SOME EFFECTS OF VEHICLE AND INDUSTRIALLY GENERATED EMISSIONS ON THE ENVIRONMENT

A thesis submitted by

PAUL LEINSTER, B.Sc., A.R.C.S.

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of London University

Department of Public Health and Water Resource Engineering
Imperial College of Science and Technology
London SW7

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Abstract

Two methods have been developed and evaluated for the sampling of volatile organic compounds in the atmosphere; one a cryogenic technique, the other entailing adsorption of these compounds onto a porous polymeric material contained in a stainless steel tube. The use of pulsed flow desorption from the sampling tube has enabled the establishment of adsorption and desorption characteristics of such systems. Identification of the organics in the atmosphere has been accomplished using gas chromatography/mass spectrometry.

Air quality has been monitored at several locations including an industrial site in the Teesside area, Heathrow Airport and various sites in London. Generally total hydrocarbons, methane, carbon monoxide and lead levels have been measured but at certain sites individual hydrocarbons and ethylene dibromide have also been determined. The concentrations of these compounds have been established in the exhaust emissions of a vehicle under test on a Clayton Dynamometer.

Terpenoid type compounds have been identified in the headspace vapours of cannabis. Four techniques were used to sample the headspace vapours; the adsorption technique developed for air pollutants, direct injection using a gas tight syringe, a solvent technique and the Elscint sampling system.

The adsorption technique has been adapted for the determination of volatile organics in water. This technique has been compared with existing procedures and has been used to determine organics in various environmental samples including an industrial effluent, motorway run-off, influent and effluent of a sewage works and river water.

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Abbreviations

ppm	parts per million
ppb	parts per billion (1 in 10^9)
ppt	parts per trillion (1 in 10^{12})
g	gram
mg	milligram
µg	microgram
ng	nanogram
km	kilometre
m	metre
mm	millimetre
µ	micron
ft	foot
in	inch
l	litre
ml	millilitre
µl	microlitre
min	minute
hr	hour
i.d.	internal diameter
o.d.	outer diameter
w/w	weight for weight
v/v	volume for volume

GLC	gas liquid chromatography
TLC	thin layer chromatography
GC	gas chromatography
MS	mass spectrometry
IR	infra-red
AA	atomic adsorption
AQC	air quality chromatograph
FID	flame ionisation detector
SCOT	support coated open tubular

EDB	ethylene dibromide
EDC	ethylene dichloride
TEL	tetraethyl lead
TML	tetramethyl lead
NMHC	non-methane hydrocarbons
THC	total hydrocarbons
COHb	carboxyhaemoglobin
NO_x	oxides of nitrogen

TWA	Thames Water Authority
EPA	Environmental Protection Agency
ECE	European Economic Community
GPO	General Post Office

PAH	polyaromatic hydrocarbons

CHAPTER 1

SAMPLING AND ANALYSIS OF HYDROCARBONS IN THE ATMOSPHERE

1.1. INTRODUCTION

It is only comparatively recently that man has become aware that the benefits of mechanisation are accompanied by undesirable consequences. One of the most serious effects of the ever increasing use of energy is the pollution of the atmosphere from combustion processes including industrial plants, domestic dwellings and mobile internal combustion engines.

The annual increase of pollutants worldwide is exponential, the rate being particularly high in the industrialised nations. Meteorological and geographical conditions add to the problem in certain areas by inhibiting the dispersion of pollutants, or by initiating the formation of secondary pollutants.

As the effects of air pollution have become more serious there has been an increase in the amount of research into every aspect of the subject. The general purpose of the research must be to provide scientific information which will facilitate the development and application of improved control methods. So that this can be accomplished, improved analytical techniques are required for the measurement of time averaged and fluctuating concentrations. As a result of the research completed much is now known of the effects on man, animals, plants and inert objects of the various pollutants which occur in the atmosphere, however the synergistic and antagonistic actions of certain pollutants when they occur simultaneously leads to problems when trying to ascribe particular effects to individual pollutants.

There are many sources of hydrocarbon air pollution of which the combustion of fossil fuels is by far the greatest. The fuels are burnt for a number of purposes including domestic and industrial heating and for the generation of power both in stationary and mobile internal combustion engines. The discharges of hydrocarbons are particularly concentrated in urban areas and close to roads and it is in these places that the worst effects are to be found. Hydrocarbons can individually or collectively cause plant damage, give rise to noxious odours or act as primary reactants in the formation of photochemical oxidants.

In view of the undesirable effects that may be caused by trace quantities of hydrocarbons in ambient air, it is important that accurate and reliable techniques are available for their detection and quantitative analysis.

Only one hydrocarbon, methane, is found naturally worldwide and it has a background concentration of 1.3 - 1.4 ppm. The natural processes that give rise to methane in the air are primarily biological, methane being produced by anaerobic decomposition of organic matter. The total background concentration of all other hydrocarbons in the air is less than that of methane.

Hydrocarbon pollutants do not remain indefinitely in the air - they may undergo chemical change or be removed to sinks such as the soil, vegetation, structures and water. A measure of a pollutant's relative permanence in the air is its half life, which can be defined as the time taken for half the pollutant emanating from a source to react chemically or be adsorbed into its various sinks. Ethylene for example has a half life of between 4 and 6 hours whereas methane has an estimated half life of 16 years. The main sink for methane appears to be the troposphere.

Natural emissions of hydrocarbons worldwide in 1969 were estimated as 480×10^6 tons a year while the estimated pollution load was 88×10^6 tons a year, however, in urban areas pollution exceeds the natural discharge of hydrocarbons. There are two primary classes of hydrocarbon pollution, those pertaining to petroleum or petroleum products and others which include coal, wood and other organic substances. The forecast of hydrocarbon emissions in the US for 1975 from combustion of prime fuels for energy conversion was 4.79×10^6 tons a year, 3.8×10^6 tons a year being emitted by vehicles. The total amount emitted is significantly lower in the UK but the relative contribution from vehicles is comparable.

The most important of all internal combustion engine fuels is petrol also known as gasoline which has a boiling point range of 30° - 200°C. The continuing increase of motor traffic since the beginning of the century has given rise to a corresponding increase in mobile combustion engine generated air pollution which is most evident in the vicinity of busy roads in urban areas.

The development of the car over the years has necessitated improvements in the composition and consistency of petrol. In particular the anti-knock characteristic of petrol has been improved. Knock is caused by preignition of the petrol-air mixture in the cylinder head which gives rise to non-stochastic thrust, the piston striking the cylinder wall. The ability of a petrol not to cause knocking is indicated by its octane number which is determined by comparing the intensity of knock caused by the test sample compared with that from a blend of iso-octane and n-heptane: iso-octane has good anti-knock characteristics and is allocated a value of 100 on an arbitary octane number scale while n-heptane of low anti-knock quality has a value of 0. The octane number of a sample is therefore the volume percentage of iso-octane in the matching blend of the two reference fuels. Crude oil contains a number of normal paraffins and therefore has to be processed to increase the proportion of hydrocarbons having a high octane number, these include aromatics (formed by catalytic reforming), olefins (from catalytic cracking or catalytic polymerisation), and iso-paraffins (obtained by isomerisation of n-paraffins, or in the alkylation process). Higher octane numbers are also achieved by the addition of anti-knock additives such as tetraethyl lead (TEL) and tetramethyl lead (TML). Addition of about 0.06% by volume provides a cheap and simple means of increasing the octane number by 5 to 10. However, unless a scavenger is added to the petrol, lead formed in the combustion process would be deposited in the cylinders, and because of this fact dibromoethane (EDB) and dichloroethane (EDC) are both added so that volatile halogenated lead compounds are formed which are emitted in the exhaust gas. This adds to the pollution problem as lead compounds are toxic and both EDB and EDC are potential carcinogens.

The products of complete combustion of petrol in the presence of excess air are carbon dioxide and water. For a combustion engine a high air to fuel ratio gives the best economy and the most complete combustion but it is not compatible with the best performance and most engines are operated below their stoichiometric point. Combustion therefore is not complete and carbon monoxide, hydrocarbons and a range of other organics are to be found in the exhaust gas. The hydrocarbons present in exhaust gas include both unburnt compounds and others resulting from cracking during the combustion process. A further factor that influences the volume of exhaust gases is the manifold vacuum which is a function of the engine load.

This is at a maximum during deceleration when there is a decrease in the volume of exhaust gases but a large increase in the percentage of unburnt fuel. The quantity of hydrocarbons emitted is also influenced by the standard of engine maintenance. It is difficult to relate the constitution of the hydrocarbons present in exhaust gas to those in the original gasoline as the combustion engine is very crude when considered as a chemical reactor, thus the composition of the hydrocarbon emissions can vary from engine to engine of the same make and model when burning the same fuel. However, there are general trends such as the higher the octane value the fuel has the smaller the quantity that is required to do a given amount of work and hence the lower the quantity of hydrocarbon emissions.

Hydrocarbons are also emitted as a result of crank case emissions and evaporation from the fuel tank and carburettor. Of the hydrocarbons emitted by cars in the UK the exhaust gases account for approximately 65% of the total, evaporation for 15% and crank case emissions for 20%. The nature of these compounds and therefore their reactivity vary according to the source. Evaporative losses are mainly the more volatile components of petrol, hydrocarbons from the crank case contain a small proportion of partial decomposition products and those in the exhaust consist mainly of decomposition products.

