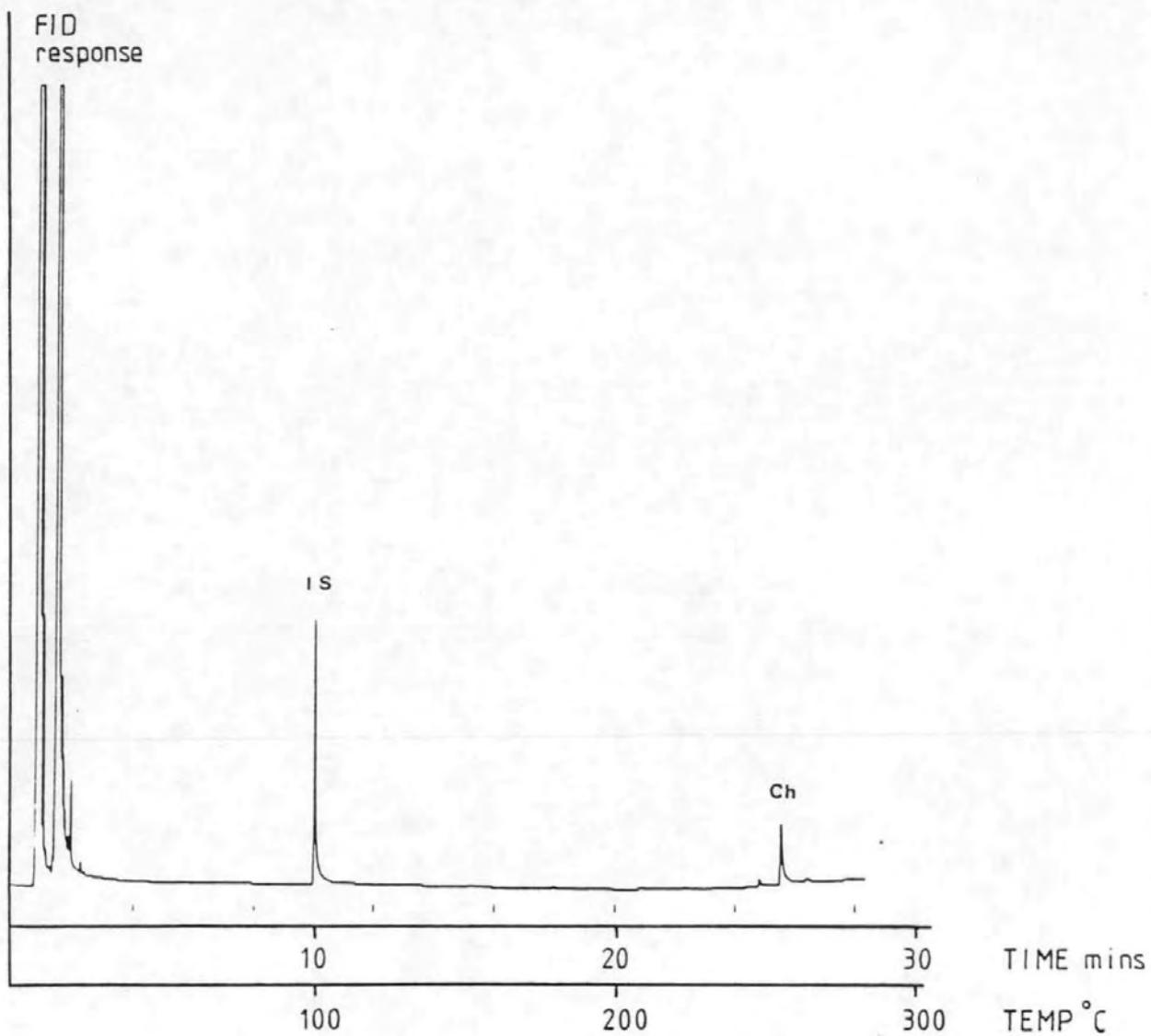


Fig 7.12

Gas Chromatogram for Chrysene Standard.

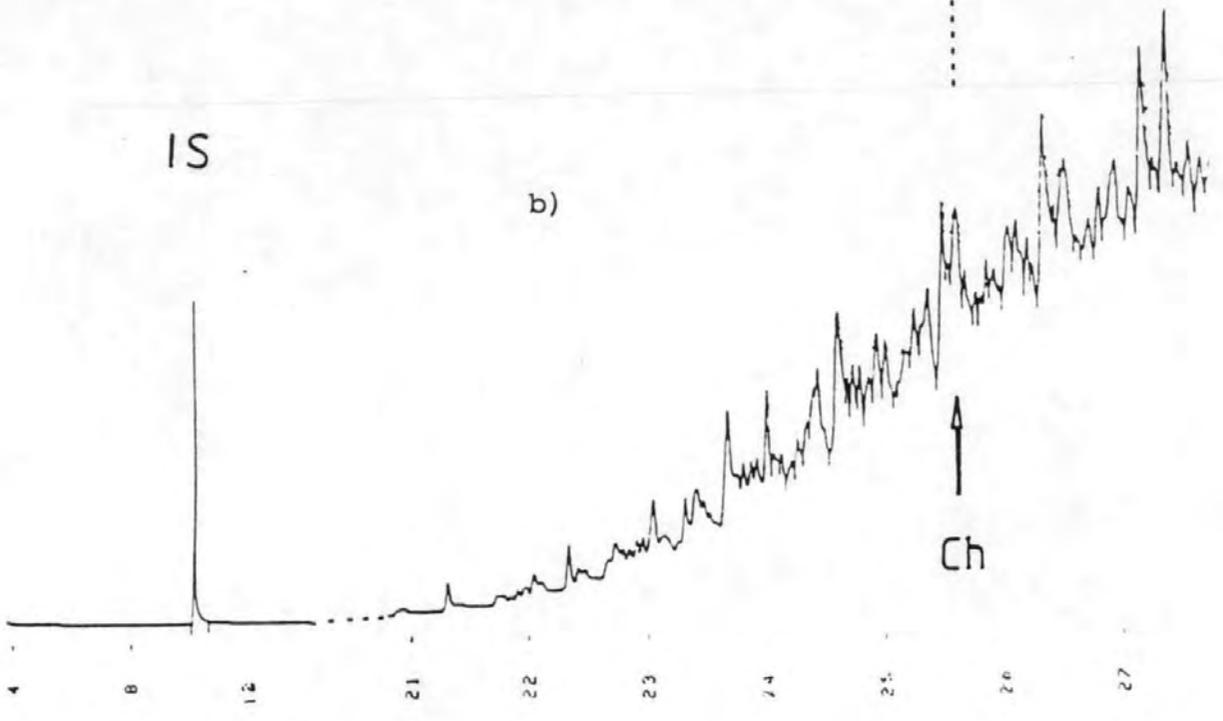
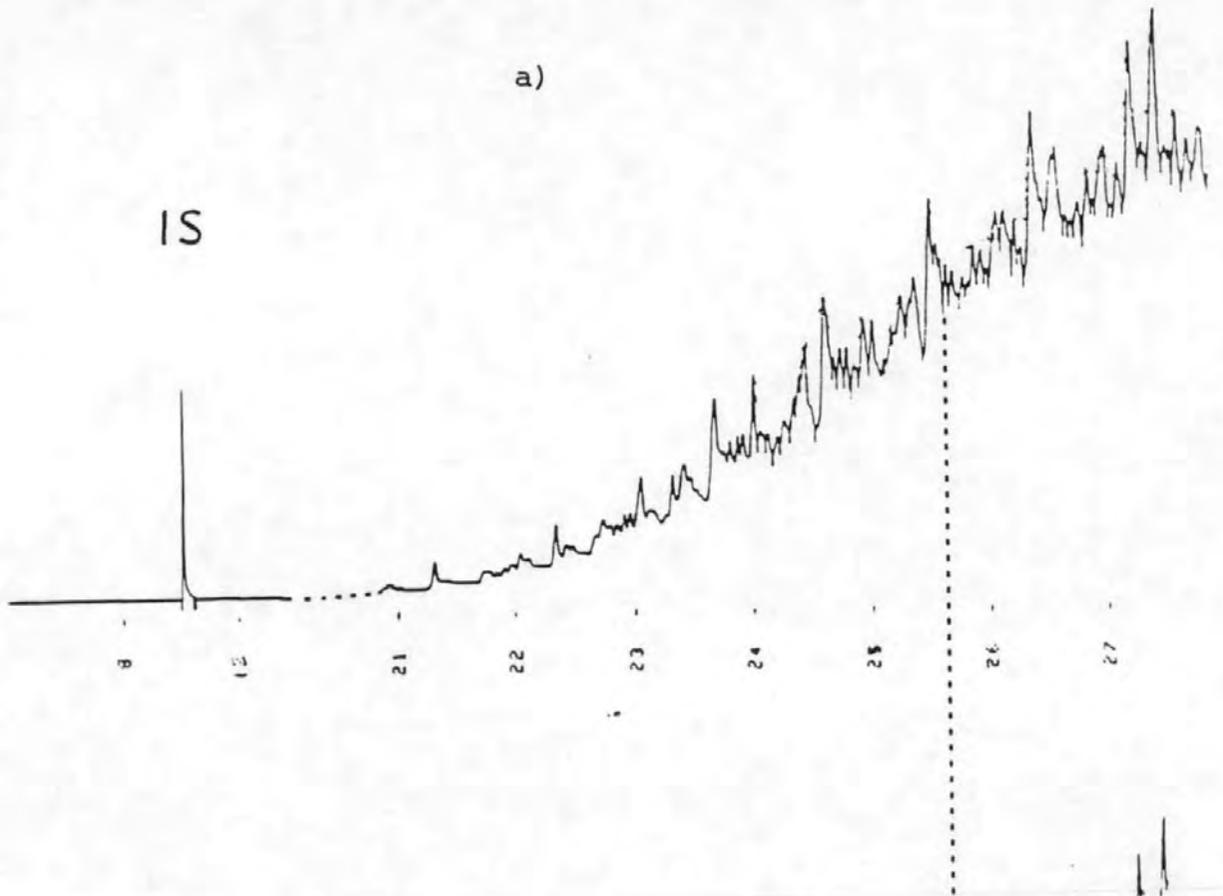


Fig 7.13 Extended Section of Part of Gas Chromatograms: a) Lubricating Oil. b) Lubricating Oil with Chrysene Added.

the integrator was altered by the addition of chrysene.

Lubricating Oil		Lubricating Oil + Chrysene		Ratio of Peak Heights	
Rtn Time	Peak Height	Rtn Time	Peak Height		
25.365	3768	25.365	4128	1 : 1.1	
25.500	6687	25.485	7260	1 : 1.09	
25.555	4639	25.525	4696	1 : 1.01	
25.690	3046	25.675	3885	1 : 1.28	
25.775	2538	25.77	2707	1 : 1.07	
25.800	3527	25.855	3793	1 : 1.07	
				Mean	1.10
				S.D.	0.0899
				C.V.	8.3%

Table 7.8 Integrator data for peaks adjacent to chrysene to compare the effect on the ratios of peak heights between chromatograms of lubricating oil with and without chrysene added.

A comparison, in Table 7.9, between the integrator peak heights and the peak heights measured manually, from an experimentally determined baseline for the internal standard in the three chromatograms, shows that the integrator data is very similar to the manual measurements. This is demonstrated most clearly by the ratios of the higher peaks to the lowest peak height for the two methods.

	Integrator		Ruler	
	Pk Ht	Ratio	Pk Ht	Ratio
Naphthalene in Chrysene	10567	1.21	4.44	1.21
Naphthalene in Lubricating Oil	8756	1.00	3.67	1.00
Naphthalene in Lubricating Oil + Chrysene	13317	1.52	5.61	1.53

Table 7.9 Similarity between integrator and ruler methods for measuring internal standard peak height unaffected by UCM hump.

The relationship does not hold for chrysene when it co-elutes on top of the lubricating oil. In this case, the ratio of the peak height for chrysene on its own, with respect to chrysene in the lubricating oil, is 1 : 2.72 for the integrator but 1 : 6.67 for the ruler. In fact, the measured height of the chrysene peak above the UCM (1.03 cm) is very close to the measured height for the chrysene on its own (1.05 cm).

In conclusion, this experiment shows that a co-eluting, non-lubricating oil compound will affect adjacent peaks to a small degree, though less so if the adjacent peak is large. There is no evidence that it has any substantial effect on the baseline.

7.4 Creating Data Sets.

The second step, once the data acquisition by integrator

had been achieved satisfactorily, was the development of a computer program to manipulate this raw data into comparable data sets.

7.4.1 Improved Data Input.

The Shimadzu integrator, used for this work, presents a final printout of data which includes three data columns of interest in this work: peak number, peak retention time and peak height. A computer program has been developed so that these 3 columns can be entered as data in their entirety. There is no selection of peaks for inclusion at this stage, the only criteria being that the data should fall within the retention time window in which the bulk of the lubricating oil elutes, in this case between 24 and 32 minutes.

The aliphatic fraction of the used lubricating oil is taken as the calibration standard. The analysis of this lubricating oil becomes the definitive version of the oil to which the samples will be compared. The calibration standard integrator data contained 60 peaks between the retention times of 24 and 32 minutes. The integrator data for the calibration standard and samples is entered into the computer in separate files. At this point, a visual inspection is required in order to identify a prominent peak in the calibration standard, and to match it with the corresponding peak in each of the samples. This information is then entered into the computer program in the form: 'Peak 35 in the calibration standard matches

peak 77 in Sample A.' The computer program then adjusts the retention times of each sample, based on the difference in retention time for the peak that has been visually matched, between the calibration standard and the sample. For instance, if in the above example the retention time of peak 35 in the calibration standard is 2 seconds more than that of peak 77 in Sample A, then 2 seconds is added to all the retention times of Sample A.

There are obvious similarities between this approach and the retention index system of Milton Lee (Lee et al. 1979). If the retention time window needed to be wider, or, a higher degree of precision were required, then the program could easily be changed to match peaks in the form of the Lee or Kovats retention indices.

Once the retention times have been adjusted the computer program draws up a new data set for each sample, which only includes the peaks in the samples which match, by adjusted retention times, with the 60 'definitive' peaks of the calibration standard. The computer program also renumbers the peaks of the samples, so that peak 35 in the calibration standard is now matched with peak 35 in each of the samples. Thus, for every sample there is a maximum of 60 possible peaks in the data set, and these peaks, if present, match by retention time the same number peak in the calibration standard.

In order to demonstrate the technique, two samples from the experimental work comparing TESSA with a dilution tunnel

filter sampling system, described in chapter 6, were used; The samples were the TES and SOF obtained from the 40 Nm load condition, and are described as TESSA 3 and Filter 3 in the following section. The technique can be illustrated by comparing the original chromatograms for the corresponding lubricating oil (calibration standard), TESSA 3 sample, and the Filter 3 sample, with their computer simulated, simplified chromatograms, shown in Figs 7.14, 7.15, and 7.16 respectively. Many matching peaks, which emphasise the similarities between the lubricating oil standard and the samples, emerge from this simplified data that are less apparent in the original data form.

7.5 Use of Statistics to Compare the Concentration of Lubricating Oil in Different Samples.

In the final step of the refined method, the previously created data sets are statistically compared, and an equation, comparing the concentration of lubricating oil in a sample with that of a calibration standard, is developed using multiple regression.

7.5.1 Comparison of Data Sets.

The timeplots for two repeat injections of the lubricating oil standard are shown in Fig 7.17. These plots are a simple display of integrator peak height against peak number. The very great similarity between them is reflected in a correlation of greater than 0.998. Small differences are nevertheless discernible, for example, pk

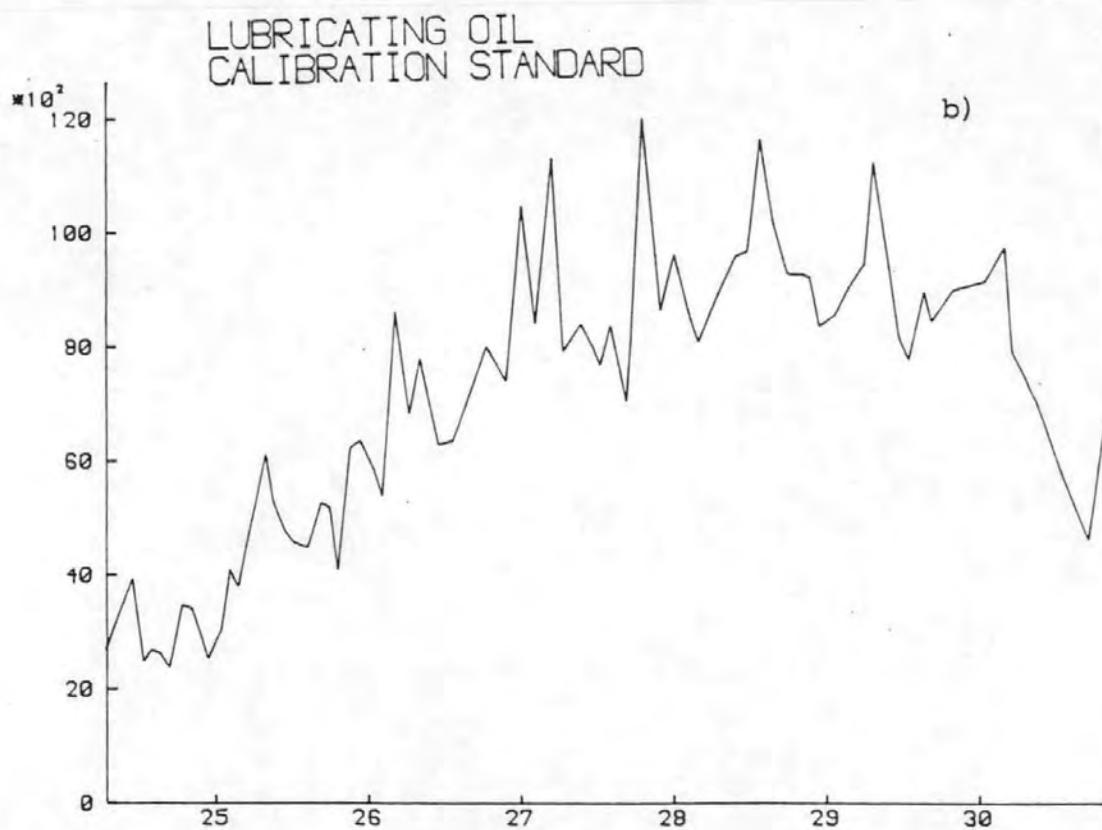
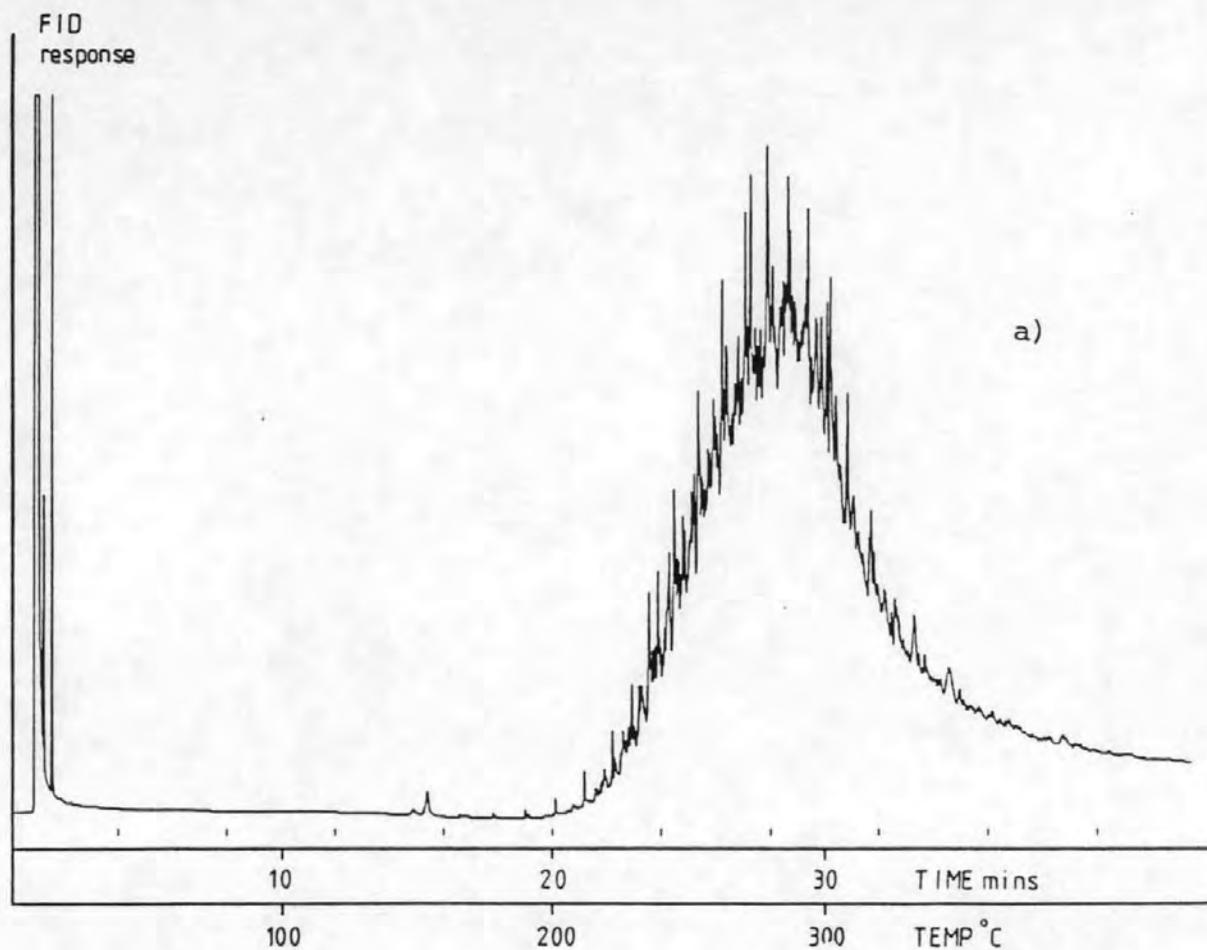


Fig 7.14 a) Gas Chromatogram for Lubricating Oil.
b) Simplified Section of Lubricating Oil Chromatogram
Simulated by Computer.

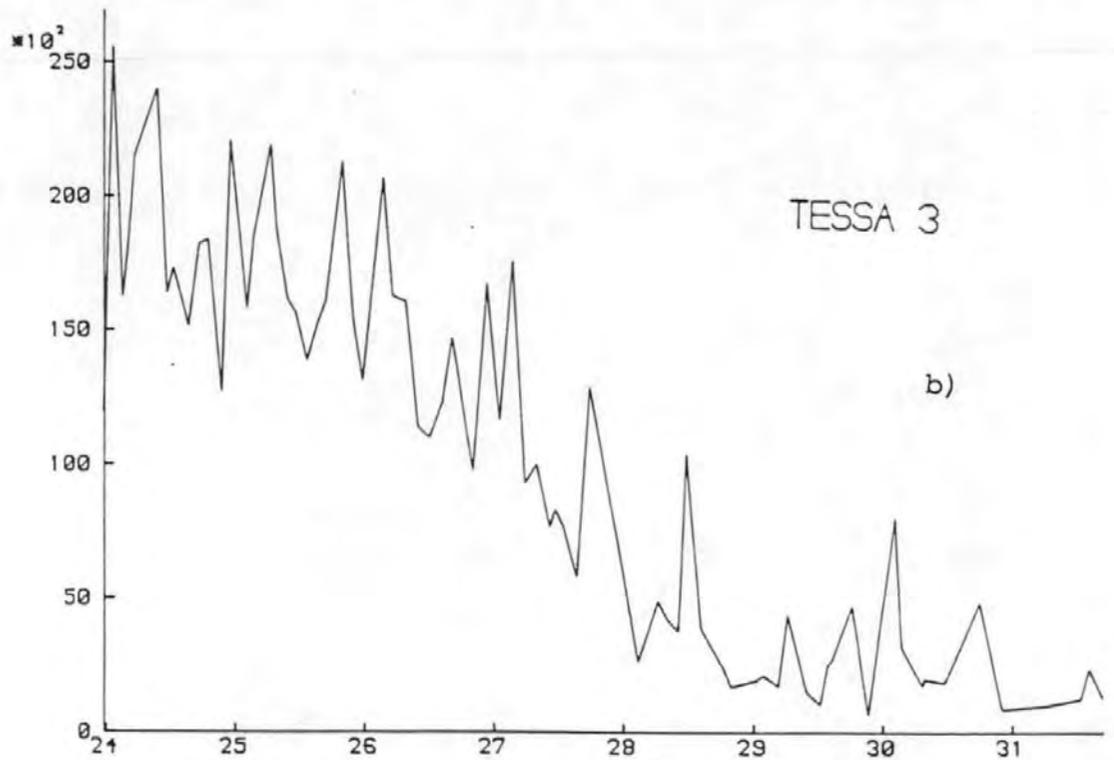
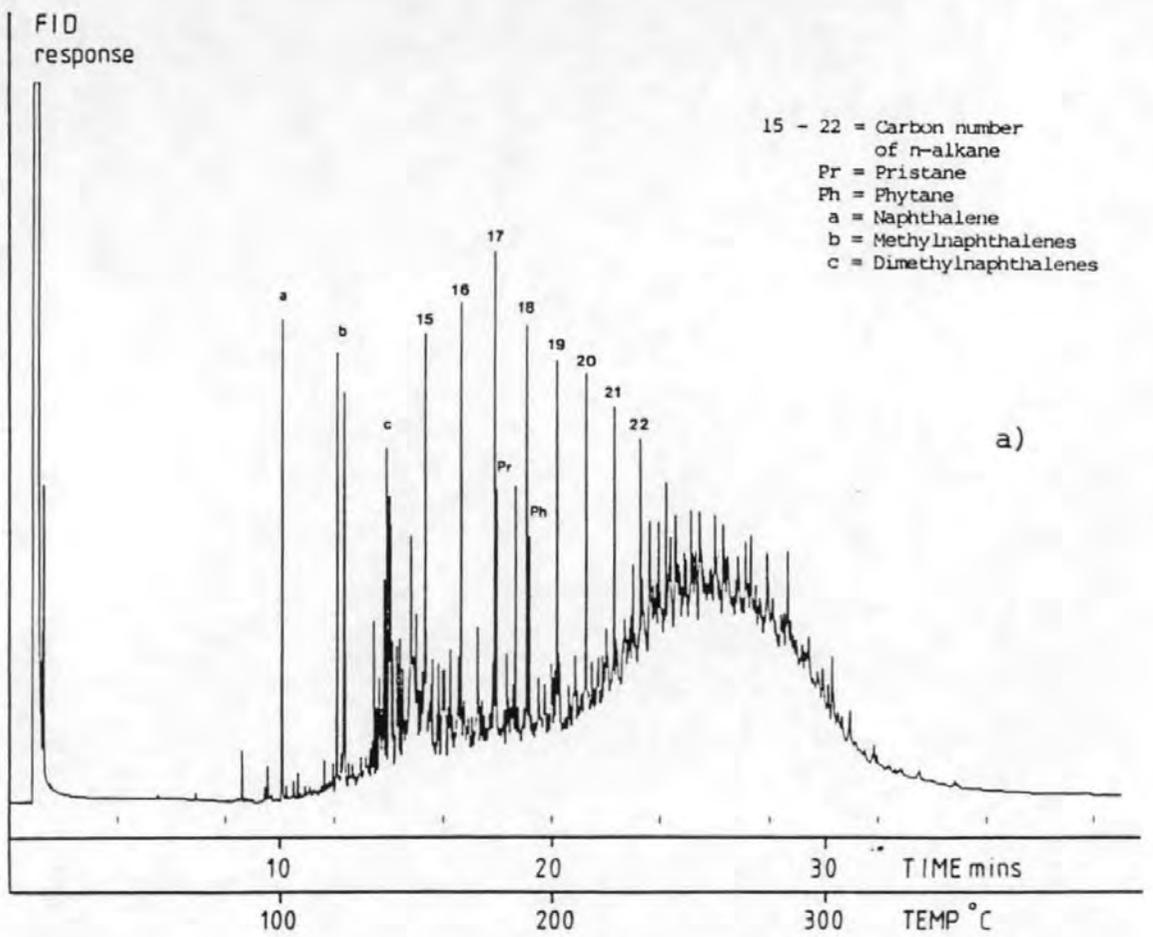


Fig 7.15 a) Gas Chromatogram for TESSA 3 Sample.
 b) Simplified Section of TESSA 3 Sample Chromatogram Simulated by Computer.