Another major fuel is diesel oil (DERV) which has a boiling point range of 150° - 400°C. A diesel engine operates at a higher air to fuel ratio than a petrol engine and thus the concentration of hydrocarbons in the exhaust gas is less. Furthermore there are no crank case emissions and little evaporation as a closed injection system is used for the fuel which is in any case less volatile than petrol. The total quantity of hydrocarbons emitted is therefore considerably lower than for a petrol engine. Diesel engines are principally installed in large commercial vehicles and the number of these vehicles on the road is considerably lower than petrol powered vehicles. The lower number together with the smaller concentration of exhaust pollutants results in a hydrocarbon load from diesel powered vehicles which is considerably lower than that from petrol powered vehicles. Futhermore, lead compounds, EDB and EDC are not added to diesel fuel.

Yet another source of hydrocarbon emissions is aircraft. There are two categories of fuel used, those for piston engines and those for gas turbines. The requirements for aviation fuel are more stringent than for petrol. For piston engines olefines are only allowable in very small quantities as they give rise to excessive gum formation. The higher grades of fuel consist mainly of iso-paraffins with a small amount of aromatic material to improve the rich mixture anti-knock performance. The main component of these high grade fuels is iso-octane and a small proportion of iso-pentane is added to improve volatility.

Aircraft gas turbines require a fuel with different characteristics from those for piston engines - the principal difference is that the anti-knock value is not important. There are two basic types of jet fuel. One is based on straight run fractions boiling in the range 150° - 250°C and is known as AVTor or ATK. The other is a wider boiling range material known as AVTag or JP4 whose boiling point range is 30° - 260°C. Since jet fuels are blended from straight run distillate components they contain virtually no olefines. The amount of aromatics is also limited because they are not as clean burning as the other hydrocarbon types causing smokiness and carbon deposition in the engine. An average JP4 contains 10 - 15% aromatics and 0.5 - 1% olefines.

Another significant source of hydrocarbon air pollution is that of heating fuels which can be in gaseous or liquid form. Hydrocarbons are also released into the air at each stage of the processing, transport and marketing of petroleum and its products and by various industrial and manufacturing processes.

1.2. Air Quality Criteria and Standards

In any study related to the levels of pollutants in the atmosphere it is essential to consider both the effects of such species on the environment, and the air quality criteria and standards which are applied to them.

A distinction must be drawn between air quality criteria and air quality standards. Criteria concern the concentrations and exposures at which the pollutant under consideration produces a specific effect and standards prescribe the legal or recommended concentration levels which should not be exceeded in a specific area and under specific conditions.

With the knowledge of the criteria it is the job of the relevant authorities to set suitable standards which should protect the health and well-being of the community but should also take account of the degree of risk and of the ability of the community to pay for the standards to be recommended or enforced.

1.2.1. Hydrocarbons

Hydrocarbons occur naturally in the atmosphere, at a level of 1 - 1.5 ppm, mainly as methane. These naturally occurring, ambient levels of hydrocarbons are not known to be harmful to man or to the environment. Whilst the effects of individual hydrocarbons at high concentrations are well known, the effects of low levels of introduced hydrocarbons in a mixture of air and other contaminants are poorly understood at the present. Many consider that most hydrocarbons cause no direct deleterious effects in man at their present or future predicted levels. However, with the possibility of synergistic reactions and the production of secondary pollutants by combinations with, or changes in, the atmosphere, e.g. the role of hydrocarbons in the formation of photochemical smog, the levels of these hydrocarbons in the air must be viewed with concern.

The possibility of cancers developing, due to the presence of PAH in the atmosphere is another field where more research is needed before standards can be closely defined. It is apparent that with the availability of more knowledge and data in the future, the present air quality criteria relating to hydrocarbons will be revised. The effects of hydrocarbons on plants, inert materials, aesthetic conditions, and a possible role in large scale meteorological changes are other fields which must be considered.

1.2.2. Carbon Monoxide

The effect of carbon monoxide on the environment is fairly well documented. It is a colourless, odourless gas, produced mainly by the incomplete combustion of carbonaceous fuels. Its health risk lies in its great affinity for haemoglobin in the blood stream, with which it combines producing carboxyhaemoglobin, thus blocking the body's oxygen transfer system. Exposure to high carbon monoxide concentrations will result in headache, dizziness, flicking of the eyes and could result in nausea, collapse, unconsciousness and finally death. The physiological effects of non-toxic levels are a function of the COHb (carboxyhaemoglobin) in the blood. This reaches an equilibrium after about eight hours, and exposure to 30 ppm carbon monoxide over this time results in a 5% level of COHb. Some levels below 5% may affect choice, discrimination, and reduce visual activity. Above 5% certain psychomotor effects are apparent. However, the long term effects of non-toxic levels of COHb have not yet been established. Carbon monoxide, at the levels encountered in ambient air, does not affect vegetation to any significant degree, whilst its effects on animals are similar to man.

1.2.3. Lead

Lead is a toxicant in the sense that an excessive accumulation in the body can result in lead poisoning, which can range from colic, to palsy, brain damage and eventually death. Atmospheric lead pollution arises mainly from the use of tetra-alkyl lead as an anti-knock agent in automobile petrol. It is primarily emitted in the exhaust as fine particulate matter. However, the pollution seldom stretches far from the road, high levels of carbon monoxide in association with correspondingly high lead levels are indicative of pollution emitted by road vehicles. The measurement of the lead in air offers a good correlation method for estimating the contribution to local air pollution from automobiles, since aircraft fuel and diesel are non-leaded. The fine lead particulate matter can enter the lungs and blood system by inhalation, but the main source of lead intake in man is by ingestion of contaminated food and water.

Plants near busy road may contain up to 500 ppm (by weight) lead. Thus although the principal source of lead is as an air pollutant, the total body load of lead arises mainly from ingestion rather than its inhalation. Concern has grown in recent years over the epidimiological effects of lead and moves have been made (especially in the USA) to use non-leaded petrol. The possible grave effects of organic lead in the atmosphere has also given rise to concern recently.

1.2.4. Air Quality Criteria

Air quality criteria, based on scientifically sound data have been brought out in the USA by the EPA. The relevant criteria for hydrocarbons and carbon monoxide are reproduced in Tables 1.1 and 1.2.

Table 1.1 Air Quality Criteria for Hydrocarbons

1. No demonstrable health effects of gaseous hydrocarbons in ambient air.
2. Injury to sensitive plants with ethylene concentrations of 1.15 - 575 $\mu g/m^3$ (1.001 - 0.5 ppm) over time period 8-24 hours.
3. Non-methane hydrocarbon concentrations of 200 $\mu g/m^3$ (0.3 ppm C) for a 3 hour period from 6.00 - 9.00 a.m. can be expected to produce a maximum hourly average oxidant concentration of up to 200 $\mu g/m^3$ (0.1 ppm) near mid-day.

Table 1.2 Air Quality Criteria for Carbon Monoxide

mg m^{-3}	1.15 mg m^{-3} CO = 1 ppm (Vol)
140	(High concentrations, 30-120 sec) physiologic stress on heart patients, COHb above 5%
120	(Intermittently through facemask) impairment in performance psychomotor tests at 5% COHb
110	
70	
60	(Nonsmokers, 90 mins) impairment time-interval discrimination, increases CCHb by 2%
50	
40	
30	(Nonsmokers, 8-12 hours) 5% COHb, impaired performance on psychomotor tests, physiologic stress on heart patients

In the USA such criteria have been used to establish air quality standards at both a federal and national level (since 1971).

Table 1.3 Air Quality Standards (USA)

Pollutant	Primary Standard, Health-Related	Secondary Standard, Welfare-Related
Carbon Monoxide	$10 mg/m^3$ (9 ppm) for 8 hr $40 mg/m^3$ (35 ppm) for 1 hr	Same as primary
Nonmethane Hydrocarbons	$160 \mu g/m^3$ (0.24 ppm) for 3 hr (6 - 9 a.m.)	Same as primary
Nitrogen Dioxide	$100 \mu g/m^3$ (0.05 ppm), annual arithmetic mean	Same as primary
Sulphur Dioxide	$80 \mu g/m^3$ (0.03 ppm), annual arithmetic mean $365 \mu g/m^3$ (0.14 ppm) for 24 hr	$60 \mu g/m^3$ (0.02 ppm), annual arithmetic mean $260 \mu g/m^3$ (0.10 ppm) for 24 hr $260 \mu g/m^3$ (0.10 ppm), for 24 hr $1300 \mu g/m^3$ (0.5 ppm), for 3 hr
Particulate matter	$75 \mu g/m^3$, annual geometric mean $260 \mu g/m^3$ for 24 hr	$60 \mu g/m^3$, annual geometric mean $150 \mu g/m^3$ for 24 hr

At present there is no legislation in the UK for the control of invisible emissions from motor vehicles and the legislation relates only to the control of 'visible' emissions.

The UK together with several other European countries have drafted common vehicle test requirements which could be used if and when legislation is introduced into the respective countries. Standards have been proposed that relate the allowable amount of hydrocarbons emitted per standard test to the kerbside weight of the vehicle.