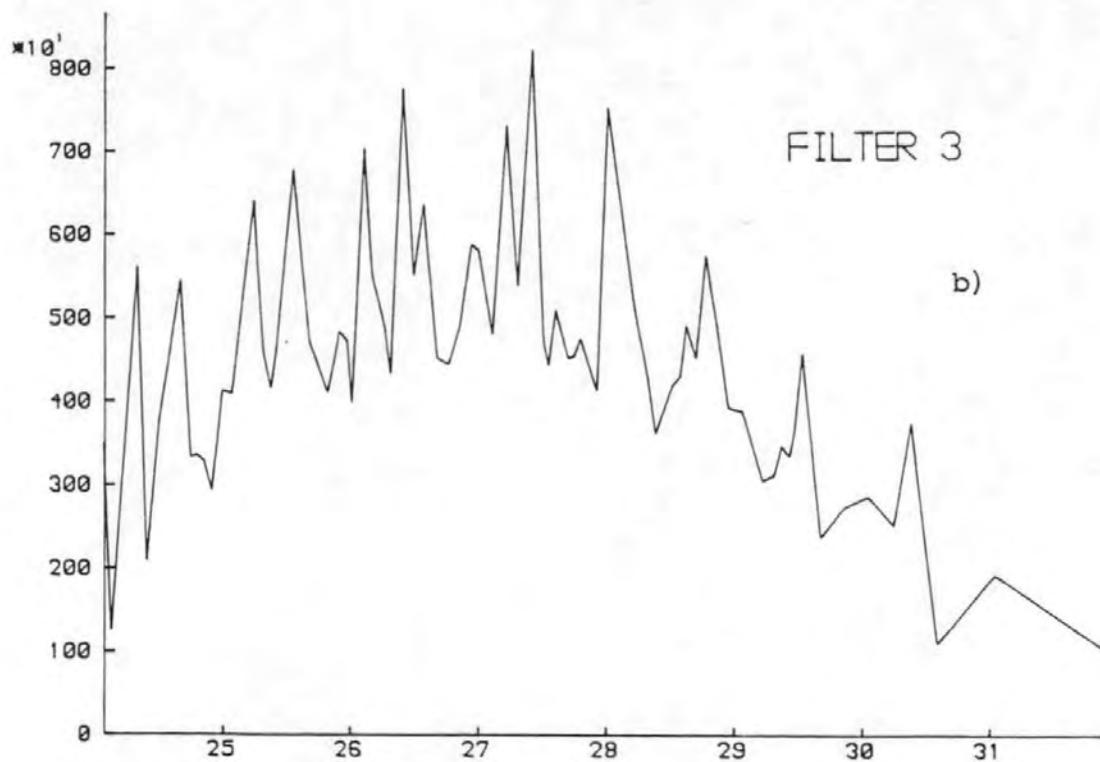
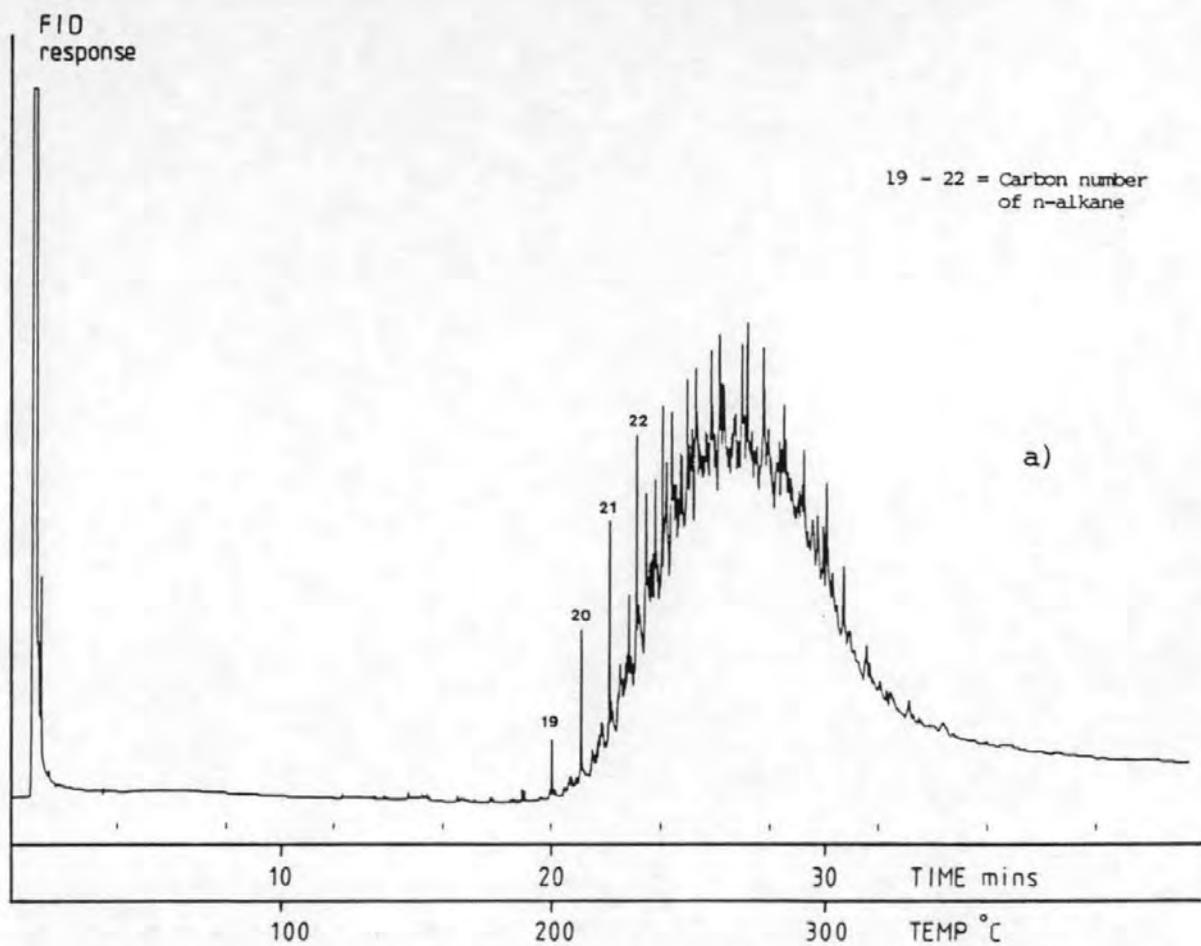


Fig 7.16 a) Gas Chromatogram for Filter 3 SOF.
 b) Simplified Section of Filter 3 SOF Chromatogram
 Simulated by Computer.

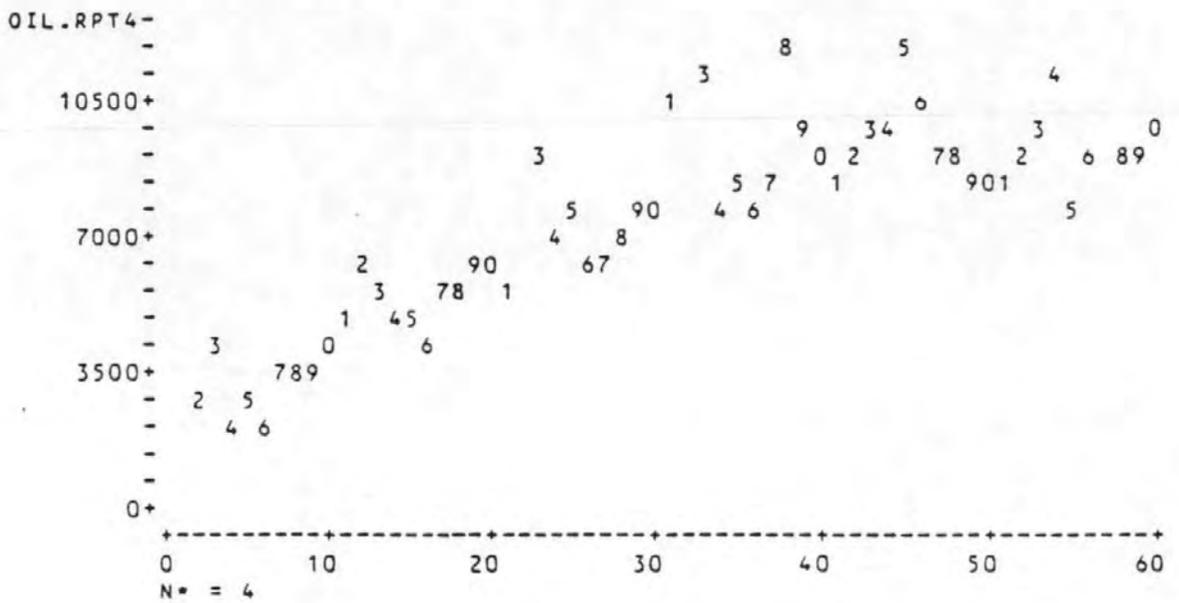
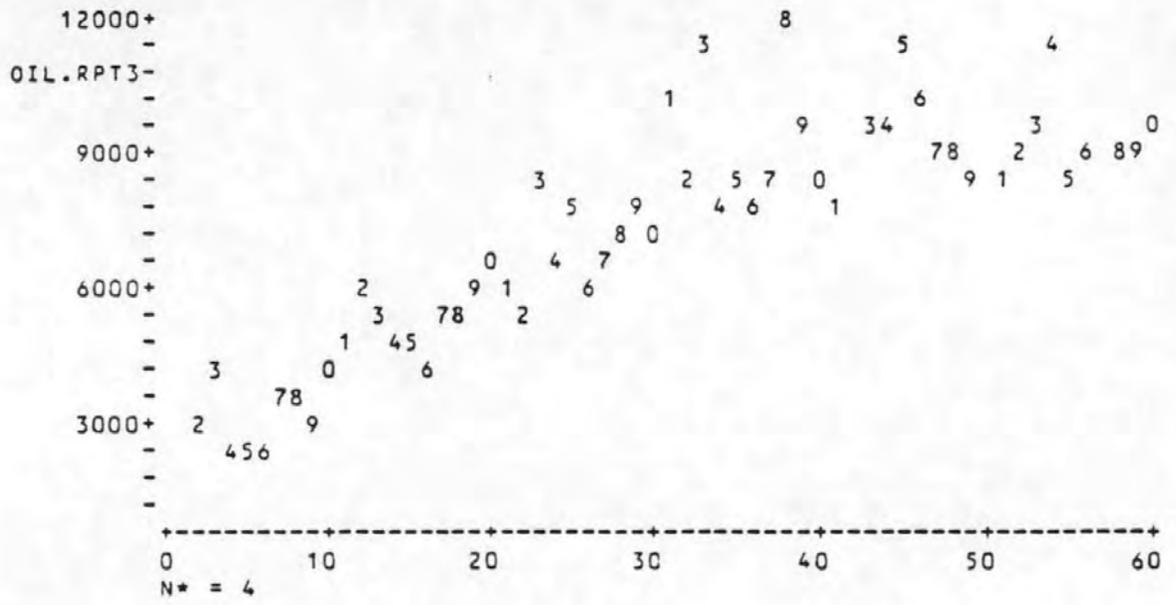


Fig 7.17 Timeplots of Peak Heights for Peaks from Two Repeat Analyses of Lubricating Oil.

26 is aligned slightly differently, with respect to pk 27, in the two plots. Another feature is the series of major peaks which clearly stand out above the rest of the peaks, in both plots, ie peak nos 3,12,23,31,33, 38,45,54 and 60. The overall pattern of the timeplot for the lubricating oil standard corresponds well to the shape of the more complex chromatogram for the oil, Fig 7.14a. Peak heights show an increasing trend up to around pk 35, which actually corresponds to the top middle of the UCM in the complex chromatogram of the lubricating oil. It should be noted that this trend only emerges because the integrator peak heights include a large part of the UCM hump.

The timeplot of peak heights for peaks from the TESSA 3 sample, that are matched with the 60 peaks in the lubricating oil, show an apparently contrasting picture in Fig 7.18a. A dominant and noticeable trend, for the first 35 peaks, is one of decreasing peak height, whereas, for the lubricating oil, the first 35 peaks showed a gradual increase in peak height. This difference results from a significant presence of non-lubricating oil compounds which have a more dominant influence on the earlier peaks than does the increase in the UCM hump due to the lubricating oil. This problem of interference from non-lubricating oil compounds only arises when these compounds have the same retention times as the 60 peaks identified in the lubricating oil.

This co-elution is termed the 'fuel-effect', although it is accepted that these compounds are not only represented by

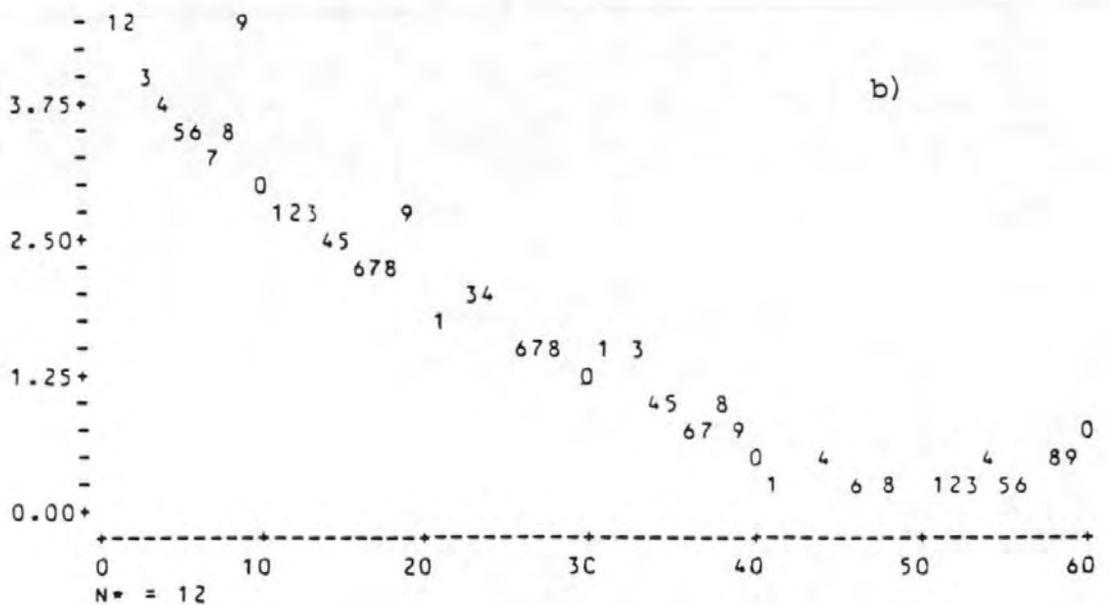
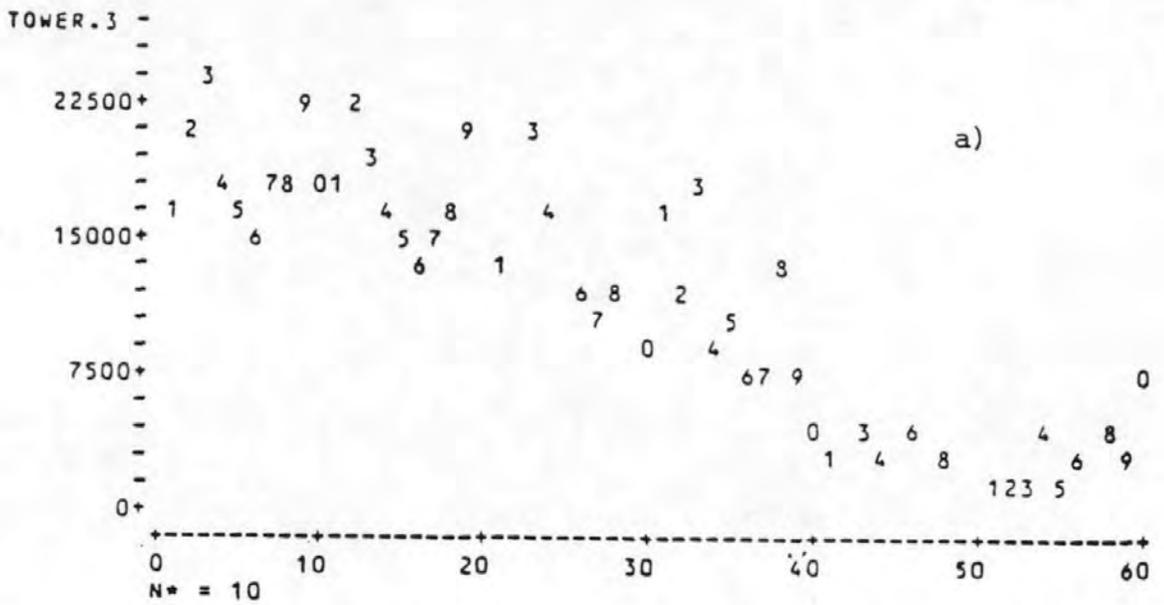


Fig 7.18 a) Timeplot of Peak Heights for Peaks from the TESSA 3 Sample. b) Ratio of TESSA 3 Sample Peak Heights Divided by Calibration Standard Peak Heights, Plotted Against Time.

unburnt fuel but by products of partial combustion in the engine as well. The fuel-effect can influence the peak heights in a sample both by enhancing specific peaks above the UCM hump and by adding to the UCM hump itself. The intention of the work described has been to model the influence of this fuel-effect sufficiently accurately that a reasonable correlation can be obtained between the 60 lubricating oil peak heights and those 50 to 60 matching peaks of a sample. This modelling is possible because the decreasing trend shows a reasonable linearity, with a tight pattern of data and little increased spread compared to the lubricating oil.

Closer inspection of the plot of peak heights for the TESSA 3 sample reveals that there is a series of major peaks which clearly stands out above the rest of the peaks. These peaks closely correspond to the major peaks for the lubricating oil standard mentioned above, and are peak nos 3, 9, 12, 19, 23, 31, 33, 38, 54 and 60. Peaks 9 and 19 correspond to peaks present in the diesel fuel, and hence do not match major peaks in the lubricating oil. Overall the relationship of each peak to its near neighbours is very similar for the TESSA sample and the lubricating oil, which suggests that the fuel-effect predominantly affects the UCM hump rather than the peaks above the hump.

The fuel-effect can be seen more clearly by plotting the ratio (TESSA 3 sample peak heights/Calibration standard peak heights) against Time, Fig 7.18b. The decreasing, approximately linear, trend over the first 35 peaks is the

fuel-effect described above. The fuel peaks, nos 9 and 19, are also very apparent and as these are effectively outliers, they are removed from the data set of the sample

Similar results can be seen in the plot of Filter 3 against Time, Fig 7.19a. The limitations of the dilution tunnel filter sampling system are such that it fails to trap lower relative molecular mass gaseous phase compounds (Trier et al.1988). The result of this is that the overall pattern of the plot of peak heights against time, for Filter 3, is much closer to the plot of peak heights against time for the calibration standard. The influence of the products of pyrolysis and partial combustion, so noticeable in the TESSA 3 sample, is much less here, although the influence is still discernible. The same major peaks are prominent in both Filter 3 and the calibration standard, as was the case with TESSA 3. Also the fuel peaks, nos 9 and 19, are again very apparent. These effects can again be seen more clearly in the plot of the ratio (Filter 3 / Calibration standard) against time Fig 7.19b.

7.5.2 Modelling the Contribution of Lubricating Oil to a Sample.

The relationship between the simplified chromatograms of a sample and the calibration standard can be modelled using multiple regression in the statistical package MINITAB. The fitted model relates, in the form of an equation, peak height for a sample, with peak height for the calibration standard, and includes a term for fuel-effect in the

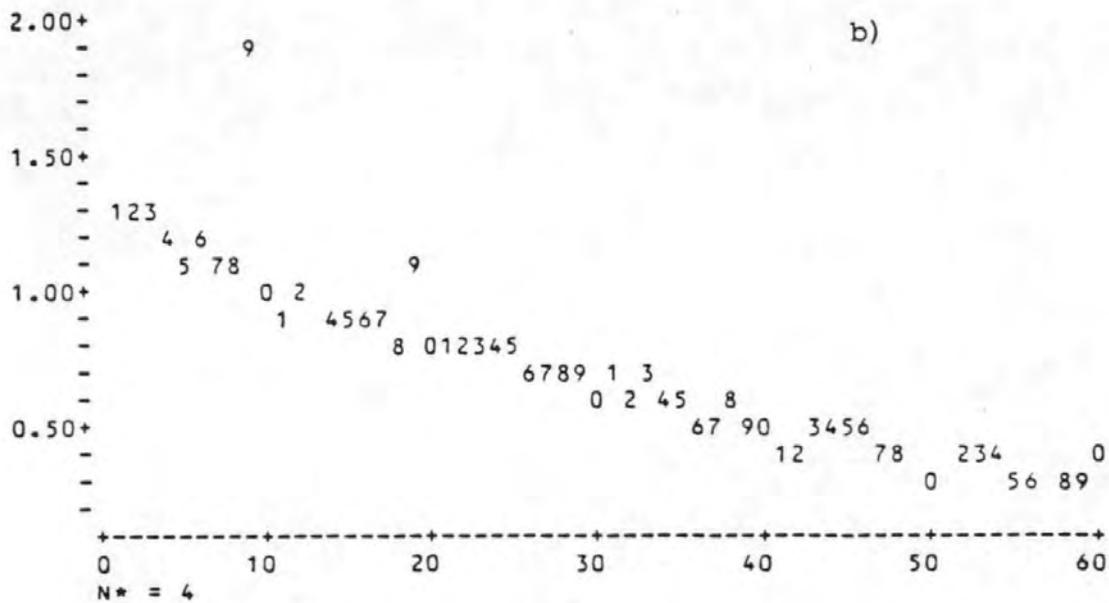
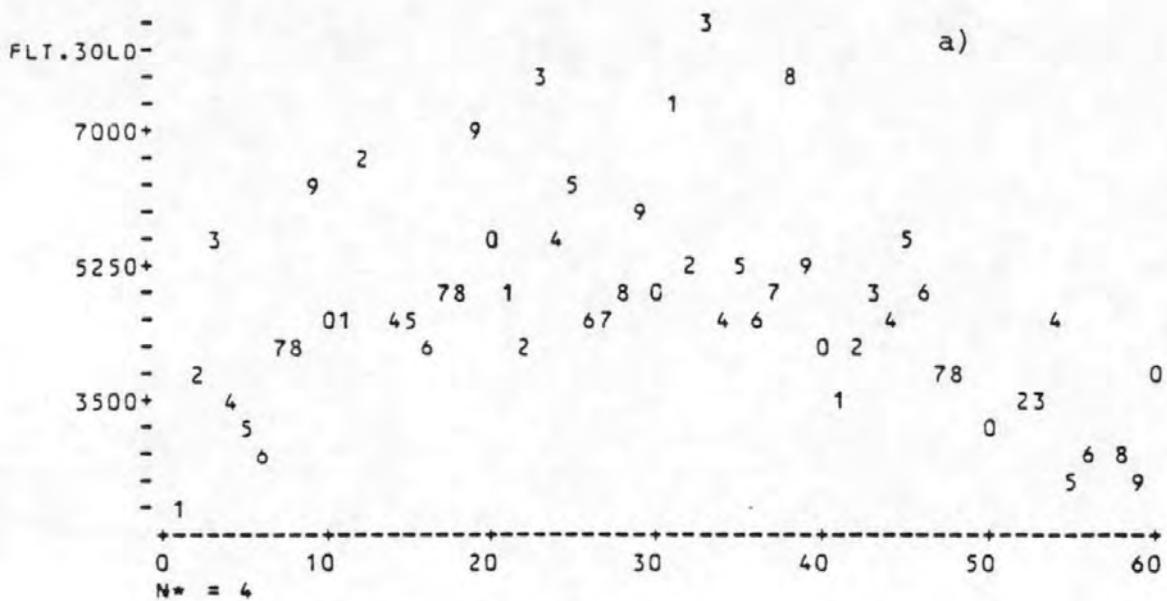


Fig 7.19 a) Timeplot of Peak Heights for Peaks from the Filter 3 SOF. b) Ratio of Filter 3 SOF Peak Heights Divided by Calibration Standard Peak Heights, Plotted Against Time.

sample. Tables 7.10 and 7.11 give the MINITAB output for multiple regression applied to TESSA 3 and Filter 3, both compared to the calibration standard.