Table 1.4 ECE Test Procedure - Standards

Vehicle weight (vw), kg	Mass of carbon monoxide (per test), g	Mass of hydrocarbons (per test), g
$vw \leqslant 750$	100	8.0
$750 < vw \leqslant 850$	109	8.4
$850 < vw \leqslant 1020$	117	8.7
$1020 < vw \leqslant 1250$	134	9.4
$1250 < vw \leqslant 1470$	152	10.1
$1470 < vw \leqslant 1700$	169	10.8
$1700 < vw \leqslant 1930$	186	11.4
$1930 < vw \leqslant 2150$	203	12.1
$2150 < vw$	220	12.8

1.3. Literature Review

In recent years considerable interest and research efforts have been invested in studies of the effects of air pollution on man and his environment. A major proportion of this activity has been directed towards the estimation of hydrocarbon levels in the atmosphere. Still more recently, interest in this general field has been concentrated on investigations into the identification and measurement of levels for groups of compounds or even individual pollutants. This literature review is concerned with the analysis of volatile hydrocarbons in the atmosphere, primarily with alkanes or with lower alkenes and aromatics as a group of unsaturated hydrocarbons. Primary sources quoted have been extracted from the literature from

1970 until the early months of 1977 - it is considered that work prior to this period has been adequately reviewed elsewhere (1). No techniques of sampling and analysis of general applicability to various environments and the wide range of potential pollutants have as yet been reported. Sampling and analytical procedures are considered separately, it should be remembered however that quantification of results will depend on the efficiencies of both procedures, and on their compatibility.

Methane, the only hydrocarbon found naturally occurring worldwide, has a background concentration in the atmosphere of 1.3 to 1.4 ppm. Other hydrocarbons found in air are derived from a wide variety of sources, the most significant of which include: oil and petroleum refineries and storage depots; chemical production and oil burning industries; commercial and geogenic gas leaks; biological processes (2); and agricultural and forest burning programmes (3). In certain forest areas terpenes are emitted by the living trees (4,5). It has been estimated that of the total quantity of benzene released to the environment more than half arises from vehicle emissions (6).

At the ppb concentrations, in which they are normally encountered in the atmosphere the hydrocarbons are relatively harmless to mammals. It has been shown, (7) however, that ethylene at concentrations as low as 0.01 ppm, and to a lesser extent other hydrocarbons have deleterious effects on various species of plant. A more serious problem is the so called photochemical smog (8,9,10), which is produced under certain meteorological conditions by the reactions of nitrogen oxides with other air pollutants including hydrocarbons leading to the formation of compounds such as ozone, aldehydes, peroxyacyl nitrates and alkyl nitrates. These reaction products can cause severe irritation of the eyes and mucus membrane. Visibility may also be reduced by the formation of aerosols of polymer molecules originating from photochemical reactions of hydrocarbons.

Specific hydrocarbons derived from different sources will have varying degrees of impact on the environment. Thus ideally it would be desirable to determine levels of individual hydrocarbons in the atmosphere. Many surveys, however, have been carried out measuring only total hydrocarbon levels, in for example, St. Louis (11), and comparing Paris with other cities (12).

A more significant survey was carried out measuring total hydrocarbon and calculating non-methane hydrocarbon levels in the USA (13) using an empirical relationship derived from previous measurements. Thus measurements of non-methane hydrocarbon levels are to be preferred to those of total hydrocarbon levels. More data may be obtained by monitoring specific compounds and a study of diurnal patterns for several aliphatic and aromatic hydrocarbons has resulted in their occurrence being attributed to automobile exhaust (14). A survey of the pollution caused by road traffic has been carried out in five towns in England over an extended period (15). A similar range of compounds has been investigated using an alternative method of evaluating vehicular emissions (16), which involved measurements in New York and New Jersey and included calculations to demonstrate the effect of wind direction on hydrocarbon levels. A study in Los Angeles has attempted to correlate hydrocarbon levels measured with possible sources of such species, and the relative significance of sources was quoted as: automobile exhausts 47%, evaporative losses of gasoline 31%, geogenic gas leaks 14%, and leaks in commercial natural gas supply systems 8%. An attempt has been made (18) to produce a distribution profile for individual hydrocarbons (benzene and toluene) over a large area (Toronto) by sampling at 12 sites simultaneously. Overall average concentrations were 13 and 30 ppb respectively but the variation in levels between individual sites reached a factor of 40. The toluene to benzene ratio has been suggested as an indication of the proportion of hydrocarbon pollution in the atmosphere produced by automobiles. Other workers (19,20) have found similar ratios to those recorded in Toronto. In Zurich, however, a far lower toluene to benzene ratio has been measured (21). Benzene and toluene have been measured (22) at levels of 23 ppm and 11 ppm respectively in the vicinity of a chemical reclamation plant.

A three month survey of a rural community in Eastern Pennsylvania showed that EPA limits for hydrocarbons (23) were not exceeded (24). However in a study of a rural area in the USA the total concentration of 30 naturally occurring hydrocarbons in the C_5 - C_{10} range was found to be 397 ppb which exceeds the EPA standard (25). Other measurements have been reported covering several molecular weight ranges and include: C_1 - C_5 by an automatic method (26); C_1 - C_5 amongst other gases associated with peat and coal (27); C_8 - C_{18} in Paris air (28); C_6 - C_{20} in Zurich (21); C_9 - C_{20} in Italy (29); and C_6 - C_{10} in the Netherlands.

1.3.1. SAMPLING

1.3.1.1. Principles of sampling procedures

The accuracy and precision of a sampling technique is of the utmost importance and such a technique must allow one to readily relate the values measured to those which were present in the environment. These requirements are of course true of all analyses and in this application inert materials such as glass, polytetrafluoroethylene (PTFE) and stainless steel should be used to reduce the adsorption effects of the walls of containers and transfer lines. Particular attention should be given to the cleaning of all apparatus and to the selection and application of any sealing or lubricating materials in order to avoid contamination.

Both the duration of sampling and the time at which samples are taken should be related to the purpose of a particular investigation. Studies on short duration pollution incidents require rapid sampling techniques, whereas in investigations into ambient levels of pollutants time-averaged results over as long a period as is practicable are desirable. German States developing legislation in respect of smog incidence are specifying half-hour sampling periods and in the USA a three-hour mean sample is prescribed (31).

1.3.1.2. Apparatus and methods for gas sampling

At the ambient levels normally encountered preconcentration (of the volatile components from a highly diluted sample) prior to analysis is usually required, however some methods in which a gas sample is analysed directly have been reported (14,26). The high volatility of the low molecular weight hydrocarbons requires the use of cryogenic trapping techniques to ensure 100% retention, whereas for the higher molecular weight compounds ($\geqslant C_6$) adsorption onto solid adsorbents is the preferred technique (32-34).

Gas tight syringes (18,34), glass aspirators and PTFE bags (18,26, 35,36) have all been used as sample containers. Ambient gas has been sampled using a modified gas pipette with 'Teflon' coated rubber seals and GC/MS analysis gave a reported detection limit of 5 μgm^{-3}(37).

The use of 'Saran' bags for the sampling of industrial atmospheres in the 200-1000 ppm range has been reported (35) and losses after three hours of 15% and 40% for benzene and toluene respectively were recorded. A remote sequential sampler has been described (38), in which spring loaded syringes are activated by a timer and the samples obtained have been stored for 18 hours without leakage. A small lightweight gas sampler for time integrated samples has been described (39). An evacuated container equipped with a critical orifice is used to collect the sample, and the sampling period is dictated by the area of the orifice and the volume of the container. The system has been evaluated for the sampling of methane, ethane, benzene and hexane.

1.3.1.3. Cryogenic systems

A battery operated system for sampling in remote areas has been reported (40), and requires approximately three litres of liquid nitrogen. This system however has been shown to have variable freeze-out efficiency and requires constant attention. A portable cryocondenser has been shown (41) to have a high enrichment capacity for large air volumes and, when coupled via sub-ambient GC to a flame ionisation detector, to give a detection limit of sub-ppb levels. A similar system has been used for the sampling of industrial air pollutants at various altitudes (42). A more sophisticated application of a freeze-out technique to ultratrace analysis has been described (43), in which a temperature gradient is applied to a tube, packed with a GLC stationary phase on an appropriate support. The main problem with freeze-out techniques is the presence of water vapour in the air. The application of drying agents prior to condensation has reduced this problem and systems based on this principle have been described (44). Separations of the contents of cryogenic traps prior to mass spectral analysis have been accomplished by thermal analysis (45) or by a preparative gas chromatographic technique (44).

Although cryogenic sampling is the only technique presently available which produces directly a true sample composition in the low molecular weight range of air pollutants, procedures involving adsorption on solid adsorbents or in liquids, coated on inert supports and acting as stationary phases, are simpler and more convenient for field sampling. Adsorption techniques suffer from high percentage losses of volatile compounds. The chemical nature of a solid adsorbent has a considerable influence on the adsorption/desorption characteristics for specific compounds, and losses due to irreversible adsorption are common, particularly when heat desorption is used.

1.3.1.4. Adsorption on activated carbon, silica gel, support bonded stationary phases or porous polymers

Activated carbon is particularly prone to irreversible adsorption of certain organic species. Recovery of solutes by solvent extraction is more complete but is also a more time-consuming and complex process. This material has, however, been used widely as an adsorbent followed by either thermal desorption (28) or by various methods for solvent extraction (21,29,46) of the adsorbed species. Carbon disulphide has been shown to be an effective solvent for the extraction of activated charcoal (21).

The usefulness of silica gel as an absorbent for sampling of environmental samples is greatly reduced by its affinity for water and the consequent influence of relative humidity on the adsorption curves for hydrocarbons. Sampling onto silica gel followed by thermal desorption of the adsorbed species, their oxidation to carbon monoxide and determination by acidimetric and coulimetric measurements has recently been reported (47). The procedure was limited by the number of adsorption/desorption cycles that could be carried out, by inadequate desorption temperatures and by variations in retention volumes for specific organic species.