Considering Table 7.10, the fitted model gives an equation in the form:-

$$\text{Pk.Ht of TESSA 3} = A + B(\text{Pk.Ht. of Calibration Std.}) + C(\text{Fuel Effect}).$$

A, B and C are constants. The actual concentration of the lubricating oil in TESSA 3 from the equation is B times the concentration in the calibration standard. Therefore the equation in Table 7.10 shows that there is about twice (1.98 times) the concentration of lubricating oil in TESSA 3 as in the lubricating oil calibration standard.

7.6 Results of Method Applied to Diesel Exhaust Samples.

The analyses of the samples and calibration standard used only the aliphatic fractions, since the used oil would fractionate similarly in them all, and it was ascertained experimentally at the outset that, after fractionation, 71.5% of the used oil eluted in the aliphatic fraction. The calibration standard and Filter 3 were analysed at a concentration of 2 mg/cm³, whilst that of the TESSA 3 was 10 mg/cm³. The equation shown in Table 7.10 indicates that the concentration of lubricating oil in TESSA 3 is 1.98 × 2,

The regression equation is
 $TOWER.3 = -14855 + 1.98 OIL.RPT6 + 612 C35$

46 cases used 14 cases contain missing values

Predictor	Coef	Stdev	t-ratio
Constant	-14855	1734	-8.57
OIL.RPT6	1.9311	0.1706	11.61
C35	611.69	24.43	25.03

s = 1544 R-sq = 94.8% R-sq(adj) = 94.6%

Analysis of Variance

SOURCE	DF	SS	MS
Regression	2	1875027200	937513600
Error	43	102557632	2385061
Total	45	1977584832	

SOURCE	DF	SEQ SS
OIL.RPT6	1	360280896

C35 1 1494746112

Continue? Y

Unusual Observations

Obs.	OIL.RPT6	TOWER.3	Fit	Stdev.Fit	Residual	St.Resid
33	12593	17603	16822	705	781	0.57 x
38	12962	12881	14494	689	-1613	-1.17 x
54	11348	4398	7627	422	-3229	-2.17R
60	9544	7993	4053	355	3940	2.62R

R denotes an obs. with a large st. resid.

x denotes an obs. whose x value gives it large influence.

Table 7.10 Multiple Regression Applied to TESSA 3.
 (C35 is the 'fuel-effect' term)

The regression equation is
 $FLT.30LD = - 5752 + 0.844 MN.OILS + 127 C44$

54 cases used. 6 cases contain missing values

Predictor	Coef	Stdev	t-ratio
Constant	-5751.8	470.3	-12.23
MN.OILS	0.84398	0.03842	21.97
C44	127.194	6.224	20.44

s = 409.8 R-sq = 90.6% R-sq(adj) = 90.3%

Analysis of Variance

SOURCE	DF	SS	MS
Regression	2	82930948	41465424
Error	51	8565122	167944
Total	53	91495968	

SOURCE	DF	SEQ SS
MN.OILS	1	12786906
C44	1	70143936

Continue? Y

Unusual Observations

Obs.	MN.OILS	FLT.30LD	Fit	Stdev.Fit	Residual	St.Resid
1	1641	2084.0	3264.8	134.1	-1180.8	-3.05R
23	9337	7772.0	6961.8	120.2	810.2	2.07R
45	12477	5762.0	6813.6	130.9	-1051.6	-2.71R
57	7729	*	1280.1	172.7	*	* X

R denotes an obs. with a large st. resid.

X denotes an obs. whose X value gives it large influence.

Table 7.11 Multiple Regression Applied to Filter 3 SOF.
 (C44 is the 'fuel-effect' term)

$$= 3.96 \text{ mg/cm}^3$$

Of the 10 mg/cm³ concentration for the aliphatic fraction of TESSA 3, 3.96 mg/cm³ came from the lubricating oil and since the weight of the aliphatic fraction for TESSA 3 was 10 mg, then the weight of lubricating oil in the aliphatic fraction of TESSA 3 was 3.96 mg. This only represented 71.5% of the lubricating oil contribution to the sample, thus the total weight of lubricating oil in TESSA 3 ,

$$= 5.54 \text{ mg}$$

The total weight of TESSA 3 was 44.9 mg so the percentage contribution of the lubricating oil to TESSA 3 ,

$$= 12.3\%$$

This represents a 3 minute sample time for approximately one fifth of the total exhaust, and expressed in terms of hourly emissions of lubricating oil from the engine,

$$= 0.6 \text{ g/hr}$$

By similar deduction for the Filter 3 sample, the total weight of lubricating oil,

$$= 4.13 \text{ mg}$$

The weight of the SOF for Filter 3 was 7.7 mg so that the percentage contribution of lubricating oil to the SOF for

Filter 3,

= 53.7%

Similarly the percentage contribution to total particulates (14.6 mg),

= 28.3%

In order to take the sample for Filter 3, 994 litres of diluted exhaust was drawn through the filter. The dilution ratio, measured by the difference in NOx concentrations in the raw exhaust and dilution tunnel, was 1.53 : 1, therefore the equivalent volume of raw exhaust sampled for Filter 3

= 646 litres

Total exhaust volume generated in an hour was 150000 litres (the small additional volume contributed by the exhaust gases produced from the combustion of the fuel is ignored). From Filter 3 results, the hourly emission of lubricating oil from the engine,

= 1.0 g/hr

These calculations have involved approximations, particularly in assessing the actual dilution ratio, and also the fraction of the exhaust sampled by TESSA, with this in mind, the results for the two samples are in

reasonable agreement, being of the same order of magnitude.

7.7 Further Comments on the Statistical Techniques.

The computer printout from MINITAB, Table 7.10, shows that there is very strong evidence, in statistical terms, that peak height (TESSA 3) depends on the peak height (calibration standard) plus the fuel effect (C35); the t-ratio for the calibration standard is 11.61 and for the fuel effect 25.03. In particular 94.8% of the variation in the 60 or so peak heights for TESSA 3 is explained by the two variables Peak height (calibration std.) and fuel effect. Peaks 33 and 38 are 'flagged' as observations which have a large influence on the final fitted model. As these are large peaks, which have already been commented on, this is not surprising.

The MINITAB program indicates approximately the 5% most extreme residuals, as a matter of course. Since 46 peaks are being used, one might expect the package to 'flag' a couple of residuals and it has done so. If these 'flagged' residuals had been particularly large (for instance with a standardised residual in excess of 3.5), then, this would have suggested the corresponding peak was in some way unusual, but neither of the 'flagged' residuals have particularly large standardised residuals. Considering the plot of the residuals against time, Fig 7.20 and the 'flagged' residuals with large standardised residuals, there is no evidence that the fitted model is not satisfactory, (Coates 1987).

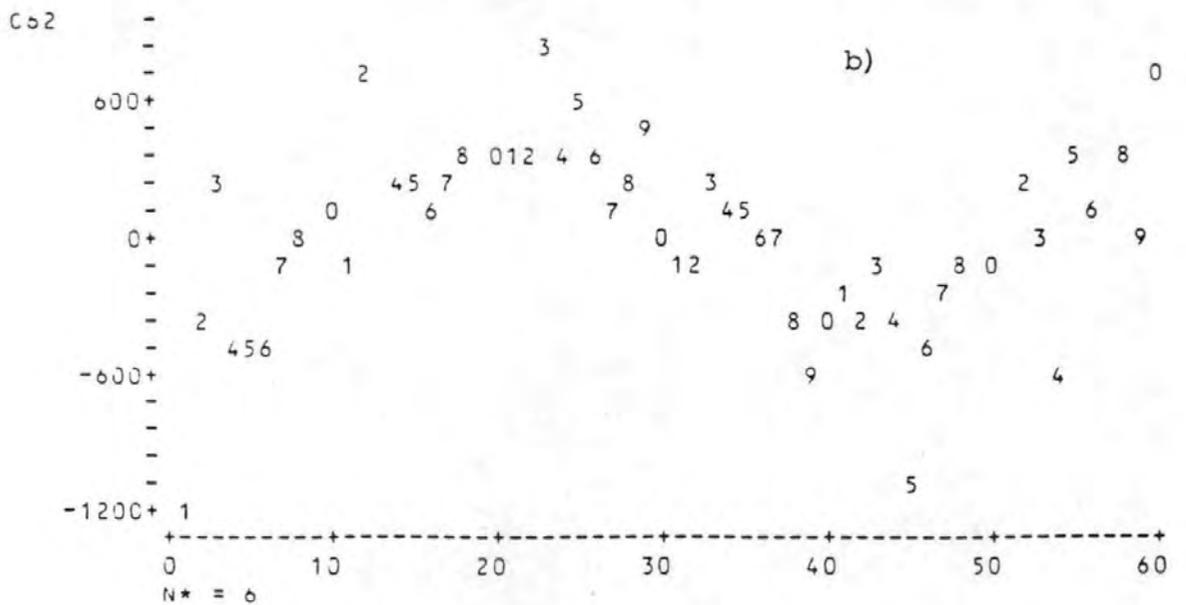
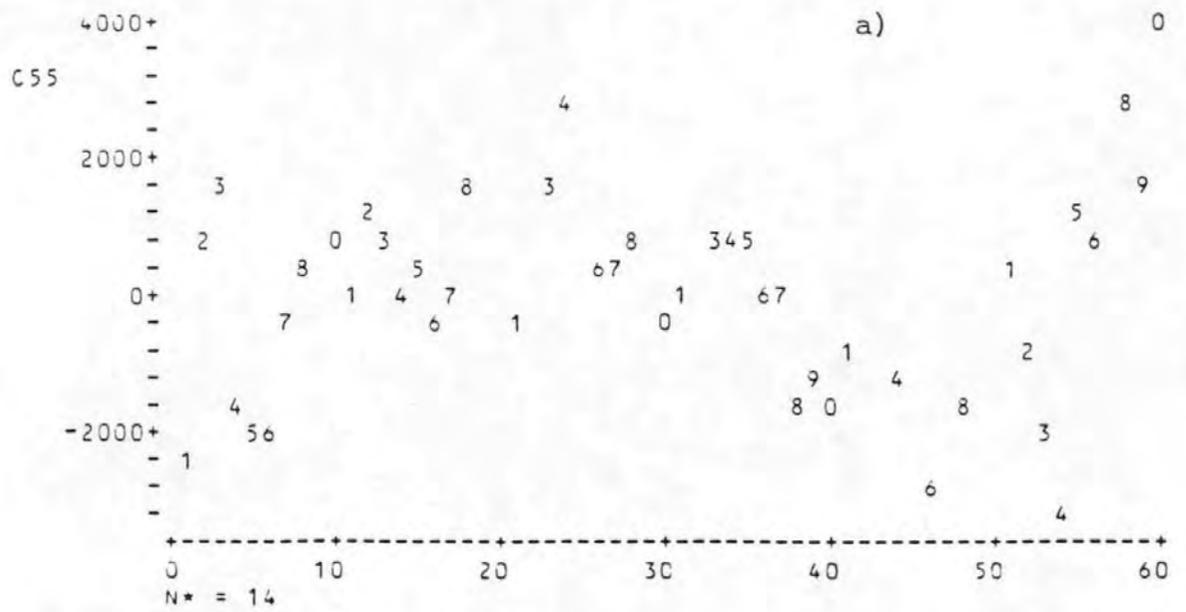


Fig 7.20 Statistical Residuals from Multiple Regression Analyses Plotted Against Time for: a) TESSA 3. b) Filter 3.

Note that had the fuel peaks, nos 9 and 19, been included in the analysis then their standardised residuals would have been particularly large thereby identifying them as unusual and suggesting that a model including them would not have been satisfactory.

7.8 Conclusions.

Two new methods have been developed for assessing the lubricating oil contribution to diesel exhaust extracts. They differ from previous methods in that they give an estimate of the lubricating oil that has passed through the combustion chamber unchanged, and do not include other material which might elute in the same retention time window. This unchanged lubricating oil has not been subjected to high temperatures and may be considered to represent oil leakage. Since lubricating oil is included in the total particulates, for the purposes of legislation, it would be advantageous to control the oil contribution to the exhaust, as a means to lowering diesel particulates. It may be easier to reduce oil leakage, i.e. oil which passes through to the exhaust unchanged, than to reduce the partially burnt oil that necessarily coats the walls of the combustion chamber and which in some small part must end up also in the exhaust. In any event, this method represents a major step forward for the combustion technologist primarily involved in controlling lubricating oil contribution to emissions.

CHAPTER 8.

Summary, Conclusions and Recommendations.

8.1 Summary.

8.1.1 Development of New Sampling System.

A new sampling system for raw diesel exhaust has been developed successfully. It is a flexible system that can sample close to the exhaust port and is also mobile enough to be moved between different engines. TESSA has the ability to sample a large proportion or even the total exhaust volume and therefore has the potential to yield large sample weights. Alternatively, sampling can be conducted over a short period of 60 seconds or less. Experiments have shown that little of the solvent-extractable material remains adsorbed to the particulates, once they have been sampled. The solvent system causes the particles to coalesce, enabling them effectively to be removed by filtering.

8.1.2 Design Assessment of TESSA.

The TESSA system has been evaluated thoroughly. The outcome has been to demonstrate that it is an effective sampling system, which minimises the formation of chemical artifacts of sampling. The temperature profile within TESSA was investigated, and the cooling capacity proven to

be sufficient. The influence of acidic gases from the exhaust was measured and their effect on a sample limited by dilution with water. The breakthrough of sample from the top exit was measured with a liquid nitrogen trap. It was found that, as long as the exhaust flow did not exceed 500 l/min, the breakthrough was minimal, (i.e less than 8% of total sample).

8.1.3 TESSA Results.

A series of experiments, undertaken with TESSA, indicated that it was an excellent means of collecting a sample for the chemical characterisation of hydrocarbons from exhaust. The results confirmed that there is a contribution to the exhaust from the fuel and the lubricating oil, as well as from combustion products, partially burnt or pyrolysed compounds, from both these sources. Two interpretative techniques were used to demonstrate how a fuller use can be made of the additional information obtained from TESSA when combined with modern analytical techniques. A significant increase in the relative concentrations of parent PAH was seen in the TES, particularly at high speed and load.

The effect of placing TESSA at the end of a 3 metre exhaust tailpipe extension was investigated and some burnout of exhaust hydrocarbons was indicated, i.e. combustion reactions continued in the elevated temperature in the tailpipe. The reduced pressure in the tailpipe, when

compared to the combustion chamber, caused a greater selectivity in burnout: the aliphatic hydrocarbons oxidised more rapidly than did the aromatic hydrocarbon compounds. Low levels of nitro-PAC were detected in the TES, close to the limit of detection, and at considerably lower concentrations than were previously found on dilution tunnel filter samples.

8.1.4 Comparison with Dilution Tunnel Filter.

A comparison of samples was made between a TES and the SOF from a dilution tunnel filter. It was found that the TES effectively sampled exhaust hydrocarbons including the more volatile constituents, and that only those hydrocarbons which remained in the gas-phase at STP, such as methane, passed through TESSA without being sampled. The results for the TES correlated closely with the UHC measurements from a HFID. The filter system, although effective in trapping particulates, collected volatile organic compounds in a somewhat arbitrary fashion; this depended on the air dilution and partial pressure of these compounds, along with their individual boiling points, to determine whether they would adsorb onto the particulate carbon, or condense onto the surface of the filter. Organic volatiles, which remained in the gas-phase, were not sampled by the dilution tunnel filter system.

Modern diesel engines, with very low particulate carbon emissions, may produce significant concentrations of

gaseous phase organics which are not scavenged by particulates and, therefore, are not effectively sampled by a filter.

8.1.5 New Methods for Calculating Lubricating Oil Concentrations in the Exhaust.

Two methods for the determination of the contribution of lubricating oil to diesel exhaust have been developed. Results using these methods have demonstrated that lubricating oil makes a significant contribution to the total particulates and in some circumstances, e.g. at low speed and load, can dominate the SOF. Control of lubricating oil leakage to the exhaust may be a useful means of lowering the total particulate emissions, which are currently subjected to tight legislative limits in the US.

The first method required a comparison of peak heights from four specific geochemical marker compounds between sample and lubricating oil. The range of results from 6 dilution tunnel filters, for the lubricating oil contribution to the SOF, was 20 - 55 %.

The second method involved a computer matching of up to 60 common peaks between sample and lubricating oil, using the data from an integrator attached to a gas chromatograph. In a comparison between a TES and SOF, taken under the same engine conditions, the contribution of lubricating oil to

the exhaust was calculated as 0.55 g/hr from the TES and 0.96 g/hr from the filter. This represented a 54% contribution to the SOF and 28% contribution to the total particulate

8.2 Conclusions.

- a) TESSA has proven to be an effective sampling system for exhaust hydrocarbons, and, when compared to a dilution tunnel filter, allowed a more complete characterisation of the organic compounds emitted from a diesel engine.
- b) The design minimises the formation of sampling artifacts: Nitro-PAC were detected in the TES, but only at very low concentrations.
- c) Little of the solvent-extractable material remains adsorbed to the particulates once they have been sampled.
- d) There is a contribution to the exhaust from small amounts of fuel and lubricating oil, passing through the combustion chamber substantially unchanged, as well as from partially burnt or pyrolysed products of combustion.
- e) Naphthalene, phenanthrene and several other PAC were shown to increase their relative concentration to their alkylated derivatives, in an exhaust sample, when compared to the relative concentrations found in the fuel. These parent compounds were being formed within the combustion chamber, as well as surviving in unburnt fuel.

f) The results from TESSA correlated closely with the UHC measurements from a HFID.

g) Aliphatic hydrocarbons in the exhaust tailpipe oxidised more rapidly than did aromatic hydrocarbons.

h) Lubricating oil makes a significant contribution to the total particulates, therefore, control of lubricating oil leakage to the exhaust may be a useful means of lowering the total particulate emissions.

i) If modern diesel engines have very low soot levels then less of the volatile organic compounds within the exhaust will be sampled by a dilution tunnel filter.

8.3 Recommendations for Future Work.

8.3.1 Further Experiments with TESSA.

a) Measure the effect of adding extra oxygen to the exhaust to increase the burnout of hydrocarbons within the exhaust.

b) Test the effectiveness of a variety of particle traps and particularly their effect on hydrocarbon emissions.

Do they encourage burnout? (Dorle et al.1987)

c) Test the hydrocarbon emissions from diesel fuels with a cetane value lower than 50, the current permitted minimum, in anticipation that this limit may soon be lowered,

(Bernstein and Tims 1984).

d) Characterise more fully the oxygenated and other polar compounds emitted in the exhaust, (Kawamura and Kaplan 1987).

e) Test the emissions of a base fuel, low in aromatics, with the addition of specific aromatic compounds. e.g 10% toluene and compare with 10% phenanthrene or pyrene.

f) Regulate the flow rate of solvent from the reservoir with the aid of a contamination-free electric pump to replace the present manual system which requires a person to be standing on TESSA during sampling.

g) Introduce distilled water, as cooling spray, into the lowest section of TESSA where exhaust enters system, rather than placing water in the collecting reservoir.

h) Design a portable frame for TESSA so that it can be wheeled between engines in the laboratory

i) Improve cooling capacity of TESSA by using a coolant with a lower freezing point than water, e.g methanol/water

8.3.2 Commercial Exploitation of TESSA.

The possibility of the commercial exploitation of TESSA should be explored. TESSA could make an attractive additional research sampling system for the combustion

technologist, particularly if it enabled a transient test cycle to be investigated in its different parts, i.e acceleration, motoring etc. It would require a number of modifications to the basic design in the following areas:

- a) The ability to take samples over a short time period of a few tens of seconds.
- b) To be able rapidly to repeat sampling.
- c) The facility to operate TESSA sampling remotely.

8.3.3 Lubricating Oil Emissions.

a) Develop the method of matching common peaks by moving towards a fully computerised assessment of lubricating oil contribution to emissions with direct access to data from a gas chromatograph. Full pattern recognition should be the ultimate goal.

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particulate matter. *Analytical Chemistry*, 54, 354-357.

APPENDIX A.

PHOTOGRAPHS OF EQUIPMENT.

A

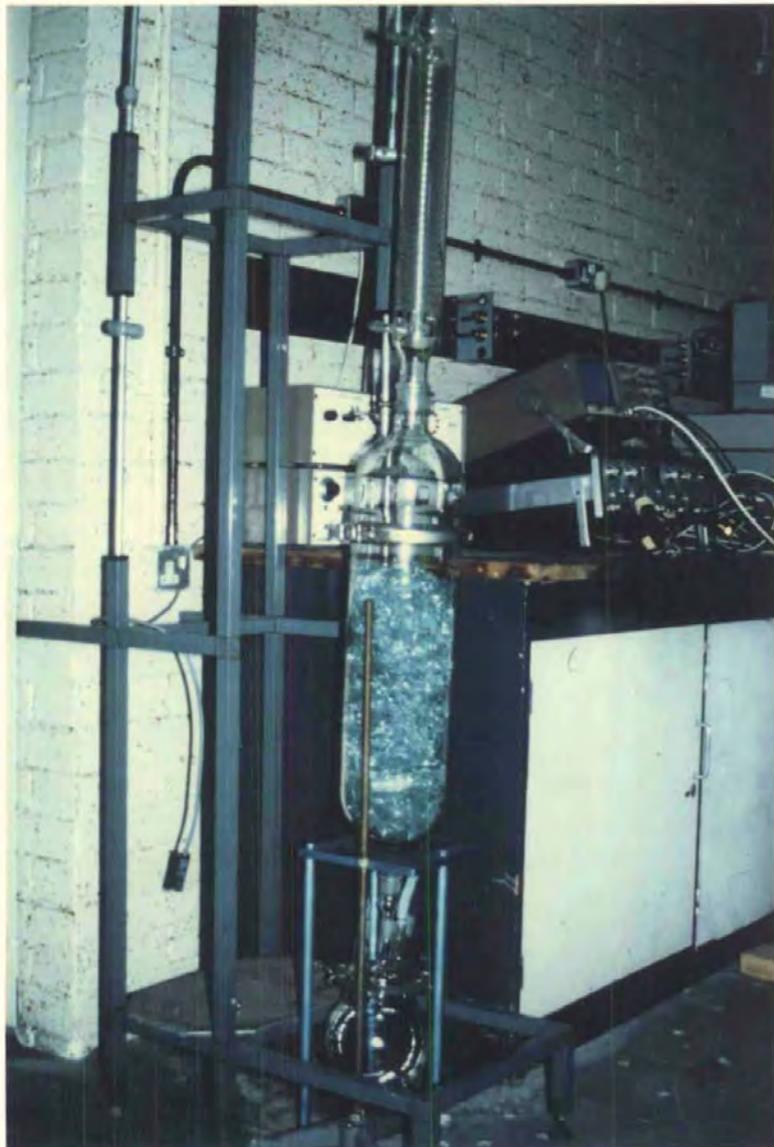


Photo A. Prototype of Tower.

B

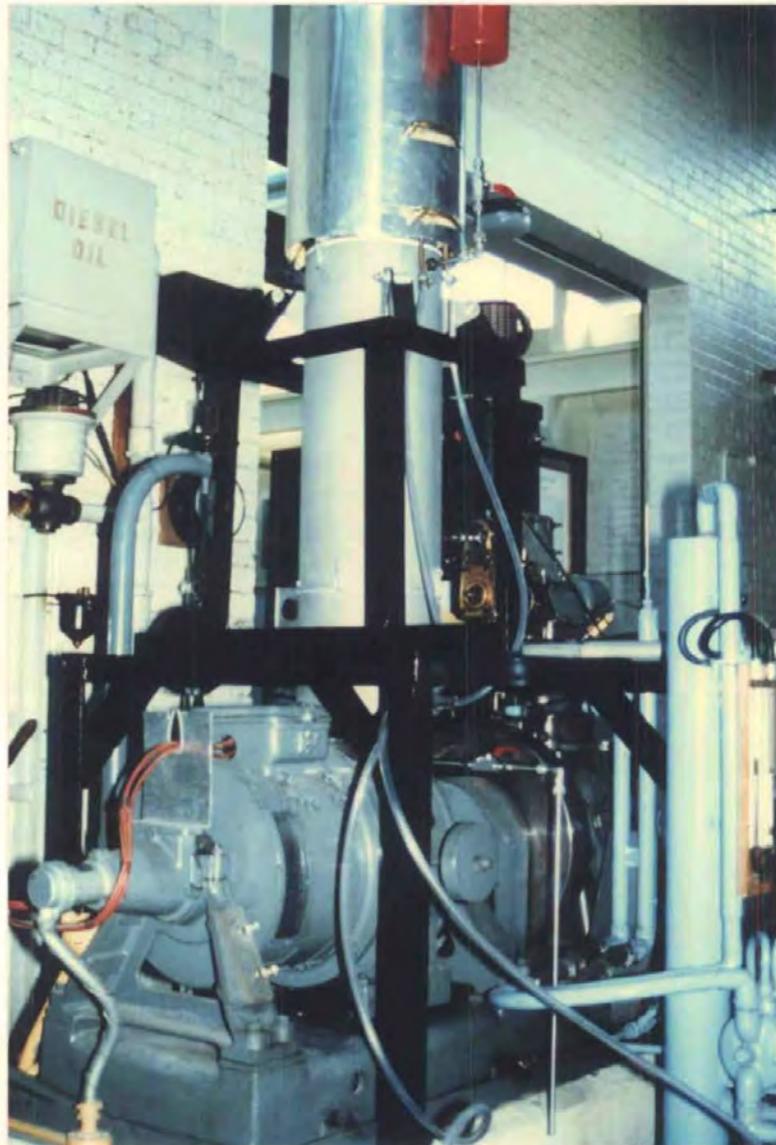


Photo B. TESSA Mounted on Ricardo E.6/T

C

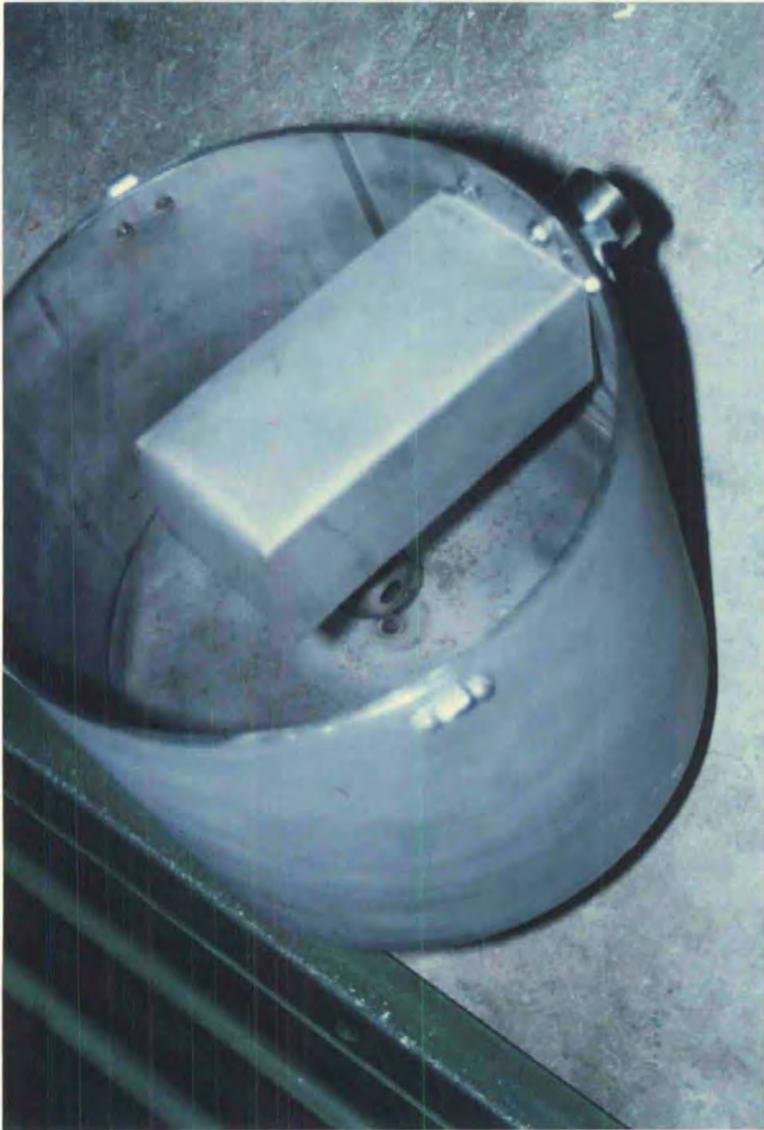
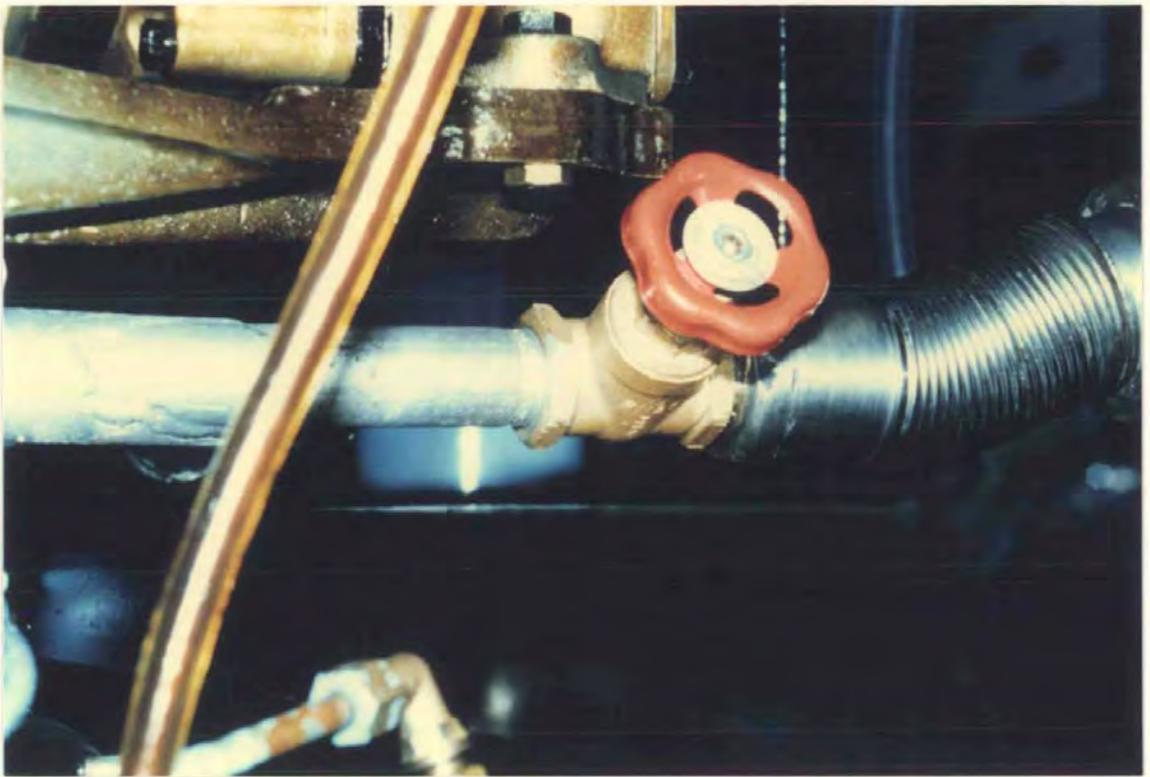


Photo C. Lower Section of TESSA Showing Shield Covering Inlet-Pipe from Engine.

D

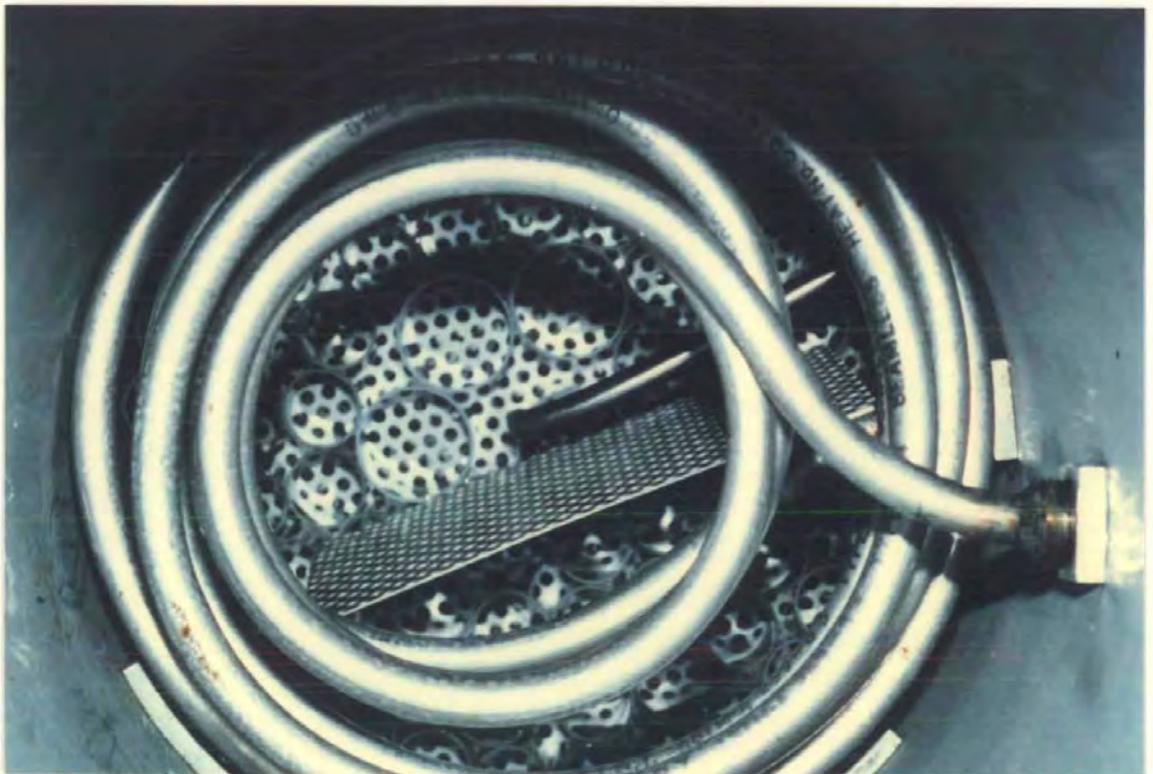


Photo D. Wire Mesh and Baffles from Top Section of TESSA.



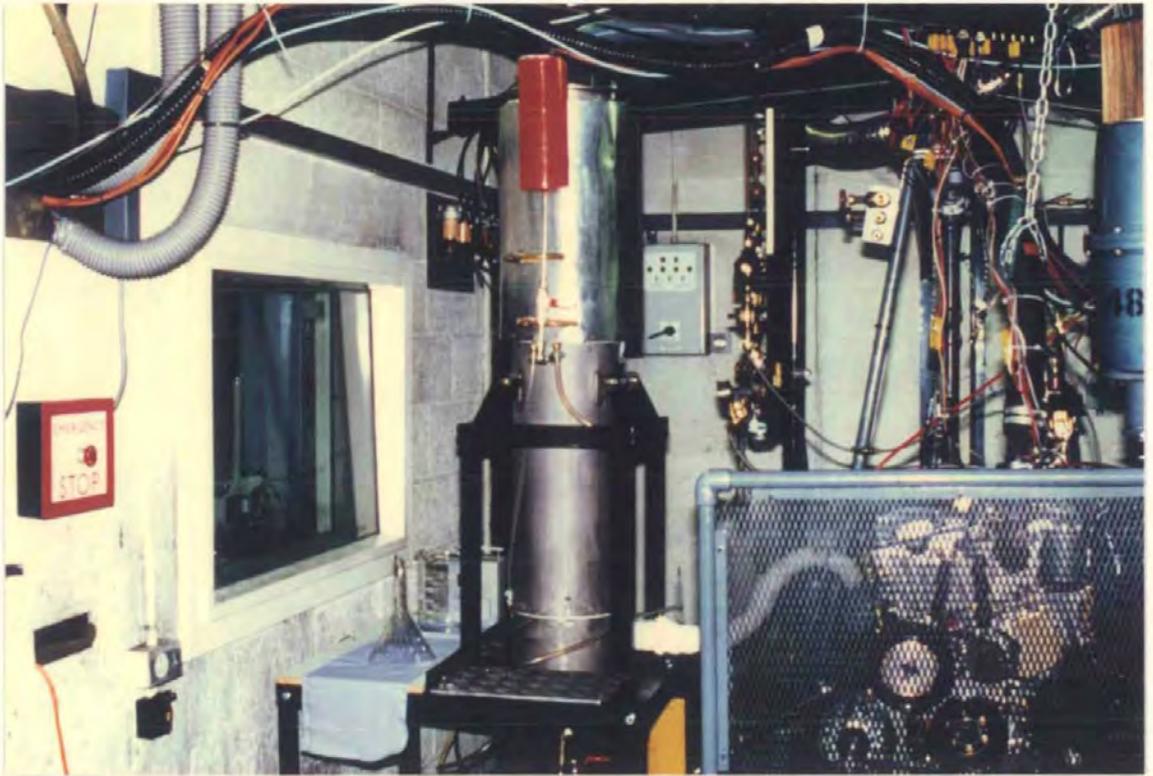
E

Photo E. Transfer Pipe from Ricardo E.6/T to TESSA.



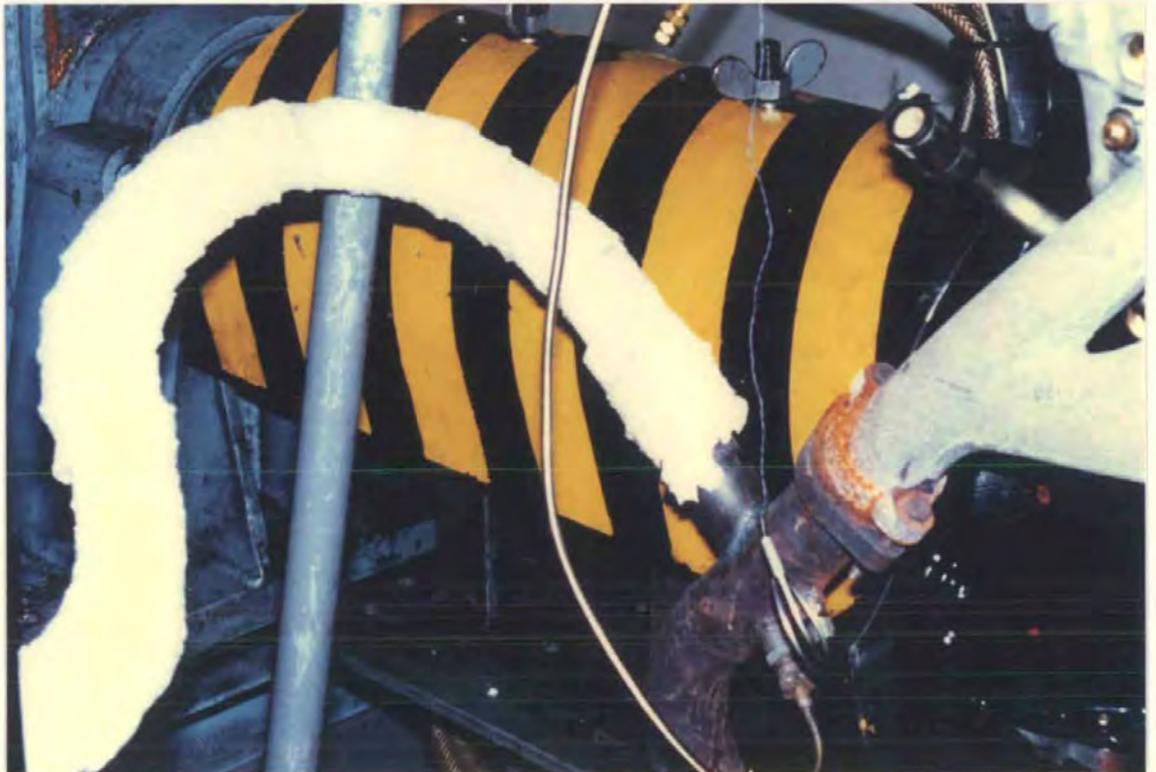
F

Photo F. Cooling Coil in Top Section of TESSA, with the Inlet Pipe from the Solvent Reservoir and the Uppermost Layer of Glass Tubing Visible Below.



G

Photo G. TESSA Set Up in Test Cell at Ricardo Consulting Engineers plc, to Compare TES with Filter Sample from Dilution Tunnel.



H

Photo H. Comparison of TESSA with Dilution Tunnel, Close-Up of Transfer Pipe Connection to Exhaust System.

APPENDIX B. - Presentations and Publications.

Resulting from the work reported in this thesis, the following papers have been presented and published:

1/.

TRIER, C.J.; PETCH, G.S; RHEAD, M.M.; FUSSEY, D.E. & SHORE P.R. Assessing the contribution of lubricating oil to diesel exhaust particulates using geochemical markers. International Conference on Vehicle Emissions and Their Impact on European Air Quality at the Institution of Mechanical Engineers, November 1987, London.

2/.

PETCH, G.S.; TRIER, C.J.; RHEAD, M.M.; FUSSEY, D.E. & MILLWARD, G.E. 1987. The development of a novel exhaust sampling technique with particular relevance to polycyclic aromatic hydrocarbons. International Conference on Vehicle Emissions and Their Impact on European Air Quality at The Institution of Mechanical Engineers, November 1987, London.

3/.

TRIER, C.J.; FUSSEY, D.E.; PETCH, G.S. & RHEAD, M.M. 1988. A comparison of diesel engine exhaust emissions collected by an EPA recommended dilution tunnel/filter with the sample from a new solvent scrubbing system. International Conference on Combustion in Engines - Technology and Applications at the Institution of Mechanical Engineers, May 1988, London.

Assessing the contribution of lubricating oil to diesel exhaust particulates using geochemical markers

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SYNOPSIS

The identification of unique geochemical markers in certain lubricating oils enables an analysis of the solvent-soluble organic fraction (SOF) of diesel particulates to assign the contribution from lubricating oil on a semi-quantitative basis. The technique involves high resolution gas chromatography and the identification of the hopane series.

1 INTRODUCTION

Diesel engines produce particulates which comprise a carbon matrix associated with a solvent-soluble organic fraction (SOF). The emissions of particulates from diesel engines are already subject to legislative regulations in the United States and these will be significantly tightened over the coming years to reduce the total weight of particulates emitted per mile. The European Economic Community is also expected to enact legislation although initially this will be less severe than U.S. Federal limits.

Previous research has shown that engine lubricating oil can make a significant contribution to the total particulate mass in diesel exhaust (1). The magnitude of the lubricating oil contribution to the SOF of particulates needs to be determined in order to identify methods which might reduce the overall particulate mass.

Methods that have been used to assess the SOF have included Thermogravimetric Analysis (TGA) which involves the gradual heating of a particulate sample. The weight loss above a certain temperature is then used to represent the weight of lubricating oil present (2,3). This method, while adequate for the determination of SOF fails to distinguish accurately between the lubricating oil contribution, unburned fuel residue and hydrocarbons synthesised in the combustion chamber, all of which may fall in the same boiling point range.

More recently low resolution packed-column gas liquid chromatography has shown that under some circumstances there is an incomplete separation of fuel oil, residual hydrocarbons from lubricating oil and combustion/pyrolysis products (4,5). Unfortunately, individual peaks that are observed from a packed column chromatograph probably represent a large number of component hydrocarbons and the whole chromatogram is largely seen as a poorly

resolved envelope. In order to obtain an improvement in diagnosis, we have used high resolution gas chromatography (HRGC) on SOF samples in order to identify individual hydrocarbons or groups of very few hydrocarbon components.

In a lubricating oil (Rotella SX40) we have identified a series of unique geochemical markers, whose precursors were produced in ancient sediments by the activities of bacteria. Subsequent geological maturation processes have modified the series of geochemical precursors to form complex cyclic alkanes known as the hopanes. The complexity and uniqueness of the structures leaves no doubt that the hopanes found and separated from an SOF must have emanated from the lubricating oil used in the engine. Detection of hopanes has previously been reported in the context of tropospheric pollution studies (6,7).

The aim of this paper is to demonstrate the HRGC separation and identification of some of the hopanes in an SOF sample and to compare them with a series of standard mixes of fuel and lubricating oil at different concentrations to achieve a semiquantitative assessment of lubricating oil in the SOF of diesel particulates.

2 EXPERIMENTAL METHODS

The fuel used throughout the experiments was UK DERV, and lubricating oil was Rotella SX40. The gas chromatography carried out on fuel and fuel/lubricating oil mixtures used the fuel fraction with a boiling point greater than 325°C. Filter samples of particulates were obtained from a standard dilution tunnel using a current light-duty diesel engine installed in a car, and comparable diesel engine mounted on a test bed. The vehicle was operated at 2400 r/min and a load of 11.6 kW whilst the test bed engine conditions were 2100 r/min and 1 bar bmep (the corresponding SOF samples are numbered 1 & 2).

SOF samples were obtained by Soxhlet extraction (8 hr) of each filter with dichloromethane (DCM). Extracts were rotary-evaporated to dryness, transferred to preweighed vials with DCM, concentrated by blowdown with nitrogen and weighed prior to final dilution for GC analysis. All solvents were obtained as GPR quality from BDH Ltd. and were redistilled in an all-glass apparatus. GC analysis was undertaken on a Carlo Erba HRGC 4160 gas chromatograph equipped with a flame ionisation detector and cool on-column injector. A 30 m by 0.32 mm I.D. Durabond DB-5 fused silica capillary column (J & W. Scientific) was used. The GC conditions were: column temperature held at 40°C for 1 minute followed by a linear temperature programme of 10°C/minute to 300°C where it was held for a further 25 minutes. GC-MS analyses were performed on a Carlo Erba Mega HRGC 5160 linked with a Kratos MS25 mass spectrometer.

3 RESULTS AND DISCUSSION

The two SOF samples of diesel exhaust particulate were analysed by HRGC and their chromatograms are shown in Figs 1 and 2. Qualitative comparisons of the chromatograms for SOF with those for individual unused fuel (fraction > 325°C) (Fig 3) and lubricating oil (Fig 4) suggest that the SOF comprises a fuel residue in which some of the hydrocarbon components have been partially removed or altered and an oil residue which is little changed. Using GC retention times in between those for the bulk of the fuel components and those for the bulk of the lubricating oil components in the SOF, increased detector responses are found. These could result from pyrolysis products. Another feature of oil products, revealed by gas chromatographic analysis for both fuel and lubricating oil, is an unresolved 'hump' comprising many complex hydrocarbons. Superimposed on the humps are individual peaks which may represent single compounds or relatively few components and, overall, the chromatograms in Figs 1 and 2 reveal complex mixtures of unresolved components. However, there are some individual peaks with retention times and recognisable patterns similar to those found in unused oil or fuel.

The filter method of collection of particulate material from a dilution tunnel, from which the SOF is extracted, is inefficient for components having a boiling point below about 325°C.

At this stage of the work it is not possible to make quantitative assessments of the contribution of lubricating oil to the SOF from particulates emitted by the engine. However, a semi-quantitative estimate can be made by capillary gas-chromatographic analysis of the gross SOF extract. This can then be used by engineers wishing to take action to reduce the lubricating oil contribution to SOF.

The lubricating oil 'hump' has so far remained an unresolved envelope. Some identifications have been possible for peaks superimposed on the hump. A particularly useful technique has been the use of HRGC linked with a computerised

mass spectrometer (GC-MS) [by selecting specific mass fragments, e.g. $m/z = 191$, (Fig 5) and using the spectrometer as a gas chromatographic detector specifically showing only those peaks having a m/z mass fragment of 191]. This produces a "mass fragmentogram" (Fig 6) in which all components not having the specified mass fragment (191) are excluded. The prominent peaks having a mass fragment of 191 in lubricating oil were identified from their mass spectra as belonging to a series of triterpanes called hopanes (Fig 5) which occur in organic sediments and crude oils from which oil products are derived.

The hopane series was used to achieve a quantitative indication of the contribution of lubricating oil to the SOF. A number of measurements associated with the hopane peaks in the SOF could have been made (Figs 1 & 2) e.g. hopane peak heights above the hump or total area of hump and superimposed peaks after an arbitrarily chosen hopane peak or other reference point. These methods were not chosen because of the uncertainty of additional pyrolysis products adding to the lubricating oil response at high retention times in an unpredictable manner. Also, hopane peaks were often small, so that peak heights or areas could be associated with inaccuracies of small measurements. Given these difficulties and uncertainties regarding the relationship between hopane peak heights and total lubricating oil response we have chosen to measure distances from each hopane peak apex perpendicularly to the base line (zero response line of a temperature programme without injected material). These distances for the four hopane peaks (C29, C30, C31(S), C31(R)) are shown in Fig 7 and were compared with corresponding measurements obtained from a series of standard analyses for varying concentrations of lubricating oil analysed in an analogous manner to SOF samples (Fig 8). Before SOF samples can be compared with calibration data from lubricating oil standards (Table 1) the relevant peak heights in the sample must be checked for their statistical validity since there may be interference from the fuel which would preclude the use of a peak. To check the sample peak heights, ratios of peaks are compared.

For each concentration of the oil standard, the ratio of the various peak heights to the C31-R peak heights are calculated (Table 2). Thus for each peak used there is a set of ratios to the C31-R peak, one for each of the different concentrations. For each peak, 95% confidence limits are then calculated using these ratios (Table 3) and any SOF peak ratio outside these limits is ignored in determining the lubricating oil concentration. The remaining peak heights are then used to calculate the lubricating oil concentration by comparing them to the calibration line obtained by the method of least squares.