The use of support bonded chromatographic stationary phases for sampling has been investigated (48) and it was shown that high concentrations of stationary phases were required in order to maximise the retention of organic species present. This method is limited to atmospheric pollutants of relatively low volatility but could be improved by sub-ambient operation.

Porous polymers with high capacities for the sampling of organics and low affinities for water provide extremely useful adsorbent species and have been extensively investigated (2,43,49-56) utilising both thermal desorption and solvent extraction. An evaluation of various organic adsorbents and their relative dynamic capacities for certain classes of compounds has been reported (32). Chromatographic packing materials studied were Poropack P a porous polymer of styrene and divinyl-benzene; Carbosieve, prepared by thermally cracking polyvinylidene chloride and Tenax GC a porous polymer, 2, 6-diphenyl-p-phenylene oxide. In this as in other recent publications (36,50,57) Tenax GC has been shown to be superior as a general adsorbent having excellent temperature stability to 380°C and proving easy to handle. In these studies relative humidity, ubiquitous background levels, repetitive use, transportation and storage were all considered. Mieure and Dietrich (54) classified the adsorption/desorption characteristics of various column packings:

Chromosorb 101 - absorbs and desorbs acidic and neutral components.

Chromosorb 105 - absorbs and desorbs low-boiling components.

Tenax GC - absorbs and desorbs basic, neutral, high-boiling components.

1.3.2. ANALYSIS

There is a need for high specificity in measuring the components of an environmental sample but it is also desirable that the analysis may be performed routinely, rapidly and with precision. The apparatus should be simple if it is required for use in a mobile laboratory. The application of GLC to the analysis of complex environmental air samples is the only really viable system with FID being the most commonly used detector. Conventional packed columns remain adequate in many applications, but in order to achieve the required separation of the broad range of components detectable and to enable accurate measurement of retention times, capillary columns are gaining increasing use. There are no accepted standard methods available for the analysis of hydrocarbons; and it is difficult to envisage the establishment in the near future because of the large variation in the analytical requirements of various applications.

Several GLC systems have been described and compared (58); the authors concluded that there is a need for better chromatographic methods designed to resolve the 50 to 100 or more readily measurable hydrocarbons in urban atmospheres. They added that methods should be developed, standardised and made generally available in order to enable more meaningful comparative and collaborative studies. There is also a requirement to reduce experimental error in identification and estimation of individual compounds especially in the correlation of the photochemical reactivity of specific hydrocarbons with the resulting oxidant formation.

Rasmussen et al (58) described: 'some of the present-best GC-column methods used in this laboratory.' They preferred a packed capillary column for the analysis of light hydrocarbons having compared its performance with both 1/8 in o.d. packed columns and support coated open tubular (SCOT) columns. The specific column used was 20 ft , 1/16 in o.d., 0.03 in i.d., packed with Durapak (n-octane, Porasil C). Sub-ambient temperature programming was found to give excellent separation of the C_2 - C_6 hydrocarbon fraction. The construction of a suitable cryogenic GC oven has been described (59). When considering methods for the analysis of hydrocarbons it is convenient to treat the compounds in groups specified by a range of molecular weights. Thus Rasmussen et al (58) considered intermediate hydrocarbons, aromatic and aliphatic (C_6 - C_{12}) compounds, and discussed their comparative chromatographic characteristics on several types of column: on open tubular columns of relatively large diameter capable of accepting high sample loadings, m-bis(m-phenoxy-phenoxy) benzene (300 ft , 0.06 in o.d.); on a system using three packed 1/8 in o.d. columns in series; and on small diameter (0.01 in i.d.) open tubular columns in conjunction with temperature programming designed to produce optimum resolution. They found a 0.02 in i.d., 200 ft OV-101 SCOT column to be most satisfactory.

1.3.2.1. Low molecular weight hydrocarbons (C_1 - C_5)

Jeltes and Burghardt (26,60) have reviewed methods available for the analysis of the C_1 - C_5 hydrocarbon fraction present in air and described an automatic GC method, claiming it to be: a relatively simple, direct and inexpensive method for sensitive and quick measurement'. Having considered both the spectroscopic and chromatographic methods available they chose to develop an automatic system for measurement of hydrocarbons : (1) maximum information; separated measurement of individual hydrocarbons, measurement of ethylene (phototoxic), 'fingerprinting' of hydrocarbon fraction (source identification); (2) facile automation; (3) as inexpensive as possible; (4) simplicity of the whole set-up; (5) quick sampling and analysis; (6) rapid results for guarding and 'alarms'; (7) specificity; (8) sensitivity. The merits of methods involving pre-concentration as opposed to direct analysis for the two distinct hydrocarbon fractions (C_1 - C_5) and (C_5 - C_9) were also discussed. A 2m x 4mm i.d. column packed with 80-100 mesh Alumina type F1 was employed for the analysis with air as carrier gas. The detection limits at a signal to noise ratio of 2 were 2-5ppb for C_1 - C_3 hydrocarbons and 7-20ppb for the C_4 - C_5 fraction. An 'AQUASORB' filter was used to remove water from the air samples. The cycle time for this system was 45 mins. including n-C_5 compounds. An automatic system for C_1 - C_5, total C_6 and benzene working on a 30 min. cycle has also been described (61).

The problems associated with the condensation of water vapour are even more significant in cryogenic sampling systems. To minimise such difficulties samples have been passed through a dessicant prior to freeze-out, potassium carbonate has been reported (44,62) to be extremely effective in this application owing to its very low affinity for organics. K_2CO_3 has been used prior to the trapping of organics in a cryogenic U-tube containing glass beads (44), and the sensitivity was quoted as 0.2ppb where the compounds were concentrated from 20 l of air with 100% efficiency. A range of dessicants has been examined (62), including both anhydrous salts such as, potassium carbonate, calcium sulphate and sodium sulphate, and adsorbents of the type Sephadex (G-100) or Linde molecular sieve 3A. The same authors considered the removal of water by its conversion to acetylene and hydrogen by calcium carbide and calcium hydride.

A cryogenic sampling system incorporating a freeze-trap containing stainless steel gauze and employing potassium carbonate as dessicant has been reported (33) to give complete recovery of all hydrocarbons boiling above -90°C with a detection limit of 0.01 part in 10^8. 50-100 litre air samples were taken and liquid oxygen was used as coolant. The transfer of the concentrate from the trap was a two stage process: initially by pressure equalisation into evacuated containers and secondly by Toepler pumps to give a residual pressure in the trap of less than 1 Torr. Subsequent analysis was by GC using retention data from several columns or with suitable samples by GC/IR.

Light hydrocarbons have been measured (14) directly using a 5 ml sample, whilst C_2 - C_5 aliphatic hydrocarbons (excluding C_4 alkenes) have been investigated (16) by a more sophisticated technique involving a silica gel packed column at liquid nitrogen temperature. The latter analysis employed an 8 ft x 1/8 in stainless steel column packed with the same silica gel substrate and operated at 30°C. The same workers have measured C_4 - C_8 aliphatic hydrocarbons and C_6 - C_{10} aromatic hydrocarbons using different trapping and analytical columns for each group. The C_4 - C_8 aliphatic hydrocarbons were trapped on a 1 ft x 1/8 in stainless steel column packed with 10% Carbowax 1540 on 60-80 mesh Gas Chrom. Z, and separated on a 300 ft x 0.06 in i.d. open tubular column coated with dibutylmaleate at 0°C. The $C_6 - C_{10}$ aromatic hydrocarbons were trapped on a 1 ft x 1/8 in stainless steel column packed with 60-80 mesh glass beads, and analysed on a 300 ft x 0.06 in i.d. open tubular column coated with m-bis-m-phenoxyphenoxy benzene at 70°C. The carbon monoxide and methane species were separated on an 8 ft x 1/8 in stainless steel column packed with 60-80 mesh 13X molecular sieve (Wilken Instrument Co.) at 70°C. The three gas chromatographic procedures produced 52 measurable hydrocarbon peaks representing the $C_1 - C_{10}$ hydrocarbons. The higher molecular weight hydrocarbons $(C_{11} - C_{12})$ were observed on occasion but at very low concentration levels. Some peaks contained unresolved shoulders. The overlap of alkane and alkene species was not a significant problem. There were interferences between benzene and some of the C_7 and C_8 alkanes, particularly methylcyclohexane. A direct comparison has been made of the resolution obtained for similar ambient air samples on a 1/8 in. x 2 m packed analytical column and on a 0.02 in x 100 ft SCOT column - the latter proving far superior (54).

Benzene and toluene have been analysed with other compounds (18) by trapping on a 1/8 in i.d. x 8 in stainless steel column packed with 20% Dow-Corning SF ≠ 20 on 60/80 mesh Columpak at dry ice/acetone temperature followed by analysis on a 1/8 in i.d. x 6 ft stainless steel column packed with 8% SF96 on 60/80 Chrom. W at 50°C.