The following examples demonstrate the method. Samples 1 & 2 are SOF extracts from filters used to trap particulates from diesel exhaust in a dilution tunnel from which solutions of convenient concentrations (Table 6) for GC analysis were prepared. The relevant peak heights and corresponding peak ratios derived

from GC analysis (Figs 1 & 2) of these solutions are shown in Tables 4 and 5. For these two samples to be acceptable for use in quantification, the confidence limits in Table 3 apply. Thus for Sample 1, peak heights 'a' and 'b' are unacceptable, whilst for Sample 2 all the peaks are acceptable. By fitting the acceptable values into the calibration data from the oil standard a good estimation of the oil contributions in the two samples can be made, (Table 7).

From the data in Tables 6 and 7 the range of percentage contributions of lubricating oil to SOF are

Sample 1	38 - 41%
Sample 2	47 - 62%

4 CONCLUSIONS

It is possible to make a rapid, semi-quantitative assessment of the contribution of lubricating oil to the SOF of diesel engine particulates using geochemical markers. The technique which has been developed uses a simple analysis of the peak ratios of a small number of selected peaks in a gas chromatogram. For the representative samples used to illustrate the technique, between approximately one third and one half the SOF of the particulate may be assignable to a lubricating oil contribution.

The current method has limitations concerned with the interpretation of selected peaks only and further analysis of the unresolved components of the oil contribution is needed to determine the survival of other oil components. In the meantime, it offers an interesting new approach to the study of the contribution of lubricating oil to the SOF of the particulates. However, analyses of other lubricating oils has shown that the hopane series is not present in all of them to the same extent as it is in the SX40 oil.

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TABLES

Table 1 Measured peak heights (peak apex to base-line) of the hopanes for a variety of lubricating oil concentrations.

Oil concentration (mg/cm ³)	Peak heights (cm)			
	C ₂₉ (A)	C ₃₀ (B)	C ₃₁ -S(C)	C ₃₁ -R(D)
0.0	-	-	-	-
2.0	1.52	1.20	1.09	0.82
4.0	3.09	2.58	2.20	2.05
6.0	5.42	4.32	3.58	3.20
8.0	7.16	6.29	5.32	4.58
10.0	9.90	8.77	7.72	7.13

Table 2 The ratio of the hopane peak heights to the C₃₁-R hopane peak height for the lubricating oil standards

Oil concentration (mg/cm ³)	Peak height ratios		
	C ₂₉ (A)	C ₃₀ (B)	C ₃₁ -S(C)
2.0	1.85	1.46	1.33
4.0	1.51	1.26	1.07
6.0	1.69	1.35	1.12
8.0	1.56	1.37	1.16
10.0	1.39	1.23	1.08

Table 3 Statistical data for the peak ratios obtained from the standard solutions of lubricating oil.

Hopane peak	Mean	Standard Deviation	95% Confidence Limits
C ₂₉ (A)	1.60	0.18	1.60 ± 0.35
C ₃₀ (B)	1.33	0.09	1.33 ± 0.18
C ₃₁ -S(C)	1.15	0.11	1.15 ± 0.21
C ₃₁ -R(D)	-	-	-

Table 4 The measured peak heights of the hopanes for the sample S0F's.

Sample	Peak heights (cm)			
	C ₂₉ (A)	C ₃₀ (B)	C ₃₁ -S(C)	C ₃₁ -R(D)
1	3.38	2.37	1.73	1.48
2	6.08	4.60	3.32	3.39

Table 5 The ratio of the hopane peak heights to the C₃₁-R hopane peak height for the samples.

<u>Sample</u>	<u>Peak Ratios</u>		
	<u>C₂₉(A)</u>	<u>C₃₀(B)</u>	<u>C₃₁-S(C)</u>
1	2.28	1.60	1.17
2	1.79	1.36	0.98

Table 6 Weights and dilutions of SOF (for GC analysis) used in calculations of lubricating oil contributions.

<u>Samples</u>	<u>Weights of</u>	<u>Dilutions for</u>
	<u>SOF extracted</u>	<u>GC analysis</u>
	(mg)	(mg/cm ³)
1	11.7	7.8
2	3.2	10.7

Table 7 Calculated lubricating oil weights for total SOF (from data in Tables 1, 4 and 6).

<u>Sample</u>	<u>Total lubricating oil weights (mg) in SOF</u> <u>from peak height data</u>			
	<u>C₂₉(A)</u>	<u>C₃₀(B)</u>	<u>C₃₁-S(C)</u>	<u>C₃₁-R(D)</u>
1	* 5.78	*4.97	4.42	4.79
2	1.97	1.75	1.50	1.71

* These values are outside the 95% confidence limits set out in Table 3 and are therefore excluded from the quoted range of lubricating oil contributions to SOF.

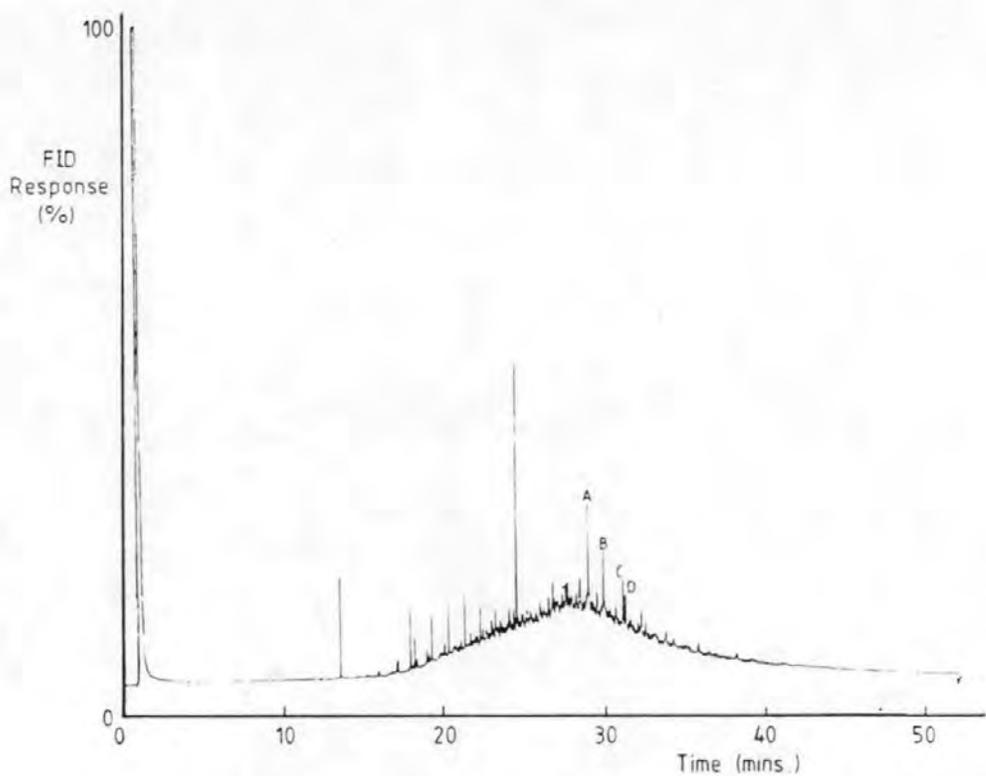


Fig 1 Gas chromatogram of the solvent-soluble organic fraction (SOF) from sample 1, a light duty diesel engine showing the hopane peaks
 A = C₂₉ - hopane; B = C₃₀ - hopane; C = C₃₁ - S-hopane;
 D = C₃₁ - R-hopane (S and R are stereoisomeric forms of the same structure)

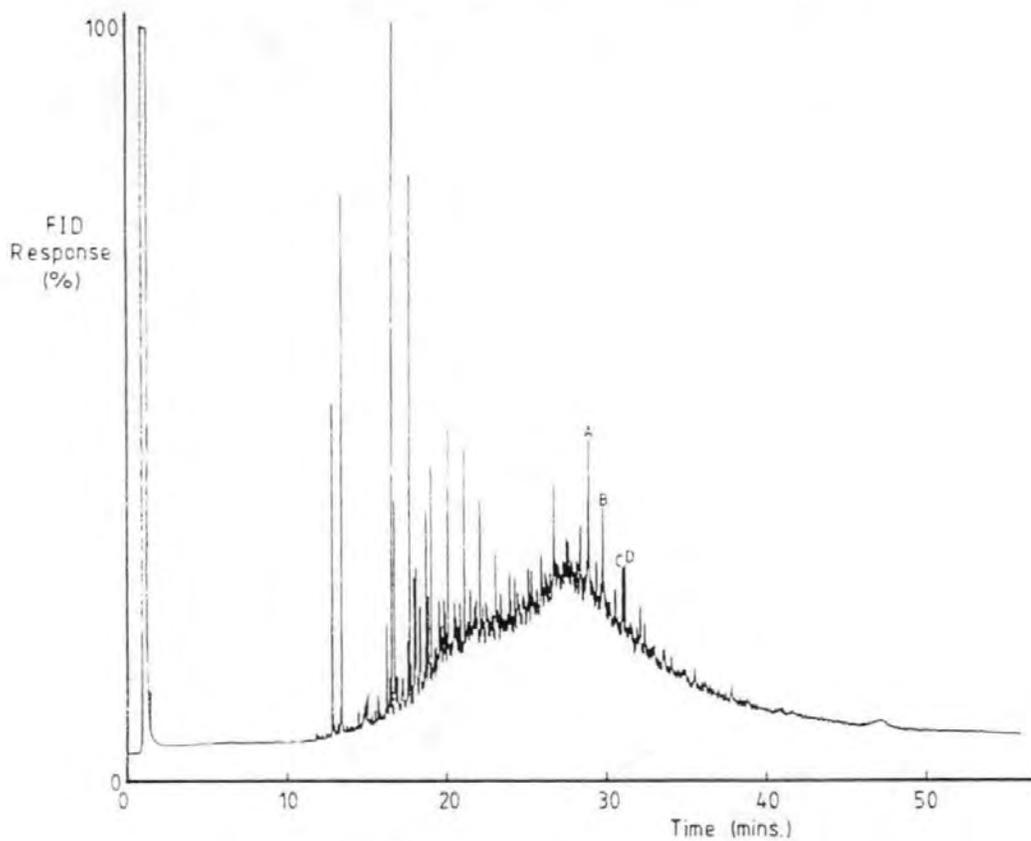


Fig 2 Gas chromatogram of the SOF from sample 2, a light duty diesel engine, showing the hopane peaks
 A = C₂₉ - hopane; B = C₃₀ - hopane; C = C₃₁ - S-hopane;
 D = C₃₁ - R-hopane

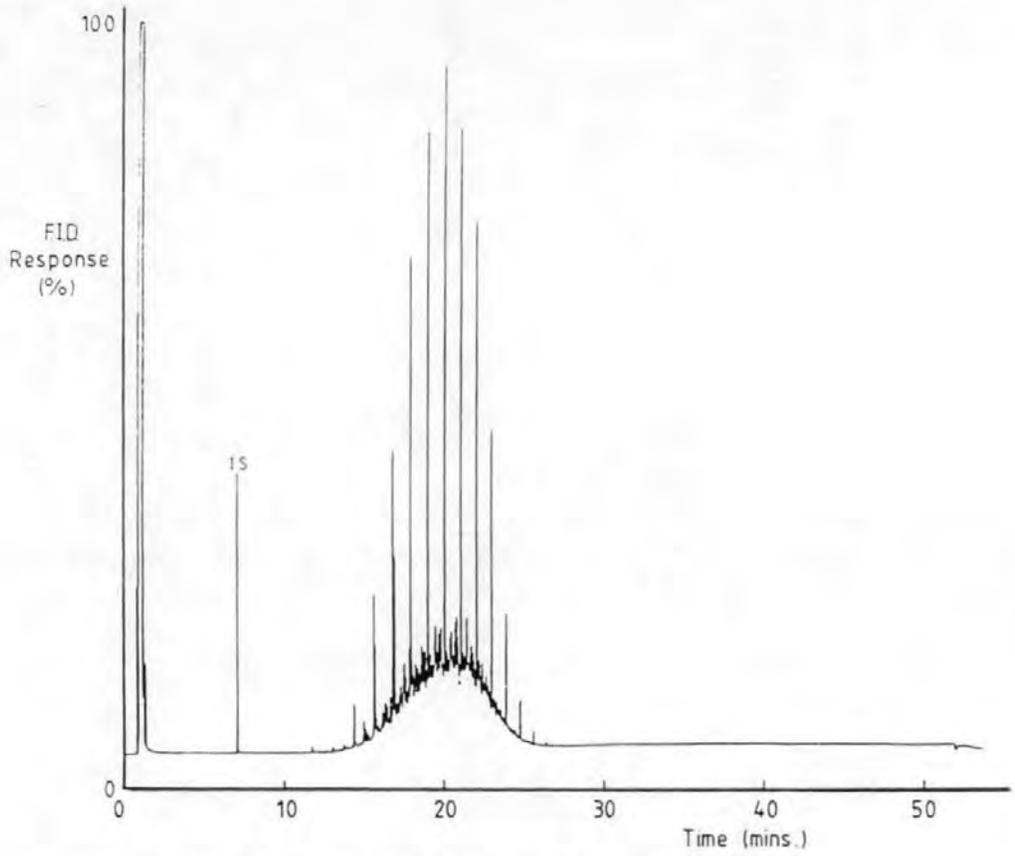


Fig 3 Gas chromatogram of the portion of fuel with a boiling point range > 325 °C. (IS = internal standard)

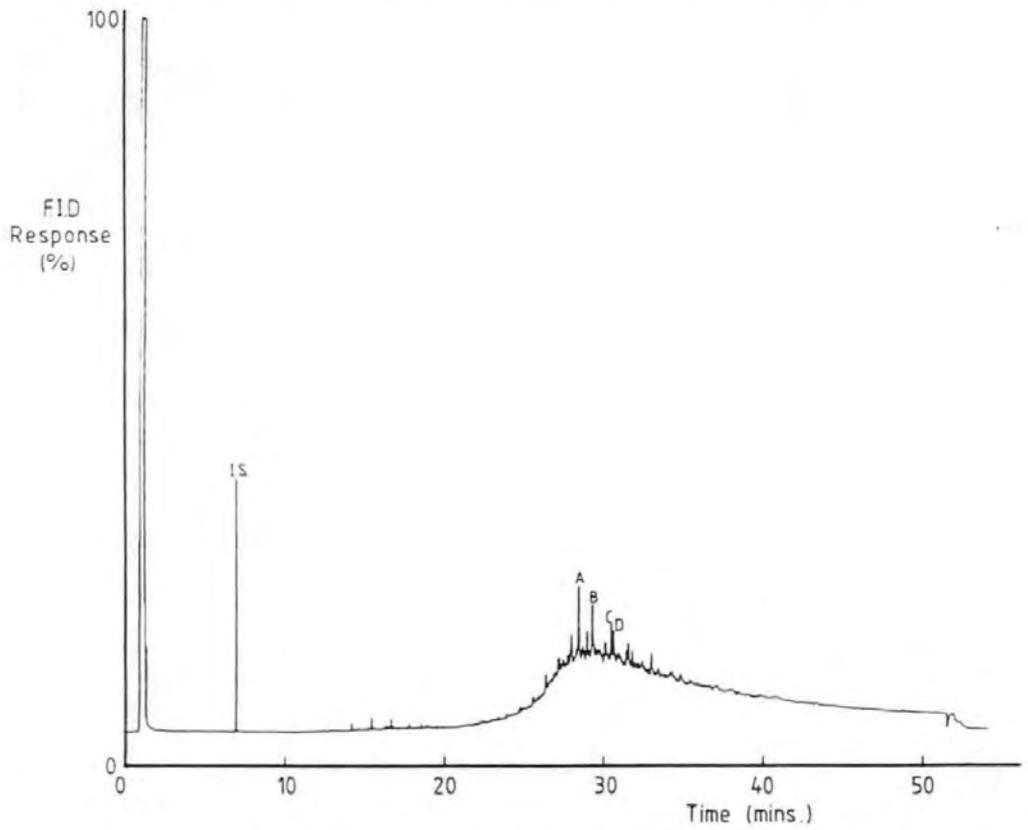


Fig 4 Gas chromatogram of the lubricating oil (SX40) showing the hopane peaks. (IS = internal standard)
 A = C₂₉ - hopane; B = C₃₀ - hopane; C = C₃₁ - S-hopane;
 D = C₃₁ - R-hopane

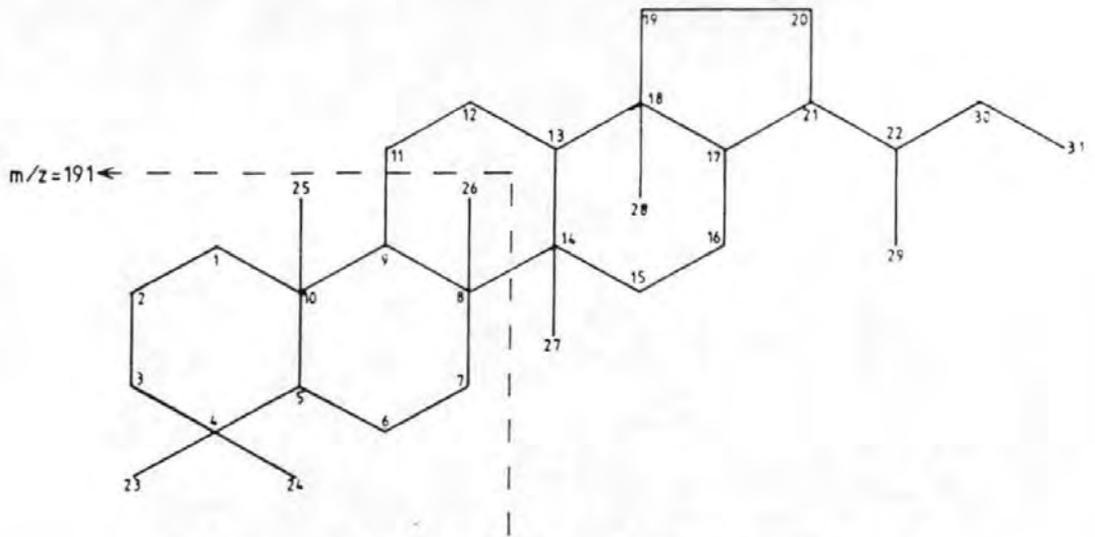


Fig 5 Diagram showing the general structure of a C₃₁ - hopane with the mass fragment m/z = 191 indicated

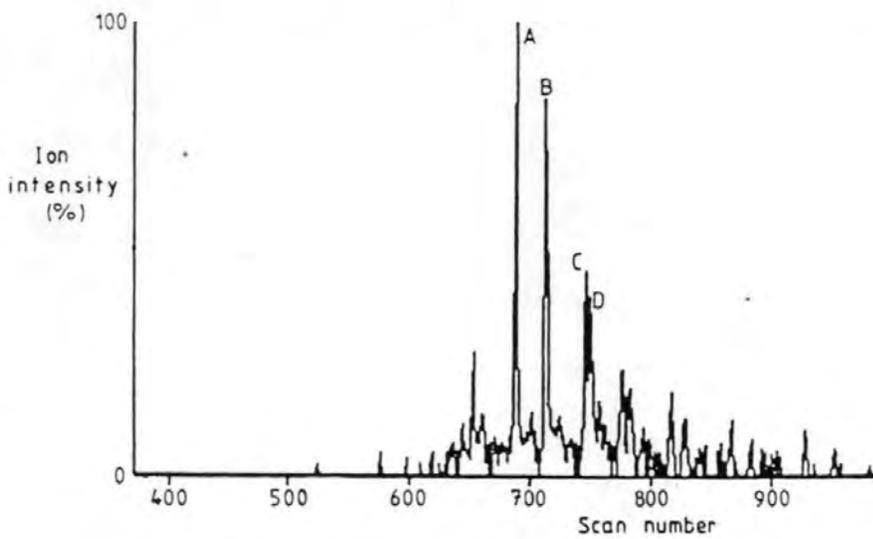


Fig 6 Mass fragmentogram for m/z = 191 of the SOF from sample 1, a light duty diesel engine, showing the hopane peaks
 A = C₂₉ - hopane; B = C₃₀ - hopane; C = C₃₁ - S-hopane;
 D = C₃₁ - R-hopane

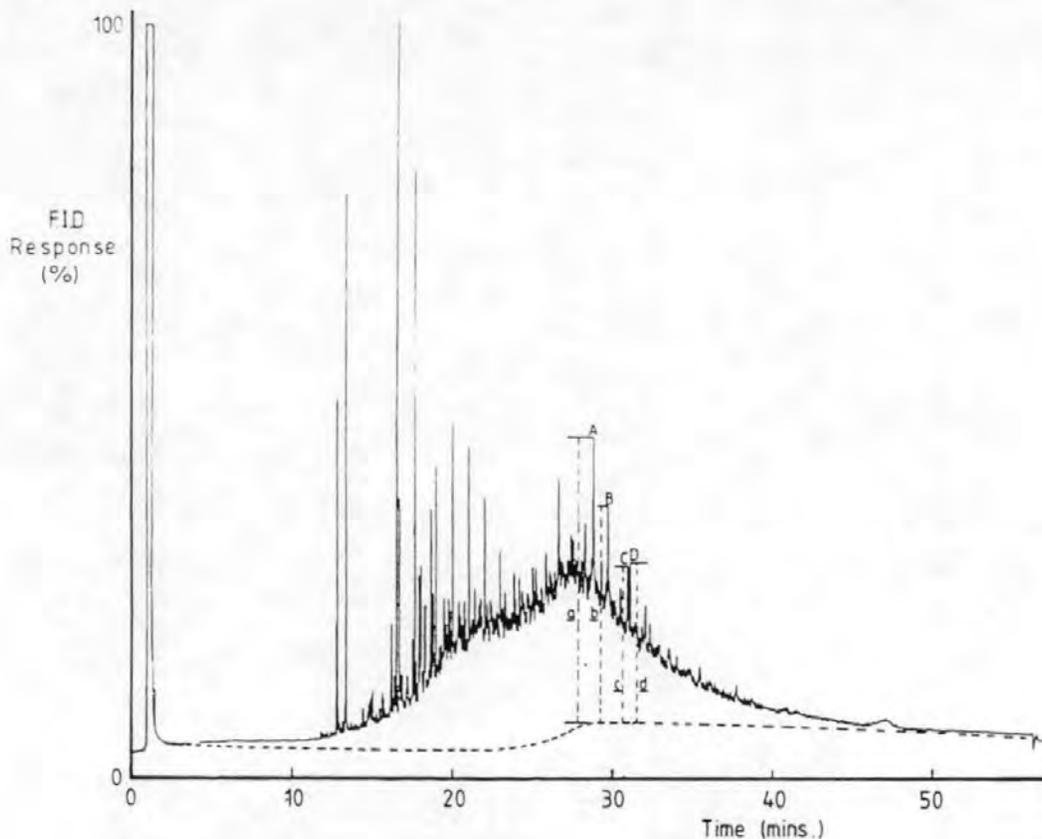


Fig 7 Gas chromatogram of the SOF, sample 2, from a light duty diesel engine, with the gas chromatogram for solvent only injection (dotted line) superimposed to show how the heights of the hopane peaks a, b, c and d were calculated
 A = C₂₉ - hopane; B = C₃₀ - hopane; C = C₃₁ - S-hopane;
 D = C₃₁ - R-hopane

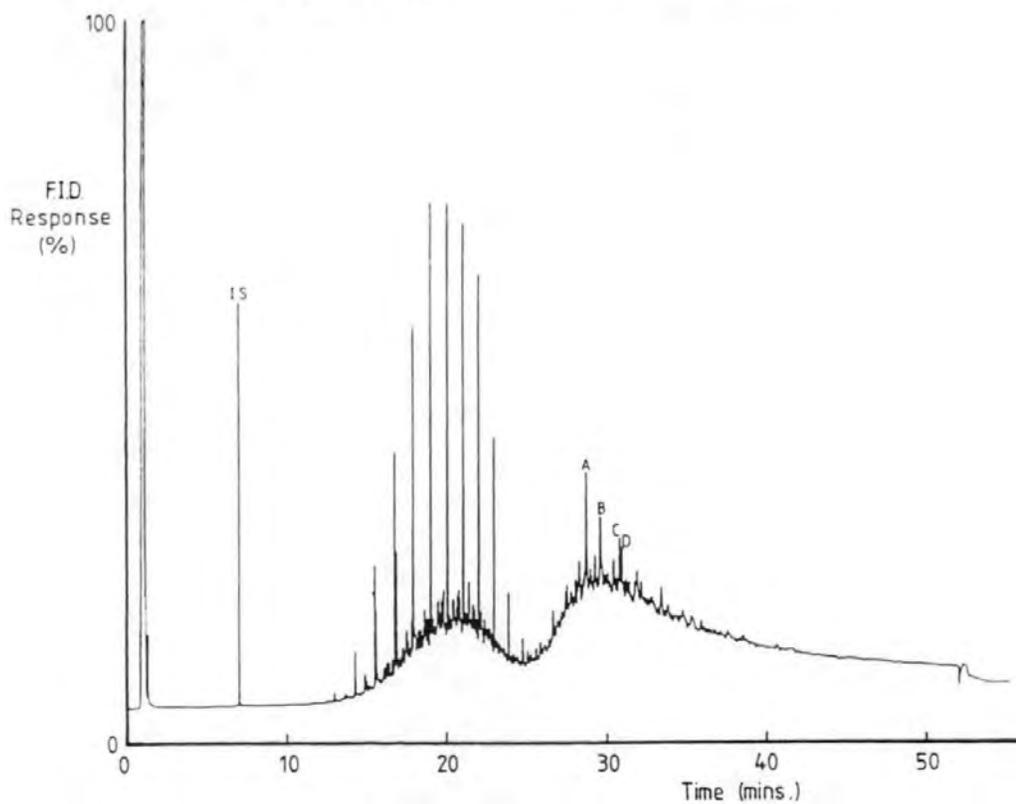


Fig 8 Gas chromatogram of a standard mix of >325 °C boiling point fuel and lubricating oil (20/80 w/w)

The development of a novel exhaust sampling technique with particular relevance to polycyclic aromatic hydrocarbons

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SYNOPSIS

A novel sampling system has been developed for use with diesel engine exhausts. Close to the exhaust valve there is a scrubbing tower arrangement which uses a solvent to capture hydrocarbons. This avoids adsorption of hydrocarbons onto particulates and many possible modes of artefact formation. The development of the system and some initial trials are described, together with the gas chromatographic analysis of samples.