1.3.2.2. Higher molecular weight hydrocarbons $(C_6 - C_{20})$

Grob and Grob (21), in agreeing with a previous worker (63) that high molecular weight hydrocarbons in the atmosphere represent a complex mixture of hundreds of compounds, considered the analysis of such mixtures as three separate components. These three components were: high resolution trace analysis on capillary columns as a necessary prerequisite; appropriate sampling of volatile organics for qualitative and/or quantitative analysis; and gas chromatographic-mass-spectrometric (GC/MS) design maintaining the full separation power of a high-resolution column and working in the nanogram range. They emphasised that the key to the possibility of injecting very dilute solutions on to capillary columns is the avoidance of stream splitting referencing their own previous work (64). They also illustrated that direct sampling was not viable for all but the most abundant species, as the majority of components were present in the 0.1-10 ppb range and 0.1 ng of an individual compound was required for positive identification. 108 volatile organic substances were identified in the C_6 - C_{20} range the majority of which were aliphatic or aromatic hydrocarbons. The samples were trapped at ambient temperature in a glass tube containing 25 mg of wood charcoal as used for cigarette filters with an average particle size of 0.08 mm. Extraction of the filters was with carbon disulphide. The analyses were carried out on two GC columns, a 120 m x 0.33 mm Ucon HB 5100 for the full spectrum (C_6 - C_{20}) and an 80 m x 0.33 mm Ucon LB550 for the volatile fraction (benzene to C_3-substituted benzenes) with temperature programming from ambient to 190°C and 120°C respectively. A more recent application of this type of technique (carbon adsorption) allied to semiautomatic sampling and chromatography on highly polar columns has been reported (65) for the analysis of C_6 - C_{20} fractions.

Using a similar approach but substituting a thermal desorption step for liquid extraction of the sampling trap Bertsch _et al_ (50) have recognized several hundred substances in the C_5 - C_{16} range and identified almost one hundred. The sampling traps used were 110 mm x 8 mm i.d. stainless steel containing Tenax GC and the GLC was carried out on 100 m x 0.5 mm i.d. nickel open tubular columns coated as described elsewhere (66) with emulsion ON 870.

Tenax GC has been used as an adsorbent (53) with the subsequent desorption step achieved by the passage of current through a heating tape attached to the sampling tube. The tube was heated to 260°C for five minutes, the desorbed components being retained at the front of the analytical capillary column at ambient temperature prior to temperature programmed elution.

Raymond and Guiochon have discussed the merits of graphitized carbon black as an absorbent for a wide range of organic compounds (67) and subsequently described (28) its use as the sampling component of a GC/MS system, with which they identified more than 70 components in Paris air. These compounds were in the C_8 - C_{18} range and predominantly aliphatic or aromatic hydrocarbons. Sampling was carried out at ambient temperature using tubes 5 cm x 4 mm i.d. packed with 0.25-0.40 g of 200-250 μ sieved graphitized carbon black. Desorption was achieved by heating the trap to 400°C within 15 seconds using an electric wire (Thermocoax) soldered around it. The analytical column was maintained at ambient temperature so that the compounds eluted from the sampling tube were retained at the column inlet; desorption usually took approximately five minutes. The analytical column used was 100 m x 0.4 mm i.d. coated with OV 101, and was operated under temperature programming between ambient and 230°C.

A "timed elution technique" has been described (20,49) involving adsorption onto a solid adsorbent followed by thermal desorption and analysis by GC/MS. The "timed-elution technique" is so-called because of the method of eluting the adsorbed species from the sample tube, which, after sampling, is placed in an oven and connected via a valve system to the analytical column. After the elapse of sufficient time to allow the establishment of thermal equilibrium in the sample tube a known amount of carrier gas is passed, calculated to flow for the precise time required to just displace the equilibrated gas phase from the sample tube into the gas chromatograph. The sample tubes were stainless steel 4 in x ½ in o.d. packed with 0.3 g Chromosorb 102, desorbed at 130°C onto the analytical column which was stainless steel 12 ft x 1/8 in o.d. packed with 5% Carbowax 20 M on Chromosorb W AW-DMCS at 90°C. Individual hydrocarbons were identified at the 20 ng. level. Applications of discontinuous carrier gas flow for the elution of adsorbed species from sample tubes are at present under study (68).

A rather complex two-stage extraction/injection system has been described (51) which was designed to overcome problems of water condensation from the air sampled. The air sample was first concentrated onto Chromosorb 102 at ambient temperature; the subsequent "thermal" desorption step was somewhat unusual in that the sampling tube was warmed only slightly above ambient but the collecting vessel (part of the injection port) was cooled to liquid nitrogen temperatures. After condensation of the organic compounds the injection port was rapidly heated and analysis was carried out on a 100 ft support-coated Carbowax 20M column temperature programmed between 60°C and 180°C.

Several reports (54,69) have appeared describing the connection of the sample collection tube directly to the analytical column. An interesting extension of this approach was presented by Mieure and

Dietrich (54), who designed their sample tube such that it could be incorporated into the injection port of their chromatograph. This design has considerable potential for less volatile hydrocarbons as it enables independent and rapid heating of sample tubes to higher temperatures than those required for analytical columns.

1.3.2.3. Mass spectrometry

Mass spectrometry is almost mandatory if definitive identification of organic compounds in environmental samples is required. Even with this powerful technique it is often difficult to differentiate between the many similar compounds which may be present, and thus considerable effort is currently being directed towards improvement of MS techniques in this application.

GC/MS systems, many of which are interfaced to computerized data handling systems are now in widespread use (45,46,49,50,70-74). A high resolution mass spectrometer coupled to a computer has been used for the analysis of multi-component air samples (75).

Experiments have been conducted (76) with a photoionisation instrument, irradiating at specific wavelengths, selected to produce ionization of trace gases and to avoid activation of major air components. Measured sensitivities and calculated detection limits are disappointing and require improvement.

A technique (77) which has found application in the estimation of refinery pollutant dispersion and in air quality control utilises a mass spectrometer modified by the incorporation of a static condensation system and gives quantitative results for hydrocarbons of ± 10% at the 5 ppm level and ± 20% at 1 ppm.

A technique has been described by which it is claimed that micro-pollutants present in the air within the concentration range of 10^{-4} to 10^{-8}% by volume may be separated and identified routinely on commercial equipment (78). Enrichment was carried out on a micro-gradient tube followed by separation on a glass thin-film open tubular column by linear-programmed low temperature gas chromatography and identified by mass spectrometry. The authors reported that significant MS data was obtained for concentrations down to 0.02 ppb.

A portable MS based vapour detection system with complete digital control has recently been described (79) which was reported to give detection limits in the ppb range with a reproducibility of approximately 5% when used with a compatible GC system.

The 'advantage' of cryogenic preconcentration of volatile trace components in air samples has recently been exploited (80) in chemical ionization mass spectrometry by using the condensed water as a secondary CI reagent gas. Further refinements in the cryogenic trap and heater system should produce lower detection limits.

1.3.3. Routine Instrumental Methods

1.3.3.1. Gas chromatography

Several commercial instruments equipped with FID are available for the continuous measurement of hydrocarbons at ambient levels. The FID is capable of providing a continuous response, which is approximately linear for hydrocarbons over a wide range of concentrations. Carbon atoms bonded to hetero atoms (e.g. O, N or Cl) give a decreased FID response, and measurements of total hydrocarbon levels can be distorted by the presence of organic compounds which are not purely hydrocarbons. Comparative evaluations of the available instruments have been reported (81,82) and their sensitivity, accuracy, portability and ease of operation discussed. Calibration techniques for such instruments have also been reported (83) using both standard calibration gases from cylinders and diffusion or permeation tubes.

FID instruments have been operated under reduced pressure (84,85) with the sample passing through the column and detector prior to entering the pump. This method has been applied to corrosive or unstable compounds. As previously noted non-methane hydrocarbon measurements are of greater significance than methane measurements as methane contributes little to photochemical reactions.

There are now many commercial non-methane hydrocarbon monitors available, the majority of which operate by producing a value for the difference between total hydrocarbon and methane levels (86). Methane and non-methane hydrocarbon levels may be monitored continuously and simultaneously using a dual flame instrument (87). A system has been described (88) which measures methane and/or total hydrocarbons by selective combustion. Selective combustion has also been used, with the incorporation of a water sorption detector, to measure hydrogen, methane, reactive and non-reactive hydrocarbons. The air is first dried and then passed into a flame, the reactive hydrocarbons being distinguished from the non-reactive species by the relative ease of their combustion. In this context the term reactive refers to the ease with which a particular hydrocarbon will undergo photochemical reaction with nitric oxide or ozone. All hydrocarbons appear to be capable of taking part in such processes, but the reaction rates are extremely dependent on molecular structure

(89). Methane is the least reactive and its estimated atmospheric residence time is up to sixteen years (90), thus in terms of urban air quality it may be considered as photochemically inert. The most reactive of such species probably only have residence times of hours in ambient air and strong sunlight (91). A total hydrocarbon analyser modified to facilitate simultaneous monitoring of ambient air for reactive hydrocarbons has recently been reported (92). The non-reactive hydrocarbons methane, ethane, propane, acetylene and benzene can be measured routinely on an instrument which has a detection limit of 0.01 ppm for each component (93). Instruments have been described (94 - 96) for the measurement of carbon monoxide and methane, in which the carbon monoxide is reduced to methane and detected by FID, with detection limits of a few ppb (97). Measurements of carbon monoxide, methane and total hydrocarbons in the range 0 - 1 ppm have been obtained automatically with a cycle time of 5 minutes (98), similarly an automatic timing device has been incorporated into an analyser to enable repetitive measurements of methane, total hydrocarbons and reactive hydrocarbons (99). An automatic gas chromatographic system, which measured carbon monoxide, methane and non-methane hydrocarbons in a single sample, has recently been described (100). In an investigation (101) into the precision of several non-methane hydrocarbon analysers the standard deviation was 0.322 ppm which is large with respect to the EPA standard of 0.24 ppm. Instruments are also available for the measurement of methane, ethylene, acetylene, carbon monoxide and total hydrocarbons (102 - 105) with detection limits in the region of 200 ppb for total hydrocarbons and 1 ppm or better for individual components. An air quality chromatograph (AQC) system has been reported (106) and evaluated for the measurements of methane, ethylene, acetylene, propene, propane, iso- and normal-butane. Methane has been separated from the other hydrocarbons in air by the use of a cryogenic trap (107). The device traps more than 95% of all non-methane hydrocarbons and when used in conjunction with a total hydrocarbon analyser makes the continuous determination of methane possible.

1.3.3.2. Spectroscopic methods

Reactive hydrocarbons can be estimated utilising the chemiluminescent reaction of oxygen atoms with unsaturated hydrocarbons at pressures of ~ 1 mbar which produces intense emission in the 700-900 nm region of the spectrum (108). Owing to the high background level of methane techniques for the determination of total hydrocarbons in air do not require exceptional sensitivity (merely a capability for precise operation at the ppm level). Although only of barely adequate sensitivity for ambient measurements, non-dispersive infra-red (ndir)(109) has been a popular technique. The sensitivity and selectivity of the method have been improved by refinements in instrumental design (110).

High resolution IR spectroscopy has been used to monitor methane in the Pyrennes (111). A problem in using IR for the measurement of trace levels of organics has been its limited sensitivity. The sensitivity has been improved (112) by using a scanning Michelson interferometer, cooled solid state detectors, fast minicomputer and multiple pass long path length cells. The spectra are analysed by the computer which minimises the interference from water and carbon monoxide and has enabled the measurement of organics at ppb levels.

Laser Raman spectroscopic techniques have been employed for the remote sensing of organics (113) and in particular for levels of methane (114, 115), ethylene (116) and acetylene and ethane (117). The detection limits for hydrocarbons using Laser Raman methods have been quoted as 1-7 ppm with a range resolution of 10 m (118). Direct current discharge emission spectra have been reported for selected organics (119). An advanced theoretical treatment of remote air pollution measurement has been published (120), in which several techniques made possible by the advent of high energy tunable laser sources are discussed and compared.

1.3.4. Methods for Specific Compounds

1.3.4.1. Ethylene (121) - Air is passed through 200 ml of a 0.1% methanolic solution of mercuric acetate at 500 ml min^{-1}. The solution is concentrated to 10 ml and a 1 ml aliquot applied to a TLC plate. After separation the band is removed and reacted with sodium borohydride releasing mercury, which is detected by atomic adsorption and is directly related to ethylene levels, which may be determined, it is claimed, to a detection limit of 0.1 ppm.

1.3.4.2. Benzene - It has been claimed (122) that benzene may by determined using a tube containing silica gel impregnated with paraformaldehyde and sulphuric acid. A critical appraisal (123) of another tube system showed that none of the tubes tested gave a result to within 25% in the 20 - 160 ppm range.

Several other 'chemical' methods which had been in use for many years prior to the advances in GC techniques have been reported (31) and may still be of value when instrumental methods are not practicable. These methods deal mainly with alkenes and aromatic species.

1.3.5. CALIBRATION

The types of analytical method described in this review do not determine the absolute amount of compound present but do measure a property of that compound which may be related to its concentration by an appropriate calibration procedure. Gas chromatographic techniques require particular care in calibration as the response of the many components of a complex mixture may vary non- linearly with relatively slight changes in operating parameters.

Gas mixtures containing very low but accurately known levels of organic compounds are extremely difficult to prepare. The techniques which are available for the generation of such standard gas mixtures fall into two categories, static and dynamic procedures. Static procedures are usually necessary in the preparation of multicomponent systems while dynamic methods are applied to the introduction of trace levels of single species into carrier or diluting gas streams.

A major problem in preparing very dilute mixtures is adsorption of trace components onto the walls of cylinders and tubing; this effect may be reduced by rigorous cleaning and careful choice of materials. Mixtures of saturated hydrocarbons in clean glass or metal containers are relatively stable. Unsaturated compounds however, especially acetylene and butadiene are slowly decomposed, particularly in the presence of water vapour and oxygen.

1.3.5.1. Static procedures

Mixtures may be prepared in glass containers or purchased as 'standard gases' in cylinders; it is often unwise to place too much reliance on commercially available standards without first checking them against their specification. Mixtures for less rigorous work can be prepared in plastic bags but these must be used rapidly to avoid excessive diffusion losses.

1.3.5.2. Dynamic procedures

Gas mixing pumps are available and the use of a two stage apparatus has enabled the production of standards down to 1 ppm concentration levels. Another system, suitable for work not demanding the highest accuracy, employs motor driven syringes.

1.3.5.3. Permeation and diffusion tubes

A more sophisticated and extremely accurate dynamic procedure employs permeation tubes, in which the component of interest as the liquid or gas phase is enclosed in a cylindrical ampoule made of plastic (often PTFE). After a certain induction period the material permeates slowly through the plastic at a uniform rate by a diffusion controlled process. An apparatus based on this principle requires precise and stable control of two physical parameters, temperatures and dilution gas flow rate. These parameters are readily controlled to within 1% and thus the overall precision of the system is high. The absolute amount of a compound released has been determined in several ways; for liquid hydrocarbons gravimetric methods are accurate and simple to perform. Such techniques allow the confident production of standards at the ppb level. Diffusion tubes may also be used to produce mixtures at similar concentrations. Although not specifically relating to their application to hydrocarbons, the principles of operation of permeation and diffusion tube devices have been extensively discussed (124 - 128).

1.3.5.4. Capillary restricted flow

In this method the calibration component to be diluted is dosed into a carrier gas stream through a restricting capillary. The concentration is calculated in accordance with the flow laws of

Hagen-Poiseuille. As the capillary radius enters these calculations raised to the 4th power it must be known precisely. This procedure has application as an absolute primary standard with an accuracy of 1-2% (129).

1.4. DEVELOPMENT OF SAMPLING TECHNIQUES

1.4.1. Introduction

Two sampling systems were developed which allow the collection of representative environmental samples for use in a mobile laboratory or at sites which have no electricity supply.

The high volatility of low molecular weight hydrocarbons necessitates the use of cryogenic sampling procedures to ensure 100% retention, whereas for higher molecular weight compounds ($\geqslant C_6$) adsorption onto solid adsorbents is the preferred technique for routine analysis. Care must be taken however, when using solid adsorbents that a valid sample is collected. Particular attention must be directed towards the determination of the 'breakthrough volume', the sampled air volume at which the compound being collected begins to elute from the tube. The breakthrough volume is related to the gas chromatographic retention time of the compounds at ambient temperature, the adsorbent acting as the stationary phase and the sampled air as the carrier gas. An equilibrium position will be reached where if the ambient concentration of the compound remains constant, the amount of the compound being adsorbed will be equal to the amount eluting from the tube.

The choice of adsorbent used in a particular situation depends upon the chemical properties of the compounds to be sampled and subsequently analysed. The following criteria must be considered: quantitative collection efficiencies and recovery of trapped vapours, high breakthrough volumes, minimal decomposition or polymerisation of sample constituents during collection and recovery, low background contribution from the adsorbent and little or no affinity of the adsorbent for water.

The parameters involved in determining the performance of the sampling system can be divided into two categories:- those related to the sampling environment such as sample flow rate, sampling time, air temperature and humidity and those related to the physiochemical properties of the adsorbent such as surface area, particle size and porosity, solute capacity, adsorption mechanism and degree of solute affinity. Furthermore, some of the factors which influence adsorbent performance are not independent of each other.

At least nanogram quantities of each compound to be identified have to be collected if a gas chromatographic/mass spectral analysis is required, but under certain circumstances, using a solid adsorbent, this may be impossible to achieve.

With cryogenic sampling techniques problems also arise, one of which is the formation of ice in the sampling tube caused by the condensation of water vapour from the atmosphere. However, this can be overcome if a suitable dessicant e.g. potassium carbonate is used. The number of cryogens available which are safe to use in a mobile laboratory, are easily transportable and give the required temperature range is limited. Liquid nitrogen has the disadvantage of trapping out oxygen from the sampled air which on rapid evaporation is liable to extinguish the flame on the flame ionisation detector. Liquid oxygen and solvent systems e.g. carbon dioxide-acetone are unsuitable for use in an enclosed environment, and the temperature achieved with solvent systems has the added disadvantage of not trapping out the more volatile compounds. With these considerations in mind a cryogenic sampling unit was designed and constructed in collaboration with Oxford Instruments.

1.4.2. Calibration

To develop and evaluate analytical procedures for gases and vapours effectively, it must be possible to prepare known concentrations of those materials in air or other gases. Gaseous air pollutants must be prepared in the microgram per cubic metre range and permeation devices offer a simple method of preparing these low concentrations. The tubes made out of Teflon emit the pollutant at a constant rate when held at constant temperature. The permeation process depends primarily on the dissolution of the vapour in Teflon, diffusion through the Teflon wall and evaporation from the outer surface, the driving force being the difference in partial pressure between the inner and outer walls of the tube. The process is highly temperature dependent and the temperature must be controlled to within $\pm$ 0.1°C.

The permeation rate F is given by:

$$F = F_o e^{-\left(\frac{E}{RT}\right)}$$

E the activation temperature is rather high (~ 10 kcal) for PTFE and therefore the rate is very sensitive to the change in temperature.