1 INTRODUCTION

Gases entering the atmosphere from diesel engine exhausts contain significant amounts of particulate carbon associated with hydrocarbons and more polar organic compounds. Vapour emissions condense and then adsorb onto highly active particulate carbon in the cooler parts of the exhaust system. Exhaust products which pass out of the engine cylinder may undergo subsequent chemical modification because of heterogeneous chemical reactions on particle surfaces. This demonstrates the need for a rapid sampling technique situated close to the exhaust port.

This paper reports a novel system which aims to sample organic compounds in the exhaust stream immediately on leaving the engine and prior to adsorption onto carbon particles. Sampling is achieved by using a solvent mixture which rapidly scavenges Polycyclic Aromatic Hydrocarbons (PAH) from the exhaust stream at high temperature. The resulting solution of PAH is removed immediately from the gas stream so as to avoid the production of increased amounts of compounds, such as nitro-PAH, suspected to be produced as artefacts in filter collection techniques. (Risby & Lestz (1)).

The requirement for an efficient sampling system is part of a wider programme designed to investigate the sources of polycyclic aromatic compounds (PAC) emanating from a diesel engine. Specifically, ^{14}C -labelled PAH will be used to 'spike' fuel or lubricating oil to allow elucidation of sources of PAC in the exhaust and of mechanisms of survival or chemical transformations accompanying the combustion processes. The sampling system must collect the total exhaust flow in order that a minimum of ^{14}C -PAH is used in any experiment.

2 REVIEW OF EXISTING METHODS

Filtration of the exhaust is the most widely utilised method of collecting diesel particulates and their associated organic compounds. The most common method of filtration sampling employed today is that recommended by the United States Environmental Protection Agency (EPA). The EPA method involves a dilution tunnel (2) and this method of filtration aims to produce a sample which is similar to that found in the immediate atmospheric environment. The process of dilution allows condensation of some hydrocarbons onto the particulate matter, whilst other hydrocarbons pass through the filter without condensing. This makes the determination of the total hydrocarbons emitted more complex as a result of their presence in both vapour and particulate form. Filtering close to the engine, without dilution, would exclude many volatile compounds. The alternative of cooling the filter and locating it close to the engine exhaust valve also poses severe problems.

Resin traps have the ability to trap all hydrocarbon material and offer an alternative to the use of filters for sampling the diesel engine exhaust. The temperature of the exhaust leaving the engine is sufficient to cause degradation of the resin, which will result in less efficient hydrocarbon collection and the possibility of artefact formation as a result of reactions between the degraded products and the exhaust hydrocarbons.

Stenberg et al. (3) described a cryogradient technique which was used to sample a portion of the exhaust. The system utilised three condensers through which the exhaust flowed consecutively. The condensers were arranged to allow the temperature to be lower in each successive condenser. The three coolants used were (a) ice/water, (b) solid carbon dioxide/ethanol and (c) liquid nitrogen. This method allowed a simple separation to be

accomplished during the sampling procedure. The most volatile components were collected by the liquid nitrogen condenser whilst the least volatile were collected by the ice/water condenser. There could be artefact formation in the ice/water cooled condenser, because the collected material is continuously in the path of the exhaust gas, as in the filter system.

Another method involving the condensation of the exhaust gas hydrocarbons was that of Grimmer et al. (4), who used a condenser followed by a filter. The system was designed to handle the total exhaust of the engine. Material collected by this system was exposed to the exhaust gas flow throughout the sampling time and this increased the risk of producing artefacts. An improved version was reported by Kraft and Lies (5) whose system produced three different types of sample - (a) the condensed material collected in a flask, (b) the material which was washed off the condenser with acetone at the end of sampling and (c) the material collected by filtration beyond the condenser. As with the Grimmer system, the majority of the sample was continuously in the path of the exhaust gas exposing the collected sample to the risk of artefact-forming reactions.

3 A NEW SYSTEM

A novel concept for sampling close to the exhaust valve has been developed in the form of a vertical, counter current mass transfer device. Exhaust products are fed directly from the exhaust valve through a transfer pipe of minimum length into the base of the tower and as they pass upwards through the tower, they are scrubbed by a downwards flow of solvent. This removes most hydrocarbons in the vapour phase before there is an opportunity for condensation onto particles. The solution of organic compounds flows out from the base of the tower and does not remain in the exhaust gas stream. This minimises the opportunity for artefact formation and also permits a mass balance to be carried out. The exhaust gases, stripped of hydrocarbons, are expelled from the top of the tower. The system, with acronym TESSA (Total Exhaust Solvent Scrubbing Apparatus) was designed to have the capacity to sample the total exhaust from the Ricardo E6 test engine used in its development.

The overall design concept for the tower is shown in Fig 1. Stainless steel was chosen for the main construction material, recognising its relative inertness under the sampling conditions. The large surface area of interaction between the solvent and the exhaust gas, which was required to ensure maximum removal of the hydrocarbons, was provided by graded glass tubing, in order to reduce chances of surface catalysed artefact formation and ensure insignificant back pressure.

Following an investigation of various alternative solvents, including hexane and propan-2-ol, the solvent chosen for stripping the hydrocarbon and more polar compounds from the exhaust gases was a mixture of dichloromethane (DCM) and methanol. This solvent mixture proved to be suitable for the removal of exhaust compounds having a wide range of polarities. The solvent mixture has

sufficient miscibility with water over a limited range of composition. Thus a single phase is still maintained in spite of the inevitable presence of water from combustion in the tower during sampling. Subsequent addition of excess water to the collected sample effects the separation into two phases, with hydrocarbons concentrated in the DCM phase. The low boiling point of DCM allowed the efficient recovery, using rotary evaporation under reduced pressure, of the Tower Extracted Sample (TES). The DCM/methanol mixture has the added advantage of low flammability.

4 ASSESSMENT OF THE CAPABILITIES OF THE NEW SAMPLING SYSTEM

During the operation of TESSA, the solvent mixture was used to scrub the exhaust gas of particulate carbon and organic compounds. The two liquid phases were separated by an excess of distilled water. The particulate matter agglomerated and was removed by a simple filtering process for further analysis. The TES was isolated from the solvent and typically a 75 mg sample was produced from a 3 minute sampling period.

A series of experiments was performed to assess the efficiency of collection of organic compounds. The filtered particulate material was Soxhlet extracted in order to assess the extent of adsorption of organic compounds onto the particulates. The total weight of each extract was less than 1% of the TES.

Losses from the top of the tower were assessed by sampling a portion of the tower effluent with a liquid nitrogen trap. The weight of extract indicated that the total losses during the sampling period were less than 8% of the TES. The tower was capable of accepting the total exhaust from the engine at a temperature of at least 350°C. At exit from the tower, the temperatures of the gases were in the range 5 - 20°C.

The possibility of artefact formation (6), particularly the production of chlorinated and nitrated compounds, is currently being investigated using electron capture- and nitrogen-specific detectors (ECD & NPD) in a high resolution capillary gas chromatographic system. The presence of acidic gases in the engine exhaust, as a result of the formation of nitrogen and sulphur oxides, also needed specific investigation and pH measurements have been made. However, the aqueous phase removes the acidic species from contact with the TES. Further forms of buffering are still being considered.

The TES isolated from TESSA runs was fractionated into aliphatic and aromatic fractions. These were compared with corresponding fractions isolated from aliquots of fuel and lubricating oil used in the engine. Peak ratio measurements within each chromatographic trace enabled preliminary matching between corresponding fractions and enabled conclusions to be drawn regarding the sources of hydrocarbon in TES (see Section 6).

The engine used for all the tests was a Ricardo E6/T with Comet MkV IDI Head and a compression ratio of 22:1. Before sampling, the engine was conditioned by running at 3000 rpm and 7.6 kW for one hour. The engine cooling water was maintained at 80°C. A period of 15 minutes at the test conditions, 2000 rpm and 3.4 kW, was allowed for equilibration.

The fuel used was BP gas oil (S.G. 0.84) and the lubricating oil was Shell Rimula X 15/40.

Before each sample was taken, the tower was washed with solvent and the inside surface of the tower was left wetted with the solvent. During the collection of the sample, the solvent mixture (DCM: Methanol, 50:50 v/v) passed continuously through the tower and 2 litres were used during the sampling interval of 3 minutes. The water cooling supply to the tower (in the jacket and cooling coils) was maintained at 5°C using a chiller. After the sample had been collected and the exhaust gas was no longer passing, the tower was washed with a further portion of solvent.

The sample was then filtered under reduced pressure using Whatman GF/F filters. The DCM phase which contained the hydrocarbons was separated and the aqueous layer was washed thoroughly with DCM. The washings and hydrocarbon-containing phase were combined and reduced in volume by rotary evaporation to 100 cm³. This concentrate was then dried with anhydrous sodium sulphate before further concentration to 2 cm³. Final concentration was achieved blowing a stream of dry nitrogen gas over the surface of the sample. Fractionation of the sample was achieved using a silica gel column. The aliphatics eluted with hexane and the aromatics eluted with DCM.

High resolution gas chromatography (HRGC) was carried out on a Carlo Erba HRGC 5360 equipped with a flame ionisation detector (FID) and fitted with a Durabond DB-5, 30 metre, fused silica capillary column (25 µm film thickness and 0.32 mm ID). The column oven programme for the analysis was as follows: 50°C for 5 minutes, 50 - 300°C at 10°C/min and 300°C for 25 minutes. Cold on-column injection of the sample was employed and a detector temperature of 320°C was maintained.

A capability for the introduction of spikes into the fuel has been provided in two ways. Firstly, an auxiliary tank is available with an injection point immediately before the filter for the pump. For radiolabel work, however, the bowl of the filter unit may be replaced by a low volume septum injection point. This allows the injection of a small volume of fuel immediately before the fuel injection pump using a syringe. ¹⁴C-labelled hydrocarbons are to be introduced by this method.

The TESSA system was used to produce a filtered sample of exhaust hydrocarbons (TES) which was separated into aliphatic and aromatic fractions. These were analysed by HRGC and the chromatograms (Figs 2 & 3) reveal the presence of both unburnt fuel and lubricating oil components when compared with the appropriate chromatograms of fuel and lubricating oil standards (Figs 4, 5, 6 & 7). The presence of additional compounds which cannot be assigned to either of these sources indicates the presence of combustion pyrolysis products.

An interesting comparison can be made between the percentages by weight found in the aliphatic fractions compared to the aromatic fractions for the fuel, lubricating oil and TES, Table 1. The distribution in the TES is very similar to that of the fuel. Lubricating oil is almost entirely represented by the aliphatic fraction. Closer inspection of the aliphatic fractions of fuel and TES (Figs 2 & 4) shows a significant trend for the survival percentage of the n-alkane series in the TES (Fig 8). It can be seen that the ratios of the higher n-alkanes relative to n-C₂₂ in both fuel and sample are very similar, Table 2, indicating that these n-alkanes in the TES represent unburnt fractions of the fuel. Increasing molecular weight reduces combustion efficiency of the hydrocarbons. Differences in molecular structure also have an influence on combustibility, so that branched and cyclic aliphatics have a different stability compared to n-alkanes.

By expanding the attenuation of the later retention times for the aliphatic fraction of TES, Fig 9, the presence of lubricating oil can be more clearly seen when compared to the standard (Fig 6). With the temperature programme utilised for these analyses, the response factor for the fuel per unit mass is far greater than for that of the lubricating oil. Thus a significant contribution from the lubricating oil to the total weight of the TES is indicated from the chromatogram in Fig 4.

When the aromatic fractions are studied a contribution of unburnt fuel to the TES similar to that found in the aliphatic fraction is indicated (Figs 3 & 5). The aromatic fraction of lubricating oil is minimal, Fig 7. Specifically, the presence of methylnaphthalenes and dimethylnaphthalenes along with methylphenanthrenes have been compared between aromatic fractions of fuel and TES. Aromatic hydrocarbon classes were identified from standards and from work reported by Rowland et al. (7). Peak height ratios of the PAH within isomeric groups relative to the most prominent member of the group, and their survival percentages are shown in Table 3.

There is a scarcity of data available in the literature relating to survival percentage of PAH in diesel engine combustion. Williams et al. (8), have surveyed the survival percentage for many PAH, albeit with a D.I. diesel engine. Comparison of the data show a higher percentage surviving for the lower molecular weight PAH in results with the I.D.I. engine here reported,

although a closer agreement is observed for medium and higher molecular weight PAH. Whilst the differences between engines used by the two research programmes has some bearing on the matter, more significant is likely to be the differences between the sampling systems employed - Williams et al. used a filter system. The TESSA system has shown itself to be particularly efficient at sampling the low molecular weight compounds typical of the fuel derived component in diesel exhaust emissions.

A wider programme is proceeding to investigate closer differences between the TESSA system and conventional filtration systems applied to exhaust samples from modern D.I. diesel engines.

For a more direct comparison with EPA filtration samples collected after cooling and dilution of the engine effluent, we intend to sample at positions down a dilution tunnel or at the end of a tailpipe using TESSA. This method will collect both particulate adsorbed hydrocarbons and vapour borne hydrocarbons from the gas stream. Exhaustive extraction of the particulate TESSA fraction would be necessary followed by combination with TES soluble material to produce a fraction that could be directly compared with EPA-SOF samples.

Differences between TES and SOF samples taken from the same position of a dilution tunnel or tailpipe could give an accurate indication of artefacts formed solely as a result of sample collection rather than resulting from the modification of compounds during adsorption to particulates and passage down the dilution tunnel/tailpipe.

CONCLUSIONS

- A novel exhaust sampling technique has been developed to the stage where it has proved to be advantageous compared to conventional filtration in sampling low molecular weight compounds, typical of fuel derived compounds in diesel engine exhaust emissions.
- The technique shows considerable promise for use in spiking experiments, in which the maximum collection of exhaust products is necessary.
- The technique offers considerable potential in the process of minimising artefact formation, as a result of the rapid quenching and subsequent removal of the sample from the exhaust gas stream.

ACKNOWLEDGEMENTS

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TABLES

Table 1 Aliphatic and aromatic content of fuel, lubricating oil and TES

Source	Aliphatic (% by wt)	Aromatic (% by wt)
Fuel	59.7	40.2
Lubricating oil	76.4	6.6
TES	34.6	25.7

Table 2 Table to show the abundance of certain hydrocarbons relative to n-C₂₂H₄₆ in diesel fuel and TES aliphatic fraction (from Figs 4 & 11).

Hydrocarbon	Ratio to n-C ₂₂ peak	
	Fuel	TES
n-C ₁₂	1.19	-
n-C ₁₃	1.76	0.07
n-C ₁₄	2.73	0.25
n-C ₁₅	3.30	1.12
n-C ₁₆	3.30	1.88
n-C ₁₇	3.27	2.31
Pristane (branched)	1.67	1.40
n-C ₁₈	2.64	1.97
Phytane (branched)	1.24	1.15
n-C ₁₉	2.22	1.85
n-C ₂₀	1.86	1.50
n-C ₂₁	1.39	1.28
n-C ₂₂	1.00	1.00

Table 3 Table to show the relative abundance of certain PAH and their % surviving.

PAH	Relative abundance compared with most abundant in isomeric group		% Surviving	Average of group
	Fuel	TES		
2-methylnaphthalene	1.00	1.00	0.097	0.106
1-methylnaphthalene	0.63	0.76	0.116	
2,6- +2,7-dimethylnaphthalenes	0.68	0.64	0.073	0.078
1,3- +1,7-dimethylnaphthalenes	1.00	1.00	0.078	
1,6-dimethylnaphthalene	0.75	0.74	0.077	
2,3- +1,4-dimethylnaphthalenes	0.38	0.41	0.084	
3-methylphenanthrene	0.81	0.88	0.102	0.102
2-methylphenanthrene	0.94	0.98	0.098	
9-methylphenanthrene	1.00	1.00	0.094	
1-methylphenanthrene	0.77	0.93	0.114	

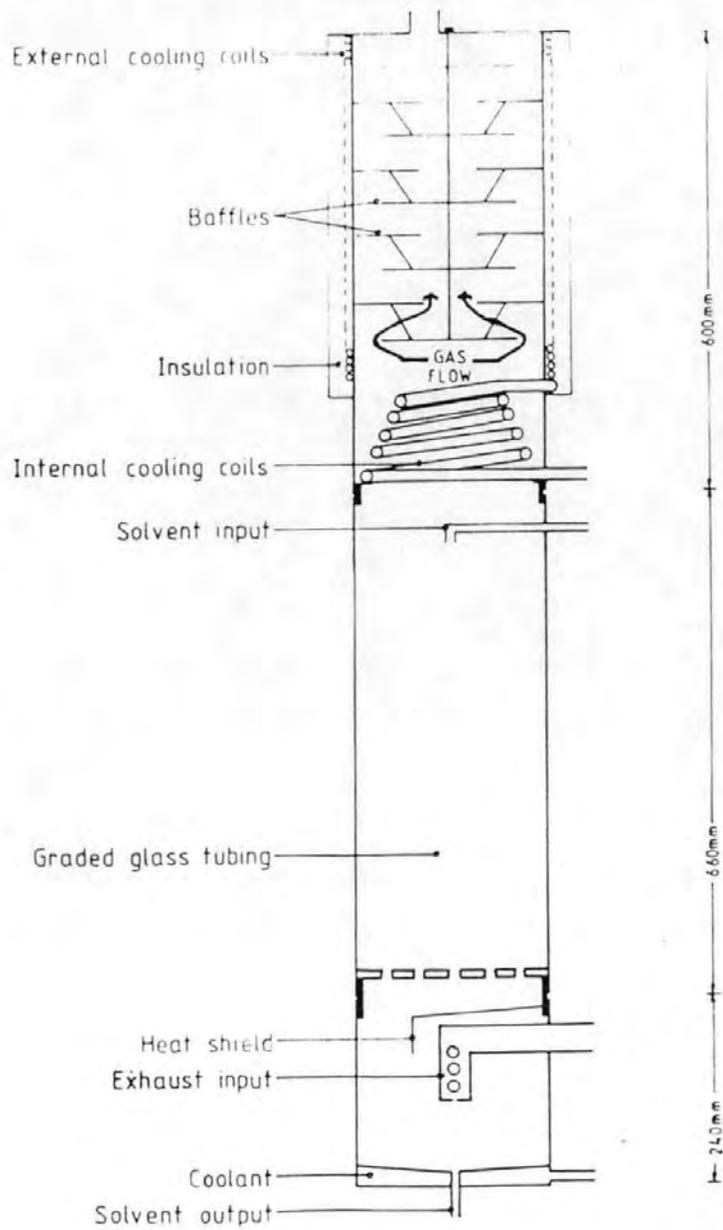


Fig 1 Schematic representation of total exhaust solvent scrubbing apparatus (TESSA)

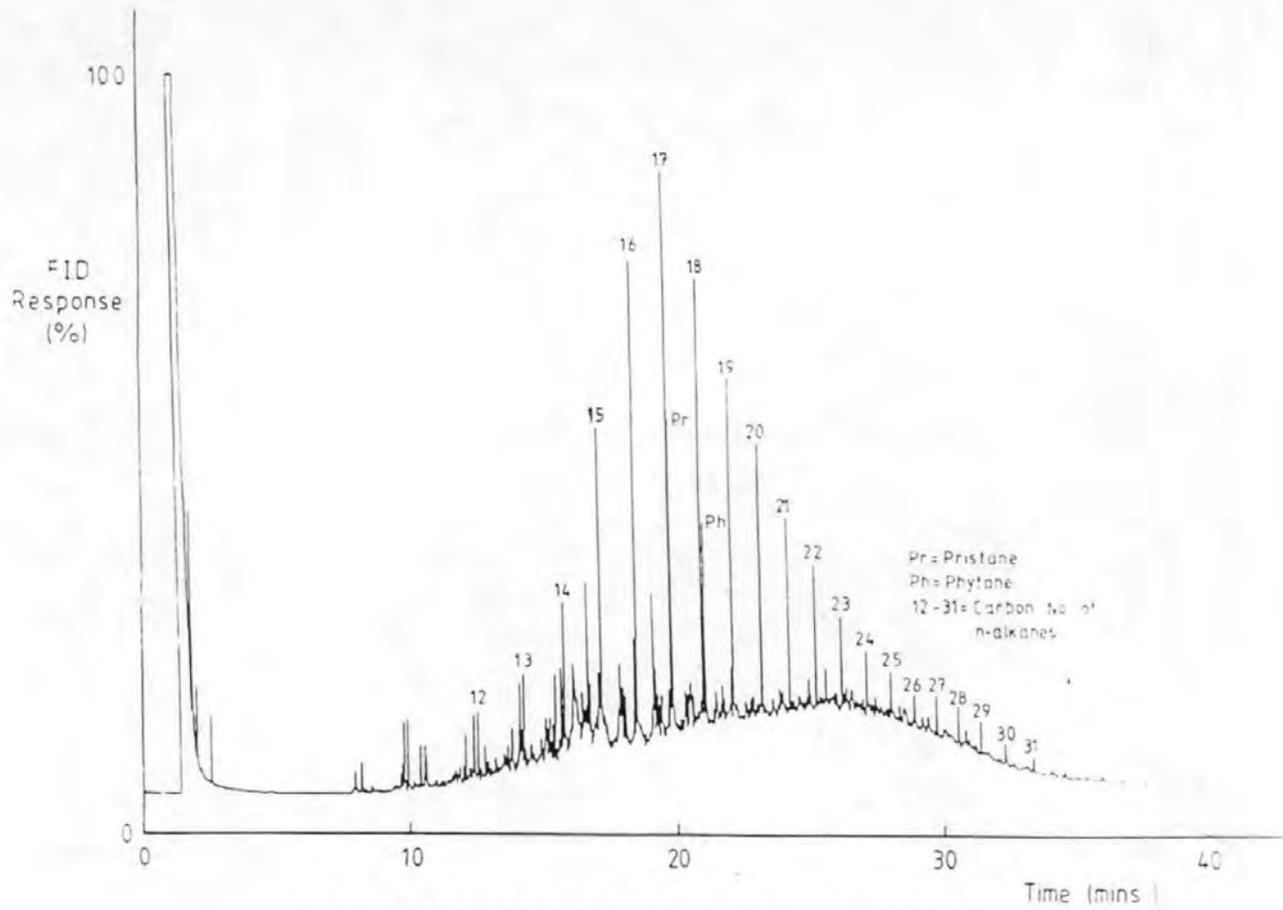


Fig 2 Gas chromatogram of the aliphatic fraction of a typical tower extracted sample (TES)