The output of the tube is directly proportional to its length and the following equation has been derived, from which the output rate at one temperature can be predicted from the known rate of another.

$$\log R_1 = \log R_2 - .2950 \left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

T is in °K

This relationship will be accurate to within 5% for a 10°C change in temperature.

Each permeation tube requires individual calibration, and this was done gravimetrically over a period of 3-4 weeks. Permeation tubes used in the experiments were either purchased from Analytical Instrument Development Inc. or made in the laboratory according to the method described by Scaringelli (124).

A model 1901 AA permeation tube oven supplied by Analysis Automation was used in the following experiments.

At 50°C the permeation rates for benzene and toluene were 1.63 µg min^{-1} and 1.25 µg min^{-1} respectively.

The cryostat was also evaluated using $C_1 - C_4$ hydrocarbon standard gas mixtures which were purchased from Phase Separation. A flow of nitrogen was passed through the 'U' tube and the hydrocarbon mixtures injected into the gas stream.

1.4.3. Oxford Instruments Cryostat

The cryostat Figure 1 has a temperature range of -196°C to 300°C. This is achieved by differential cooling and heating between liquid nitrogen and a 240 watt cartridge heater. The sampling tube can be temperature programmed so that there is some separation of material prior to its introduction into the gas chromatograph.

The liquid nitrogen can is surrounded by two independent vacuum chambers. The inner chamber contains the liquid nitrogen can with an integral carbon adsorption pump. The outer vacuum space contains the 'U' tube, heat exchanger, heater and temperature sensors. By having two independent vacuum chambers interconnected via an isolation valve it is possible to change the 'U' tube without removing the

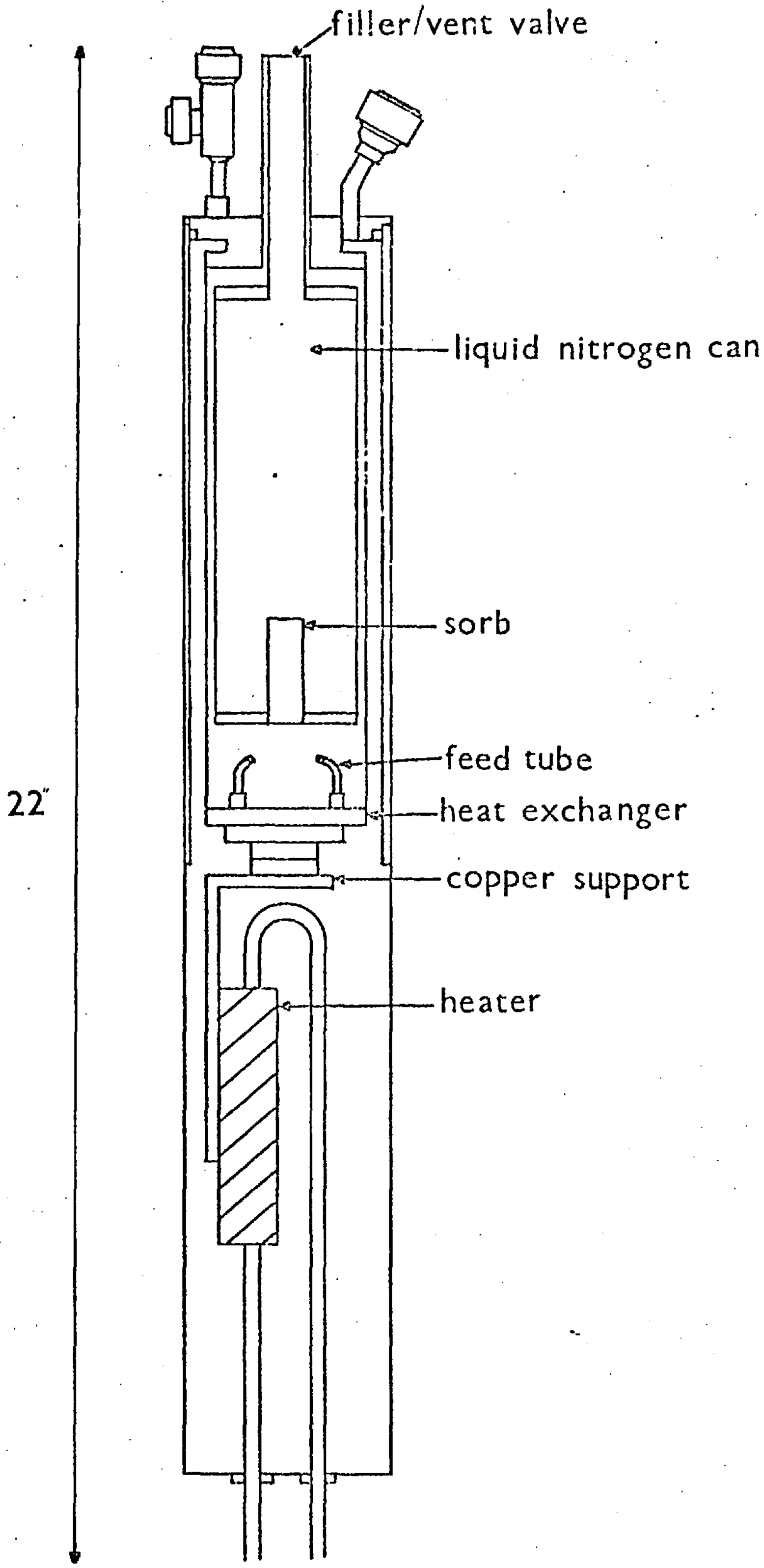


FIGURE 1 Oxford Instruments Cryostat

refrigerant. The 'U' tube is only packed with adsorbent along the length of the cartridge heater. Once the sampling temperature has been achieved and the can refilled with liquid nitrogen, the supply will last for approximately 4 hours.

In a remote area with no electricity supply, sampling is carried out at -196°C. Prior to analysis liquid oxygen that has been condensed out in the 'U' tube, can, with controlled heating, be slowly evaporated so that it does not interfere with the subsequent chromatographic analysis of the adsorbed material.

1.4.3.1. Mode of Use

The required sampling temperature is set on the temperature controller. Once sampling is complete the cryostat is connected to a 6 port valve on the gas chromatograph which is connected into the carrier gas flow just prior to the injection port. The flow is switched to travel through the 'U' tube and the temperature programme to elute the adsorbed material commenced. Sampling and elution are always carried out with opposed gas flows.

1.4.4. An Adsorption Technique for Sampling Hydrocarbons at Ambient Temperatures

Heat desorption for the recovery of the adsorbed material was preferred to solvent extraction for the following reasons. If solvent extraction is used as a method for removal of the hydrocarbons, considerable sample dilution occurs. Micro Soxhlet extractions have been used as a means of reducing dilution, but they still suffer from loss of the more volatile components of the extracted material. A further disadvantage, particularly where volatile organic materials are involved is the limiting source pressure that can be tolerated in a mass spectrometer system. Not only would the solvent mask several compounds being separated in the gas chromatograph, but it would limit, very considerably, the detection of small quantities of material passing into the ion source.

Ambient levels of hydrocarbons necessitate total desorption of the adsorbed material if relatively short sampling periods of 15-60 mins are used so that the subsequent GC analysis is satisfactory.

1.4.4.1. Mode of Use

The organics of interest are collected by passing the gas stream to be analysed, at a controlled rate through a stainless steel tube packed with a solid adsorbent.

Desorption and analysis are carried out by attaching one of the sample tubes to a Carle valve which is connected to the gas chromatograph carrier gas line just prior to the injection port. The valve is contained in a thermostatically controlled oven capable of being heated to 300°C. Following connection the whole system is warmed to 200°C whilst carrier gas passes through a closed loop on the valve. When this temperature has been reached the carrier gas is diverted to flow through the tube. The carrier gas is left to flow continuously through the sample tube to achieve complete desorption of the adsorbed material.

1.4.5. Pulsed Flow Desorption of Adsorbent Tube

A modification of the solid adsorbent technique was devised to give more information about the breakthrough volume of the adsorbed material on the adsorption tube. Instead of allowing the carrier gas to flow continuously through the tube to effect complete desorption, the flow was pulsed through the tube, by means of a valve system.

1.4.5.1. Mode of Use

After sampling onto the adsorbent, desorption is accomplished using an automated gas sampling valve system. Two Carle 6 port sampling valves are linked in series and connected into the carrier gas line just prior to the injection port. The whole system is enclosed in a thermostatically controlled oven which can be maintained at any temperature up to 300°C, the carrier gas being allowed to flow through a loop on valve 1. Valve 2 selects the tube to be eluted and a timed elution is carried out with the aid of a preset valve actuator. This, when operated, opens valve 1 for a known period. A timing device is fitted to this actuator so that valve 1 can be opened automatically at set intervals in the range 15 secs to 30 mins. The length of time the tube is heated, the temperature to which it is heated, the time of each elution and the time between elutions all have to be standardised to obtain reproducibility.

1.4.6. Evaluation of the Sampling Systems

The sampling devices described in Sections 1.4.3. and 1.4.4. were evaluated so that they could be used with confidence to sample ambient concentrations of hydrocarbons.

A check was made on the purity of the nitrogen carrier gas to ensure there was no contribution to the results obtained from this source. No significant interference was discovered at the normal permeation rates used but at low permeation rates the nitrogen was purified by first passing it through a packed 'U' tube cooled in liquid nitrogen. When using the permeation tube system the sampling devices were connected directly to the outlet of one of the oven tubes.