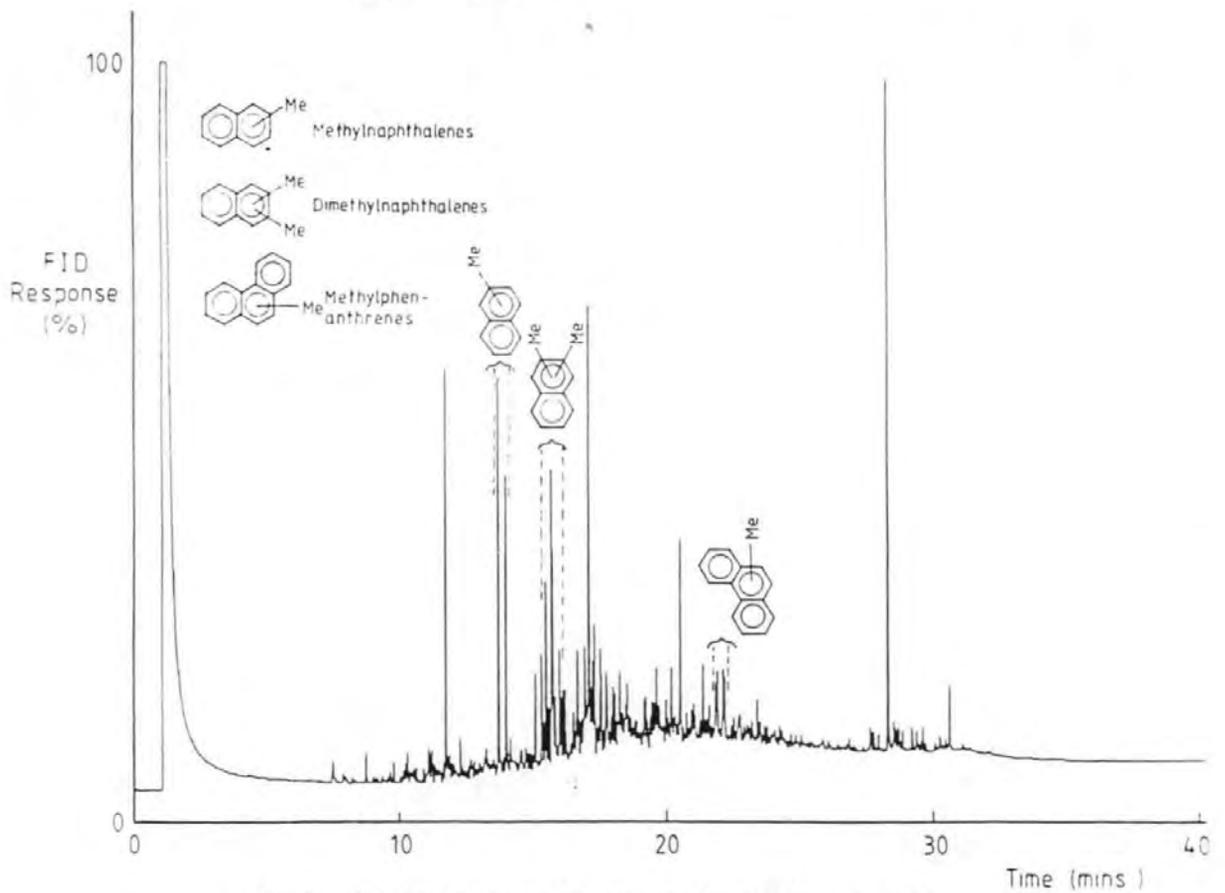


Fig 3 Gas chromatogram of the aromatic fraction of a typical TES

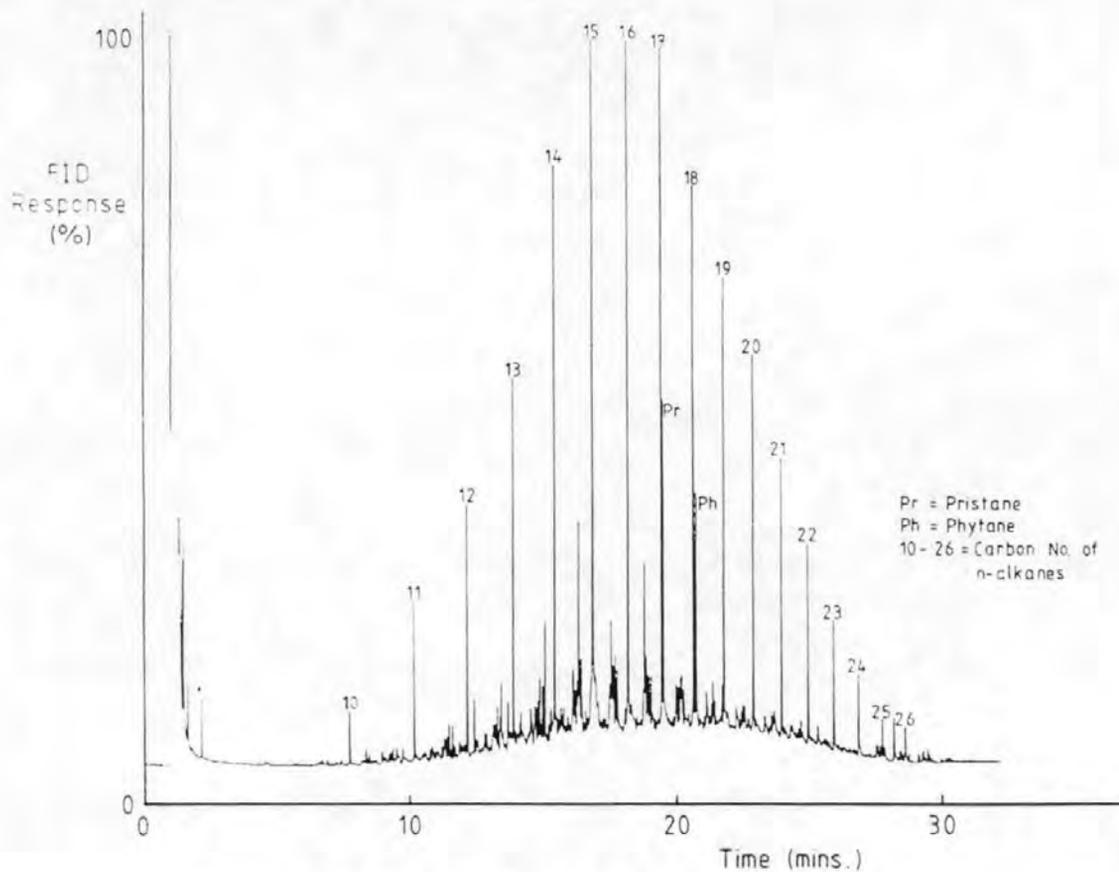


Fig 4 Gas chromatogram of the aliphatic fraction of the diesel fuel used

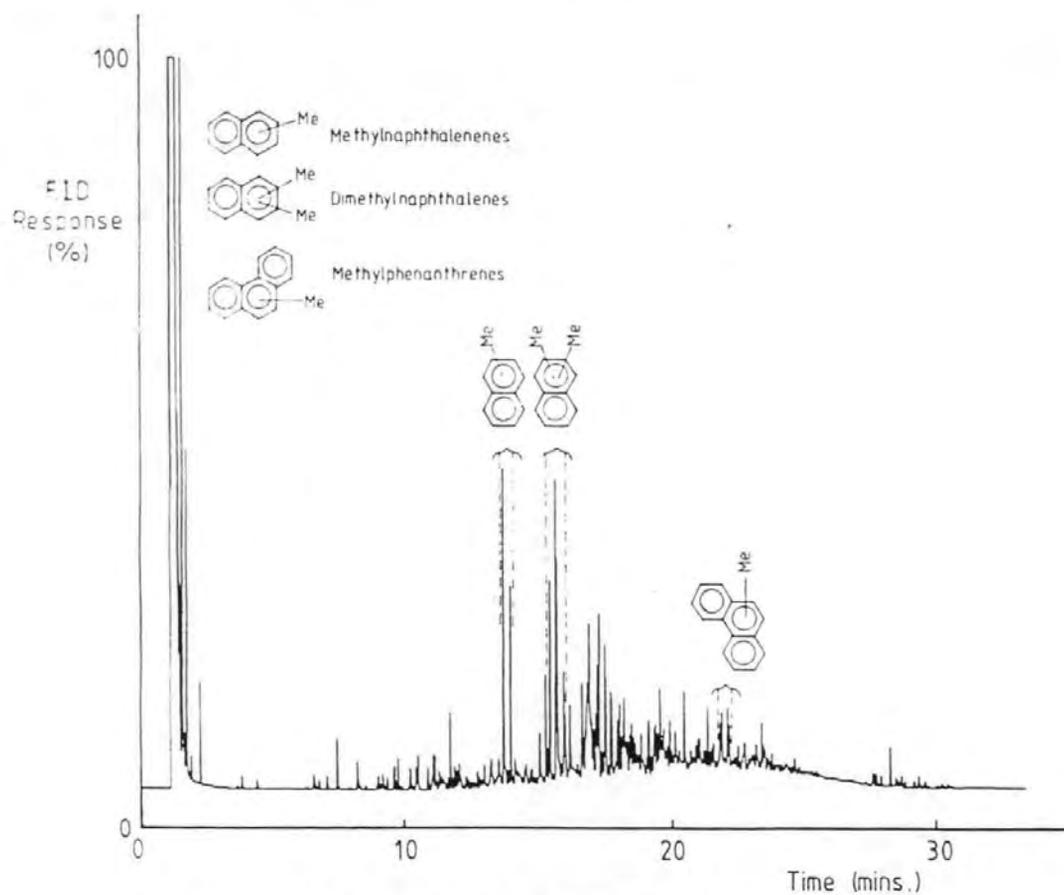


Fig 5 Gas chromatogram of the aromatic fraction of the diesel fuel used

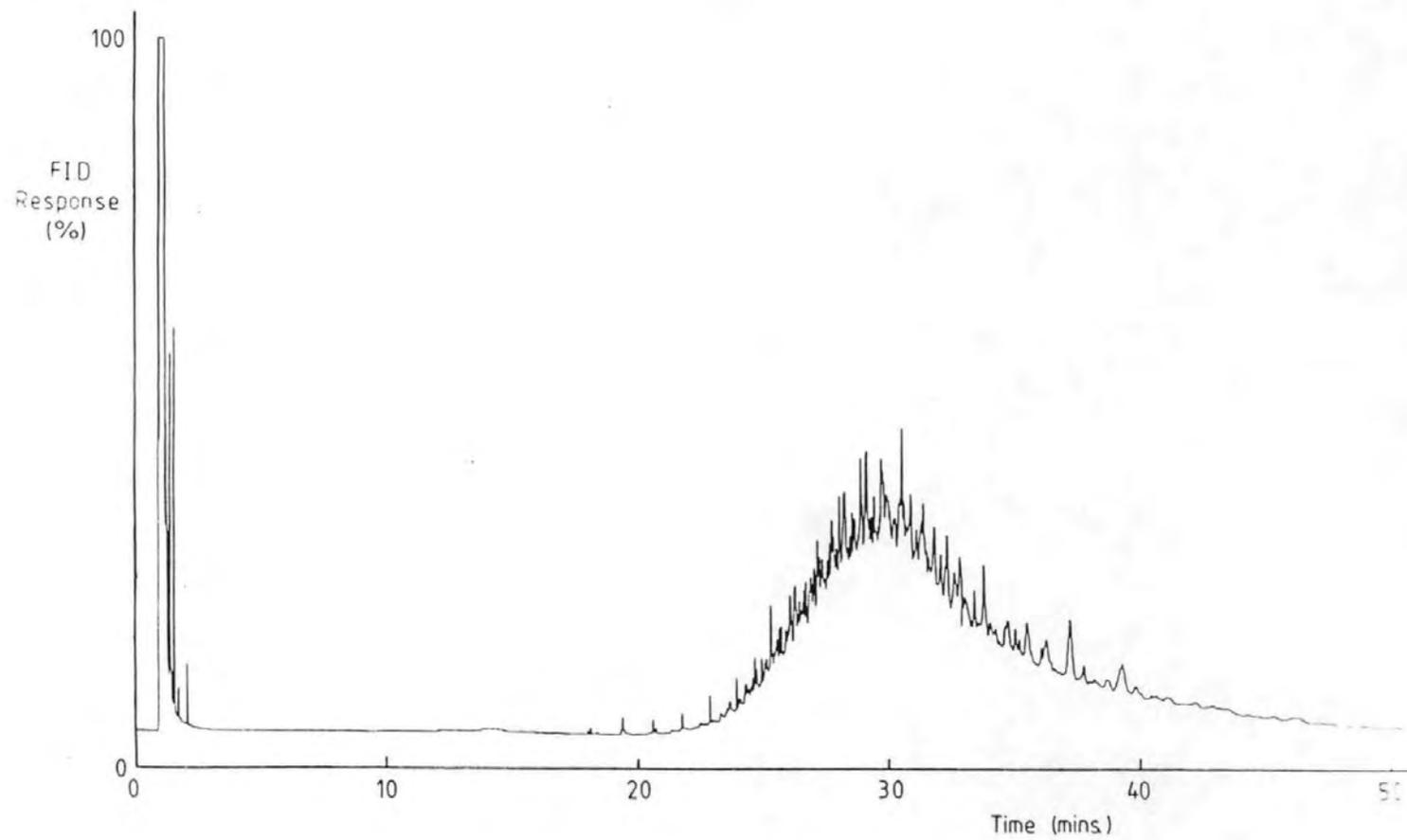


Fig 6 Gas chromatogram of the aliphatic fraction of the lubricating oil used

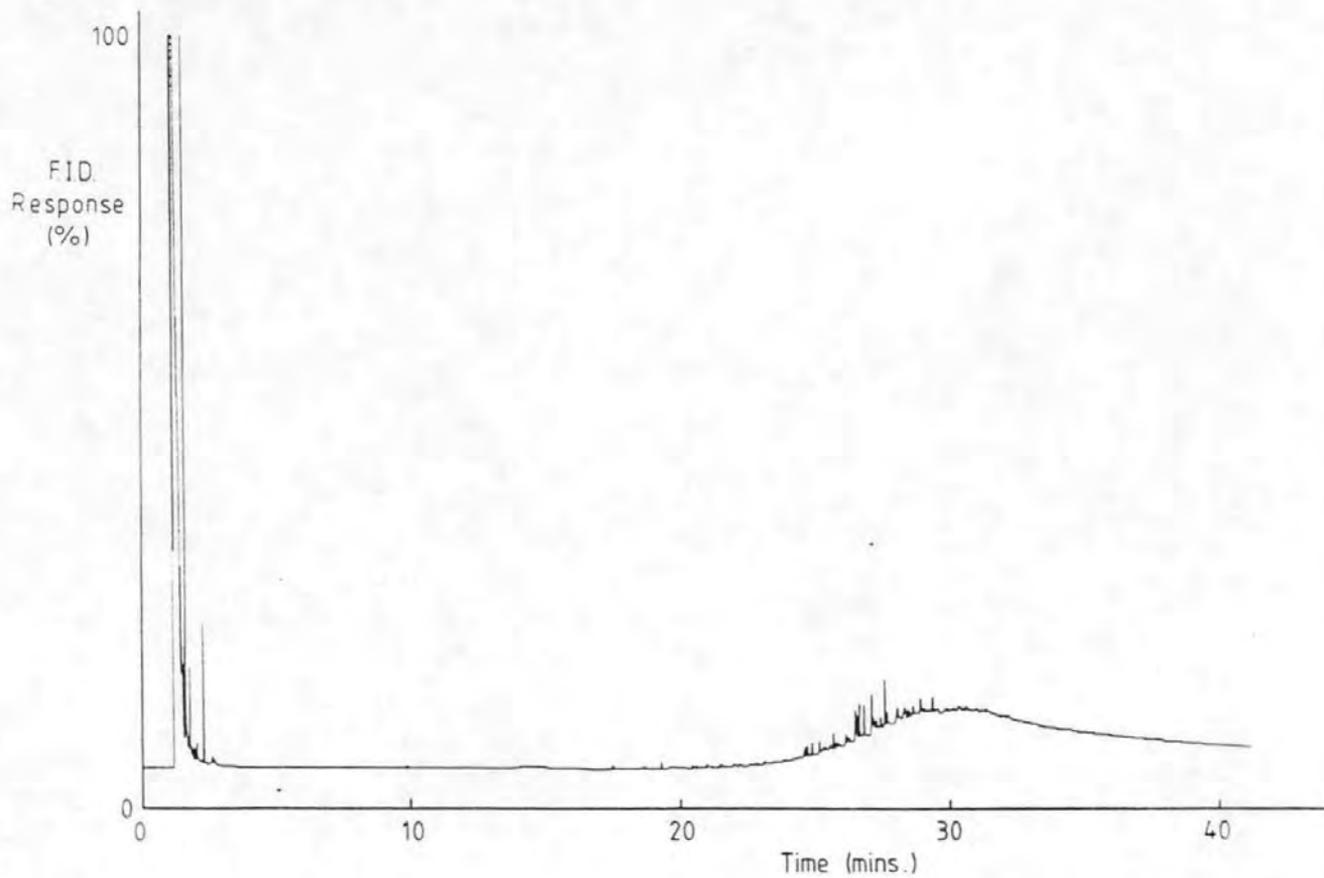


Fig 7 Gas chromatogram of the aromatic fraction of the lubricating oil used

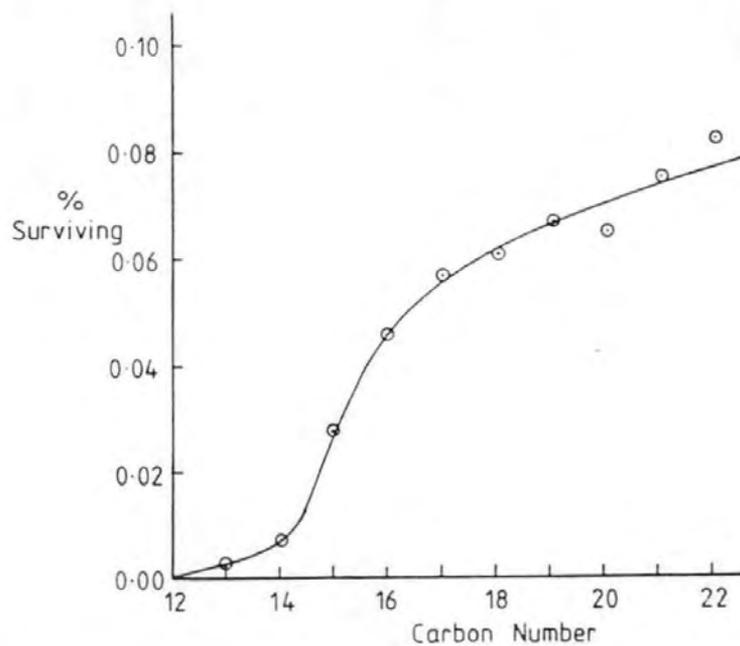


Fig 8 Diagram to show how the increase in per cent surviving relates to increase in the carbon number of the n-alkanes

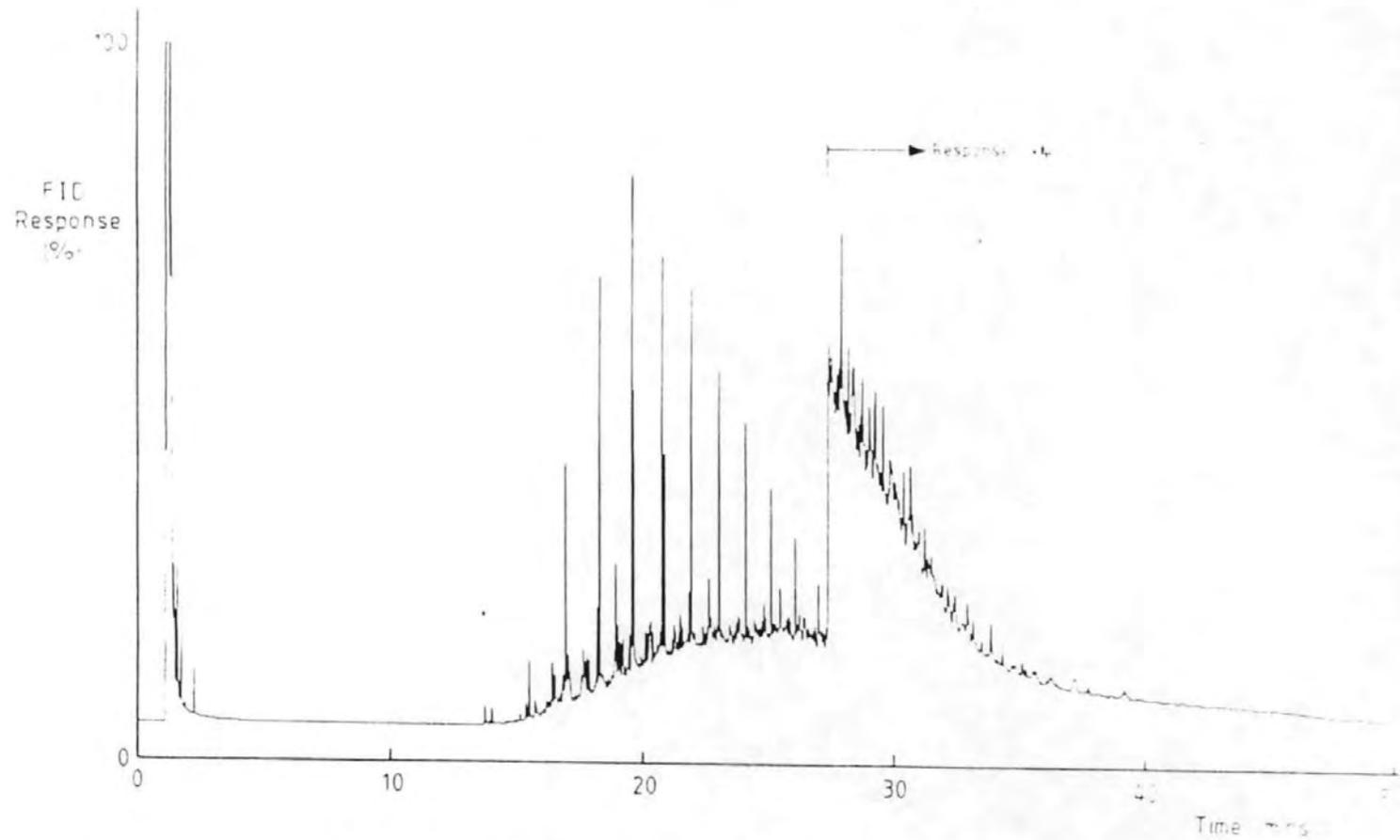


Fig 9 Gas chromatogram of the aliphatic fraction of a typical TES with the later retention time attenuation increased to emphasize lubricating oil contribution

A comparison of diesel engine exhaust emissions collected by an environmental protection agency recommended dilution tunnel/filter with the sample from a new solvent scrubbing system

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SYNOPSIS

A new solvent scrubbing exhaust sampling system has been used to take a representative sample of the organic compounds, along with particulates, present in diesel exhaust from a modern four-cylinder IDI passenger car diesel engine. The samples obtained have been directly compared with filter samples taken with a dilution tunnel, using the same engine under identical conditions of speed and load. Significant differences between the samples are demonstrated, indicating that the dilution tunnel filters discriminate against the low molecular weight, more volatile components, which may remain in the gaseous phase if particulate levels are very low. The TESSA system effectively characterises this group of compounds, which make a significant contribution to urban air pollution, and thereby offers additional information to the monitoring of unburnt hydrocarbons by conventional flame ionisation detection.

1. INTRODUCTION

The development of a novel exhaust sampling technique has previously been described, and the acronym TESSA (Total Exhaust Solvent Stripping Apparatus) assigned to the system (1). In the TESSA system, exhaust products are fed into the base of a stainless steel tower and as they pass upwards through the tower they are scrubbed by a downward flow of solvent. The tower was originally designed to ensure complete recovery of radiolabelled tracers surviving from the fuel, but it has also proved useful as a sampling device for the organic species in the gaseous phase and those adsorbed onto particulates. When sampling close to the engine it is possible to quench and isolate most of the organic species before they have become adsorbed to the carbon particulates.

In the experiment described below, the TESSA system was connected to a light-duty diesel engine close to the exhaust manifold, whilst further down the exhaust a standard dilution tunnel system was connected enabling filter samples to be taken in the manner recommended by the United States Environmental Protection Agency (EPA). In this way the TESSA sample gives an indication of the type and concentration of organic material leaving the engine, whereas the filter sample is indicative of the organic species, associated with exhaust particulates, which enter the atmosphere. It is likely to reflect further reactions that may occur in the exhaust pipe or on the filter in the dilution tunnel (2). Furthermore, filtering of the lower molecular weight, more volatile

organic compounds, such as 2 and 3 ringed aromatics, which may remain in part within the gaseous phase, is not completely effective (3). A normal procedure is to monitor the total unburnt hydrocarbon (UHC) levels in the exhaust by means of a flame ionisation detector (FID) to give an indication of those compounds not trapped by the filter; the TESSA system offers additional information on these compounds because it traps gas-phase as well as particulate bound organics.

2.0 EXPERIMENTAL METHODS

2.1 Facilities available

A test bed was used with a modern passenger car IDI ca. 2-litre, 4 cylinder, naturally aspirated diesel engine. The engine was fully controlled and monitored by computer, including exhaust gas analysis, [NO_x, CO/CO₂, HC, and O₂] Air Fuel Ratio (AFR) & Bosch Smoke.

In order to enable the TESSA system to be connected to the main exhaust pipe, a short (60cm) transfer pipe was added very close (15cm) to the exhaust manifold.

From earlier measurements taken with a single-cylinder test engine, (Ricardo E6), the maximum capacity of TESSA was estimated to be 500 l/min, when using a solvent volume of 2 l and a sampling time of 3 minutes. The back-pressure exerted by TESSA on the exhaust system was only 4.9cm of water. Previous research has indicated that the load on the engine is the most significant engine operating

parameter effecting the emission of Polycyclic Aromatic Hydrocarbons (PAH) and their derivatives (4). It was therefore decided that the experiment to be carried out would be done at a constant engine speed of 2500 rev/min, whilst varying the load. Because TESSA could not handle the total exhaust flow from this engine it was necessary to split the exhaust. With the minimal backpressure exerted by TESSA, it was possible to distribute the exhaust gases between the transfer pipe and main exhaust approximately in the ratio of the cross-sectional areas of the respective pipes, (approximately 1:4 was achieved). A measurement by manometer at the top of TESSA during the sampling gave a reading of 5.7cm of water, which was similar to that achieved in previous tests. Further tests, with the single cylinder engine and TESSA showed that temperatures within TESSA were acceptable even when temperatures within the transfer pipe reached 550-600°C, (see Fig 1). In fact the maximum temperature of the transfer pipe, as measured by a thermocouple inserted into the gas stream during the experiments described here, did not exceed 480°C.

2.2 Test procedure for TESSA

The engine was conditioned by running at full-load and speed for one hour before selecting 2500 rev/min and the chosen load. The system was further conditioned for 15 minutes. The valve in the transfer pipe was kept fully closed during this procedure. For effective use of TESSA, exhaust gases were never passed through it without the presence of a solvent flow, and so the internal surfaces of the tower remained remarkably clean. Only static engine conditions can be sampled at the present time and a range of typical operating conditions was selected to give a comprehensive picture of the changes in emissions from full to low load.

At the end of the conditioning period, the valve on the transfer pipe was opened fully and a TESSA sample was taken in the manner described in a previous paper (1). A solvent mixture of dichloromethane (1 litre) and methanol (1 litre) was passed down the tower, on a once-through basis, over a 3 minute period during which the exhaust was flowing up the tower and out the top before being vented to atmosphere. During its passage through TESSA the exhaust stream was stripped of the soluble organic compounds as well as any particulate carbon. Exhaust components which are gases at STP emerged from the exit of TESSA. The residence time of the solvent in TESSA was minimised since it drained to a reservoir where it was removed from further exposure to exhaust material. The reservoir itself was partially filled with distilled water (2 litres) which acted to dilute acidic species and caused the solvent mixture to separate into two phases. The organic species of interest, particularly PAH, remained in the dichloromethane layer removed from further reaction with the acidic species in the aqueous phase. Recovery experiments have been undertaken and show good recovery (>90%) for most of the PAH, except for naphthalene which is exceptional in that it has an appreciable solubility in water. In addition, naphthalene has a volatility which makes it difficult to recover quantitatively during work up.

2.3 Filter Samples

Filter samples were taken at a temperature below 52°C, after air dilution. Only part of the exhaust was drawn off into the dilution tunnel and the exact dilution was monitored and adjusted by comparing the concentration of NO_x in the exhaust before and after dilution. A volume of diluted exhaust was drawn through each filter for a sufficient sampling time to ensure a particulate loading per filter of around 10 mg; the exhaust volume was accurately recorded for each sample.

2.4 Analytical Procedures

The sample from TESSA was filtered under reduced pressure immediately after sampling. The dichloromethane fraction was then extracted by liquid/liquid partition. The sample was concentrated by rotary evaporation under reduced pressure at 35°C, transferred to a preweighed vial where any remaining solvent was removed by nitrogen blowdown. The TESSA extracted sample (TES) was then ready for fractionation prior to analysis. These steps have been described more fully in an earlier paper (1).

The filter samples were extracted with a Soxhlet apparatus for 12 hours using dichloromethane as the solvent. The resulting extract, the soluble organic fraction (SOF), was then rotary evaporated in a similar manner to the TES sample. Both samples were fractionated into aliphatic, aromatic and polar fractions by column chromatography using silica and consecutive elution by hexane (15cm³), dichloromethane (15cm³) and methanol (15cm³).

High resolution gas chromatography (HRGC) was carried out on a Carlo Erba HRGC 5360 equipped with FID and fitted with a DB-5, 30 metre, fused silica capillary column, (25 µm film thickness and 0.32mm I.D.). For each analysis the following temperature programme was used: At the start, after injecting the sample, a temperature of 50°C was held for 5 minutes. A temperature ramp was then used to raise the GC temperature to 300°C at 10°C per minute and finally the temperature of 300°C was maintained for a further 25 minutes.

3.0 RESULTS AND DISCUSSION

The exhaust emissions were routinely monitored for hydrocarbons during the sampling procedure using a probe in the exhaust and a heated transfer line kept above 190°C to prevent condensation of material before reaching an FID. The SOF and TES results can be compared with those for the UHC in Fig 2. The general picture is one of increasing hydrocarbon emissions as load decreases. This is as one might expect from a modern engine where the high air-fuel ratios at low load lead to localised over-lean conditions for full combustion to be effected, whereas the problem of over-fuelling prevalent in older engines at high load is well under control (5). The variations in the TES are not very different for the four load conditions. The data for the TES represents the results for only one experiment and need to be

repeated to confirm the trends, in particular the low reading for the 20Nm load.

These results can be compared with published data for an on-the-road, 1.8 l IDI diesel engine tested under similar steady state conditions (6). The results for the UHC and total particulates are of the same order of magnitude for both sets of data, however, the Bosch smoke figures are much lower for the engine used in the present test, see Table 1. Alkidas (7) correlated Bosch smoke, total particulates and extracted particulate (carbon) and found a similar correlation to that shown in Fig 2.

Examination of the gas chromatograms for the aliphatic fractions of the fuel and used lubricating oil from the engine test, shows a familiar homologous series of n-alkane peaks (Fig 3). These are in an approximately normal distribution around the carbon numbers C_{14} - C_{15} for the fuel and C_{26} - C_{27} for the lubricating oil. It can be seen in the GC trace of a TESSA sample (see Fig 4a) that the homologous n-alkane series is still prominent but has shifted in its distribution towards n- C_{17} and is less normal in its distribution.

The compounds of lower GC retention times than the n- C_{14} peak comprise mainly light aromatics such as alkyl naphthalenes, which have unintentionally been eluted with the aliphatic fraction in the column chromatography fractionation. The percentage survival from the fuel of these alkyl naphthalenes is calculated in Table 2, and an increasing trend with lower load can be seen.

For these calculations the assumption has been made that all the alkyl naphthalenes originate from the fuel, which is supported by the very similar distribution and relative peak heights for these compounds in both the fuel and TESSA samples. The survival of the alkyl-naphthalenes shows similar trends to those of the UHC and SOF: an overall increase as the load decreases when the data is considered in terms of weight of emission (mg) per gram of fuel burnt. (See Table 3). Other workers have published similar results (8). It is interesting to note that the total particulates remains roughly the same at all loads, but the contributions from the SOF is much more load-dependent.

The TES chromatogram in Fig 4a has two prominent regions of peaks; the first is low molecular weight material up to n- C_{20} which mainly originates from the fuel. The similar n- C_{17} /pristane, n- C_{18} /phytane ratios between the TESSA and fuel chromatograms support this conclusion that the lighter, more volatile, material in the exhaust sample is in fact unburnt fuel. In the second area, beyond n- C_{20} , a series of peaks protrude from a broad hump of unresolved complex material (UCM). Although this material in large part corresponds with the molecular weight range of lubricating oil, it is broader and also includes a wide range of compounds in the lower molecular weight region at the beginning of the UCM, which have probably formed in the engine through partial combustion and pyrolysis of fuel and oil.

Close inspection of the filter sample (Fig 4b) shows a far heavier dominance of material in the boiling range of the lubricating oil. By expanding the chromatogram, many of these peaks

can be matched between the lubricating oil and the filter sample in terms of corresponding retention times and relative peak areas. Only a few of the n-alkanes typical of the fuel are present. These are the less volatile compounds above n- C_{19} which are only present in low concentrations barely rising above the outline of the UCM hump. In contrast to the TESSA sample, none of the lighter aromatic compounds such as alkyl-naphthalenes are present in the filter sample. However, the lower boiling point area of the UCM hump exhibits the same broadening which results from compounds not present in the lubricating oil. This indicates that chemical processes within the cylinder transform some of the fuel and lubricating oil without completing the combustion of these products.

These results confirm a significant contribution of lubricating oil to the filter samples and to a lesser extent the TESSA samples. Cuthbertson et al. (9) have shown that filter samples can trap more of the low molecular weight material than was apparent in this experiment. One explanation for this difference can be found in the very low Bosch smoke readings. In other words, the present engine on test produces very little carbonaceous soot but appreciable amounts of lubricating oil in its exhaust emissions. Soot with its very high surface area is known to be highly effective in scavenging the light organic material from the gaseous phase. Organics adsorb strongly onto the carbon particulates and are trapped with the particulates on the dilution tunnel filter. In such a dilution tunnel sampling system it is suggested that there is insufficient soot to scavenge the gaseous phase organics, which therefore pass through the filter. These gas phase organics are however included in the measurement of the total unburnt hydrocarbons by FID and, of course, are fully trapped by the TESSA system.

The situation described highlights a limitation of the tunnel dilution and filter method, which depends for the efficiency of collection of vapour phase organics from the engine on the presence of sufficient particulate matter with a large surface area of contact to scavenge the organics. In modern engines, in which particulates are at low levels in the exhaust, much of the vapour phase organic compounds may not be trapped by a filter. However, Amann and Siegl (10) do suggest that in considering the processes of adsorption and condensation the bulk of extractable material is acquired by the particulates after the exhaust gas is mixed with dilution air. If the level of dilution in this experiment was too low, it may also in part explain why the particulates did not effectively scavenge the gas-phase organic compounds.

The ratios of the TES to SOF and TES to UHC in Fig 5, are of interest. At high load, the TES is eight times greater than the SOF and the lighter molecular weight material has not been trapped on the filter. At low load the lubricating oil contribution becomes more significant, in relation to the total particulates, and the ratio is closer to unity. The TES/UHC ratio remains fairly constant at just over 1:1. The TESSA system thus compares reasonably well with the UHCs. Some very low molecular weight gaseous hydrocarbons are

detected as part of the UHC but are not registered in either the TES or SOF. On the other hand, some losses occur for the UHC through the condensation of high molecular weight material in the heated line to the FID, (11) most of the compounds that make up the lubricating oil, for instance, have boiling points which are much higher than 190°C. However this material is collected by TESSA.

4. CONCLUSIONS

The TESSA system has been shown to be a capable sampling device for organic species in diesel exhaust emissions, particularly those species that remain in the gaseous phase, allowing a more complete characterisation.

Some degree of bias has been confirmed in the way that the dilution tunnel filter sampling system discriminates against low molecular weight volatile organic material. This bias can distort the apparent contribution of lubricating oil to exhaust emissions. However this work has confirmed that, particularly at low load, lubricating oil can make a significant contribution to total particulates (12).

Modern diesel engines, with very low elemental carbon particulate emissions, may produce significant concentrations of gaseous phase organics which are not scavenged by particulates and therefore are not effectively sampled by a filter system.

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Table 1 Comparison of Smoke Bosch Number, between engine used in present work and a similar engine reported in literature

Torque, Nm	Medium		High	High
	Low	Low		
IDI from literature 1.8 litre (4)	0.9	0.9	1.0	1.5
IDI present work ca. 2.0 litre	0.1	0.3	0.4	0.7

Table 2 Percentage survival of lower molecular weight PAH in the TESSA samples

Torque, Nm	20	40	55	100
Naphthalene	0.209	0.070	0.088	0.020
Methyl-Naphthalenes				
2-methyl	0.096	0.030	0.027	0.008
1-methyl	0.121	0.034	0.046	0.012
Dimethyl Naphthalenes (Dmn)				
2,6- and 2,7- Dmn	0.082	0.034	0.023	0.010
1,3- and 1,7- Dmn	0.074	0.928	0.014	0.007
1,6- Dmn	0.065	0.023	0.014	0.006
1,5- Dmn	0.070	0.029	0.012	0.005
2,3- Dmn	0.073	0.028	0.012	0.005
1,2- Dmn	0.077	0.036	0.022	0.008

Table 3 Exhaust emissions expressed as mg. per gram of fuel burnt at different load conditions

Torque, Nm		20	40	55	100
UHC, FID	mg/g	2.34	1.11	0.83	0.38
TES, Tower	"	1.24	1.34	1.01	0.60
SOF, Filter	"	0.77	0.49	0.24	0.07
Total Particulates	"	0.97	0.93	0.90	0.90

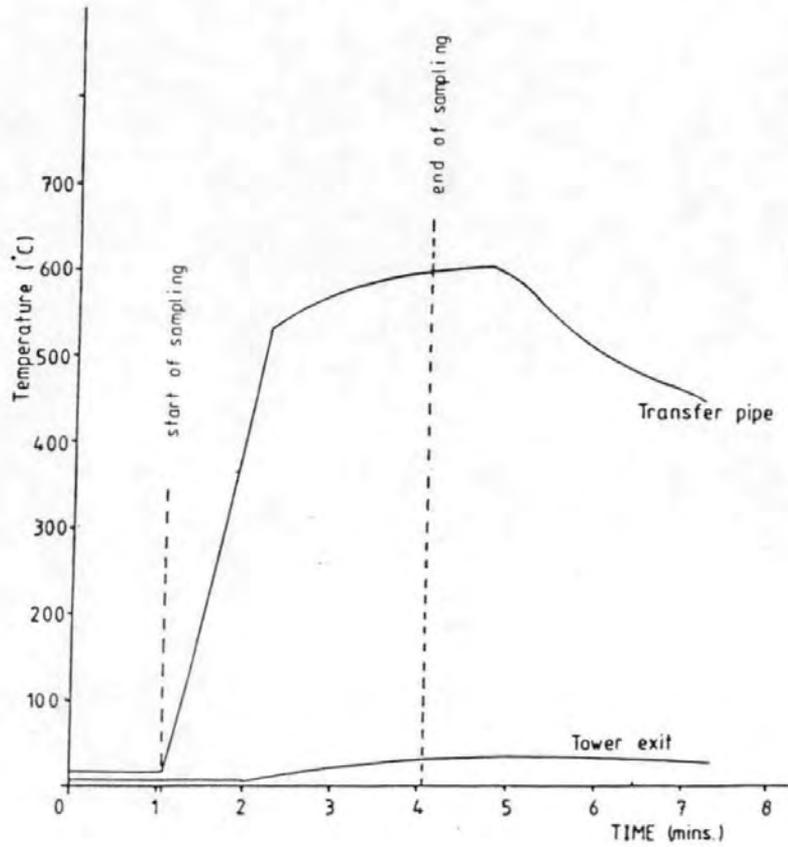


Fig 1 Graph showing temperature profile during sampling between transfer pipe and exit from total exhaust solvent stripping apparatus (TESSA) measured with Ricardo E6 single-cylinder indirect injection (IDI) diesel engine operated at high speed and load

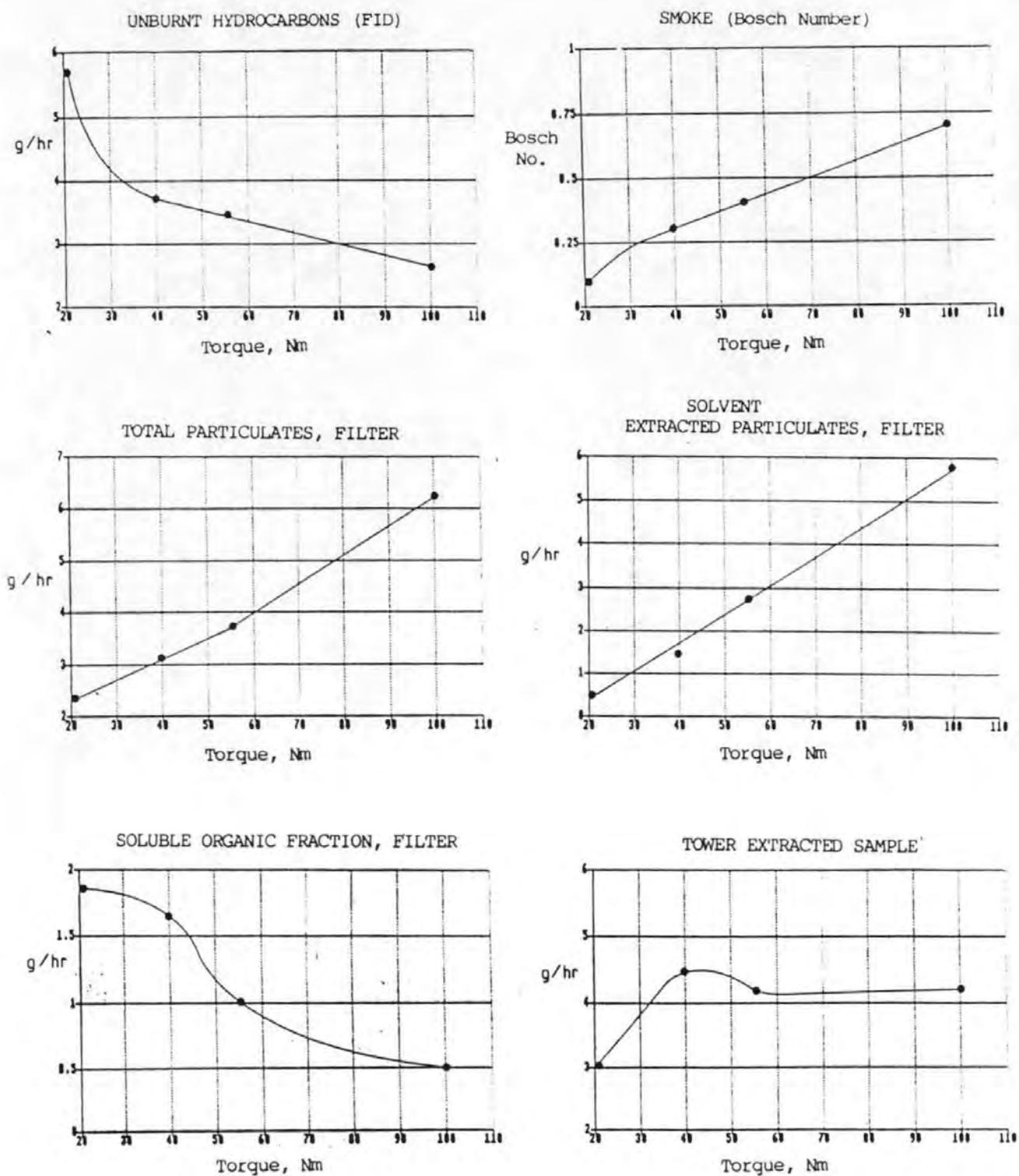


Fig 2 Summary of unburnt hydrocarbons, smoke emissions and emission rates measured by TESSA and filter (all in g/hr) for the in 2.0 litre IDI test engine operated at a constant speed of (2500 r/min)

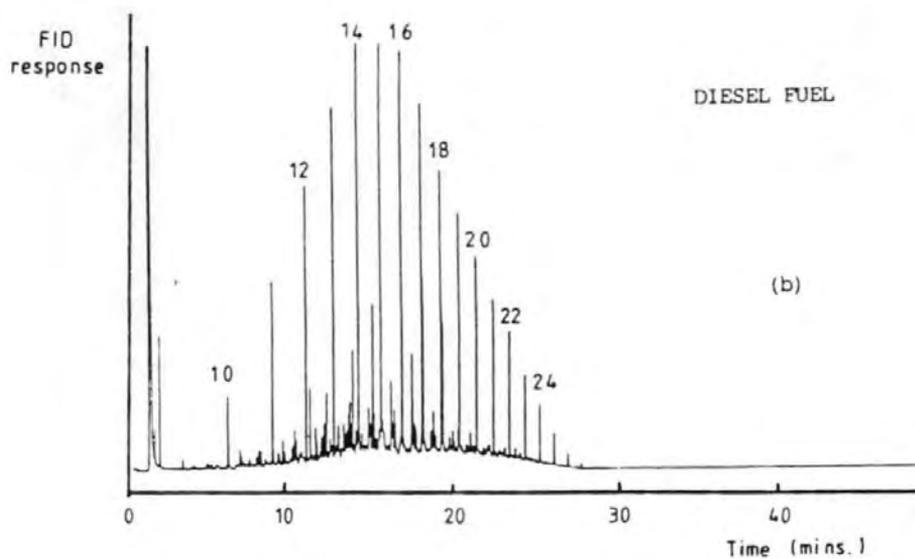
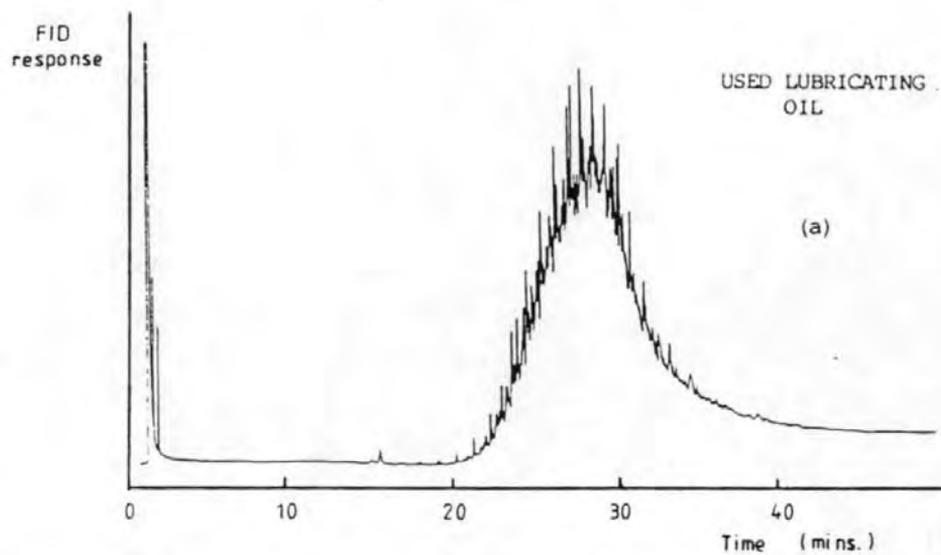


Fig 3 Gas chromatograms for the aliphatic fractions of the lubricating oil (a) and the diesel fuel (b) used for the engine tests (numbers identify even-numbered n-alkanes)

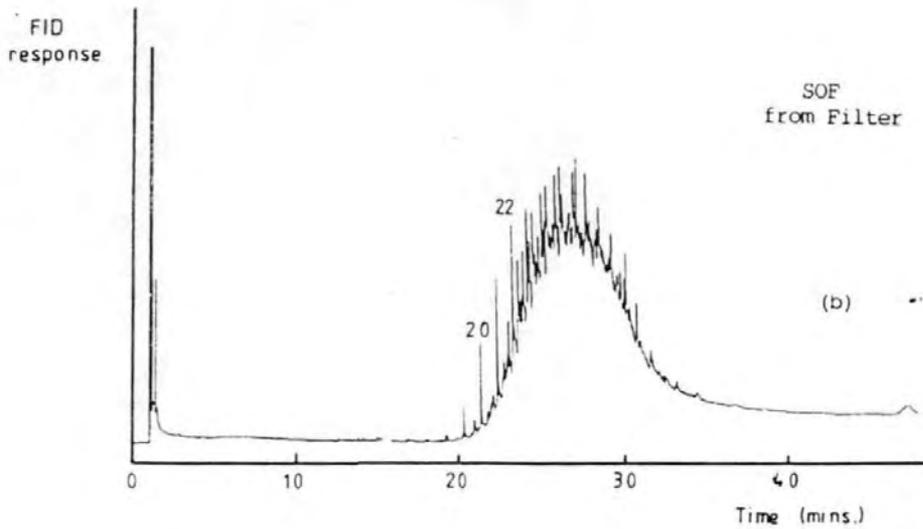
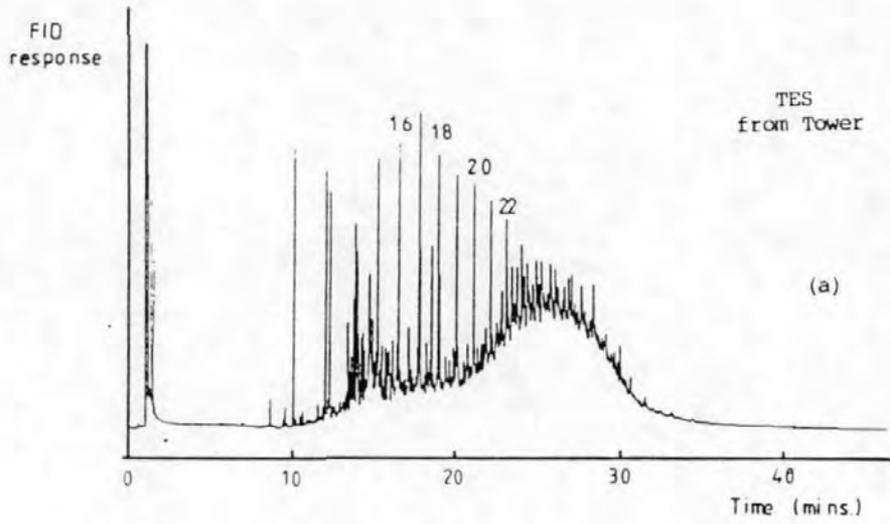


Fig 4 Gas chromatograms for the aliphatic fractions of a TES sample at medium load from
 (a) TESSA
 (b) a soluble organic fraction (SOF) sample from the filter
 (numbers identify even-numbered n-alkanes)

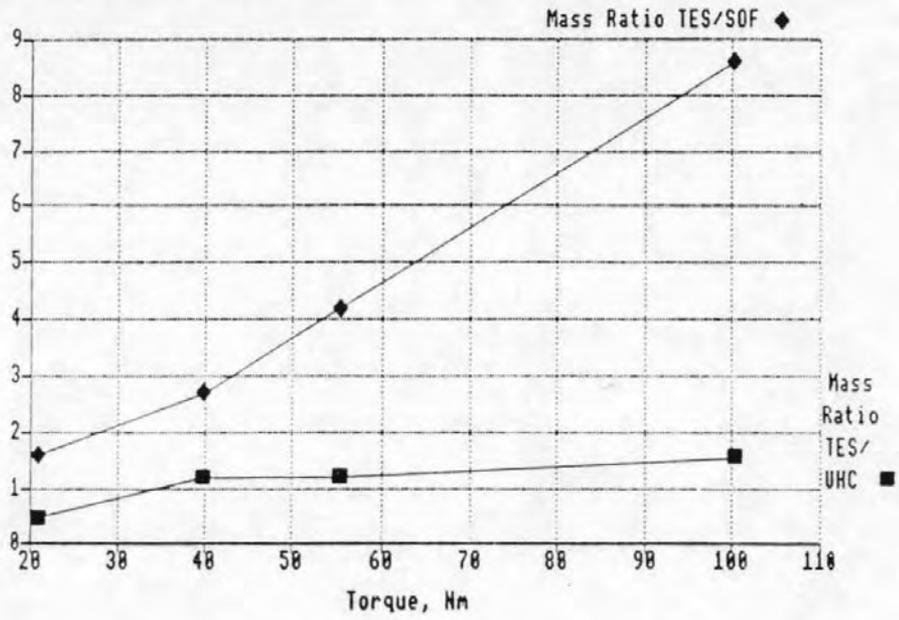


Fig 5 Graph showing the ratio of TES to SOF and TES to unburnt hydrocarbon (UHC) for the engine tests with the in 2.0 litre IDI multi-cylinder diesel operated at constant speed (2500 r/min) and varying load conditions

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