For testing the Oxford Instruments sampler with C_1- C_4 hydrocarbon mixtures a continuous flow of nitrogen was passed through the cryostat and the standard gas mixes injected into this through a septum in the carrier gas line.

When testing the effectiveness of dessicants the carrier gas stream was first bubbled through water then passed through the drying tube and then to the sampler.

1.4.6.1. Preparation of the Sampling Tubes

The sampling tubes were constructed by packing 0.35g Chromosorb 102 into 3 x ½ in o.d. stainless steel tubes. Each end was plugged with glass wool and the tubes purged at 230°C with a carrier gas flow of 20 ml min^{-1} for 24 hours. On heating, the polymeric beads shrink and it was necessary to repack the tubes after the initial purging, and then purge for a further 12 hours.

1.4.6.2. Gas Chromatographic Operating Conditions

Separation of the eluted material (with a carbon number greater than 6) was performed on a Hewlett Packard 5700 gas chromatograph. The column was 20 ft x 1/8 in o.d. stainless steel column packed with 3% OV7 on Chromosorb W AWDMCS. The nitrogen carrier gas flow was 30 ml min^{-1}. Separation of the C_1- C_5 hydrocarbons was accomplished using an 8 ft x 1/8 in o.d. stainless steel column packed with Chromosorb 102. The nitrogen carrier gas flow was 30 ml min^{-1}. This column allowed separation of these compounds at ambient temperature, which is desirable for routine analysis in a mobile laboratory.

1.4.6.3. An Evaluation of the Oxford Instrument Cryostat

In all of the following experiments the cryostat 'U' tube was packed with glass beads.

Reproducibility and Accuracy

The reproducibility of the cryostat was first tested by sampling replicate amounts of benzene and measuring the resultant peak areas, the cryostat being operated at -50°C with a carrier gas flow rate of 80 ml min^{-1}.

Table 1.4. Sampling Replicate Amounts of Benzene

Benzene	Peak Area
8.15 µg	159, 154, 158, 164, 158 mean = 159 ± 5 6% Error

These results are similar to the scatter that are obtained from direct injections of benzene onto the gas chromatographic column, and are typical of the spread of results obtained in the subsequent experiments where only the mean value from five determinations is reported in Tables 1.5 - 1.9

Known quantities of benzene and toluene were sampled, operating the cryostat at -50°C with a nitrogen carrier gas flow rate of 80 ml min^{-1}. The results obtained were compared with direct injections onto the analytical column of similar quantities of these compounds.

Table 1.5. A Comparison of Measurements Obtained Using the Cryostat with those Obtained by Direct Injection of Benzene

CRYOSTAT		DIRECT INJECTION	
µg	Peak Area	µg	Peak Area
1.63	33	1.76	31
4.89	91	3.52	65
6.52	127	5.28	92
8.15	158	7.04	150
10.59	226	11.26	221
12.22	245	14.08	269
15.48	316	21.12	404
16.30	327		

Table 1.6. A Comparison of Measurements Obtained Using the Cryostat with those Obtained by Direct Injection of Toluene

CRYOSTAT		DIRECT INJECTION	
µg	Peak Area	µg	Peak Area
1.25	28	1.63	32
3.75	70	3.26	62
5.00	97	4.89	90
6.25	117	6.52	139
8.12	154	10.43	201
9.37	183	13.04	244
11.25	234	19.56	366

These data illustrate that the results obtained using the cryostat are very similar to those obtained by direct injection, the difference over the range measured being 4%. An error of this magnitude could be attributed to inaccuracy in measuring the peak area and to a slight variation in the carrier gas flow rate when it passes through the cryostat which will effect the response.

Effect of Sampling Flow Rate

The effect of sampling flow rate on the amount of the compound adsorbed was investigated and the results presented in Tables 1.7 and 1.8. The cryostat was operated at -25°C.

Table 1.7. Effect of Sampling Flow Rate on the Quantity of Benzene Trapped

ml min^{-1}	Peak Area	% Efficiency
80	93	100
190	92	99
400	81	87
680	66	71
880	53	57
1150	36	38
1350	24	26
1550	14	15

Table 1.8. Effect of Sampling Flow Rate on the Quantity of Toluene Trapped

ml min^{-1}	Peak Area	% Efficiency
80	70	100
400	69	99
680	67	96
880	66	94
1150	61	87
1350	55	79
1550	50	72

These data clearly demonstrate that as the sampling flow rate increases the amount of benzene and toluene trapped decreases. The rate of decrease is faster for benzene which might be expected as it has a lower boiling point (80°C) than toluene (110°C).

Effect of Sampling Temperature

The sampling flow rate was 400 ml min^{-1}, the tube packed with glass beads and 4.89 µg of benzene and 3.75 µg of toluene were sampled in each instance.

Table 1.9. Effect of Sampling Temperature on the Quantity of Benzene Trapped

Temperature °C	Peak Area	% Efficiency
50	4	4
25	43	49
0	72	79
-15	82	90
-40	89	98
-75	91	100

Table 1.10. Effect of Sampling Temperature on the Quantity of Toluene Trapped

Temperature °C	Peak Area	% Efficiency
75	4	5
50	34	48
25	50	71
0	63	89
-15	67	96
-40	69	99
-75	70	100

These data demonstrate that the amount of benzene and toluene trapped increases with a decrease in the sampling temperature. At any given temperature above that at which 100% retention occurs, there is more toluene than benzene trapped. This is again consistent with the difference in their boiling points.

Sampling C_1-C_4 Hydrocarbon Mixtures

Sampling was carried out at -180°C to prevent oxygen condensing in the 'U' tube. The C_2-C_4 hydrocarbons were trapped quantitatively at flow rates of up to 200 ml min^{-1}. To trap methane quantitatively it was necessary to pack the 'U' tube with a solid adsorbent.

However, in a field sampling situation where the mobile laboratory was being used it would not be essential to trap methane as it can be determined routinely using a Beckman Air Quality Chromatograph. It could however act as a comparison between the two techniques.

Use of Dessicant

From the literature it appeared that potassium carbonate would prove to be the best dessicant. When tests were carried out results showed that potassium carbonate was effective in trapping the water and yet did not trap any of the hydrocarbons of interest, therefore a potassium carbonate column was used when sampling, to prevent the formation of ice in the sampling tube.

Sampling C_1- C_{10} Hydrocarbon Mixtures

Standard compounds in the C_1- C_{10} range were sampled and analysed reproducibly and repetitively, excepting methane. Some separation of the compounds was possible by temperature programming the 'U' tube prior to introduction into the gas chromatograph.

The standard mixtures were produced by injecting known volumes of the C_5- C_{10} hydrocarbons into a glass vessel which was warmed to aid evaporation of the liquids. C_1- C_4 hydrocarbon mixtures were then injected into the vessel. Aliquots of this mixture were then used to test the cryostat using the same method as used for the C_1- C_4 hydrocarbons.

It was again impossible to quantitatively trap methane at -180°C. This however can be of some advantage when taking environmental samples because the concentration of methane in the atmosphere is usually two orders of magnitude greater than that of other hydrocarbons and it can complicate the gas chromatographic analysis of the sample.

Conclusion

The cryostat has several advantages over other sampling techniques that are currently available. It is easily portable which is advantageous when sampling in remote areas and the results obtained are consistent. By the choice and control of the sampling temperature it is possible to ignore certain of the more volatile compounds, however, if required, it is possible to sample and then subsequently analyse the complete C_1-C_{12} range of compounds from one sample. A certain amount of separation of the adsorbed material prior to introduction in the gas chromatograph is possible by temperature programming the 'U' tube. With the cryostat it is possible to sample large volumes of air with confidence that a truly representative sample is being collected. This is important when a gas chromatographic/mass spectral analysis is required and nanogram quantities of each compound to be identified must be collected.

Greater breakthrough volumes are achieved when sampling at subambient temperatures. Samples collected in this manner may be stored at ambient temperature with no apparent loss of hydrocarbons with 5 or more carbon atoms.

1.4.6.4. An Evaluation of Chromosorb 102 as an Adsorbent for Sampling Organics at Ambient Temperature using Pulsed Flow Desorption

Samples were collected on Chromosorb 102 and the tubes were then placed in the oven and the temperature allowed to stabilise at $130^{\circ}C$ for periods of time in the range 10 - 60 minutes, the configuration of the tube in the oven being of the utmost importance. Two characteristic types of trace may be obtained from a sampling plug. The first is produced when the direction of gas flow is similar in both the sampling and elution phases. A second type is generated when sampling and elution are carried out with the gas flow in opposite directions. This is illustrated in Figures 2 and 3. By pulsing the carrier gas flow through the sample tube it was possible to deduce from the traces obtained the chromatographic characteristics of the sample plug, and using these the breakthrough volume was calculated.

After some initial experiments sampling on to different tubes, it was found that the variation in pressure drop across individual tubes affected the retention time and therefore the breakthrough volume. However, when the pressure drop across the tubes was the same the traces obtained were almost identical. A value for the pressure drop was determined as a function of the change in flow indicated on the rotameter when the adsorbent tube was removed from the exit pipe of the permeation tube oven. It is given as $\frac{F2-F1}{F2}$ where F2 is the gas flow rate indicated on the rotameter with the tube removed and F1 is the gas flow rate at which sampling occurred.

The number of elutions to the peak maxima gives an indication of the retention time of benzene on the sampling tube.

The tubes in the following experiments were all eluted with the carrier gas flow passing in the same direction as when sampling

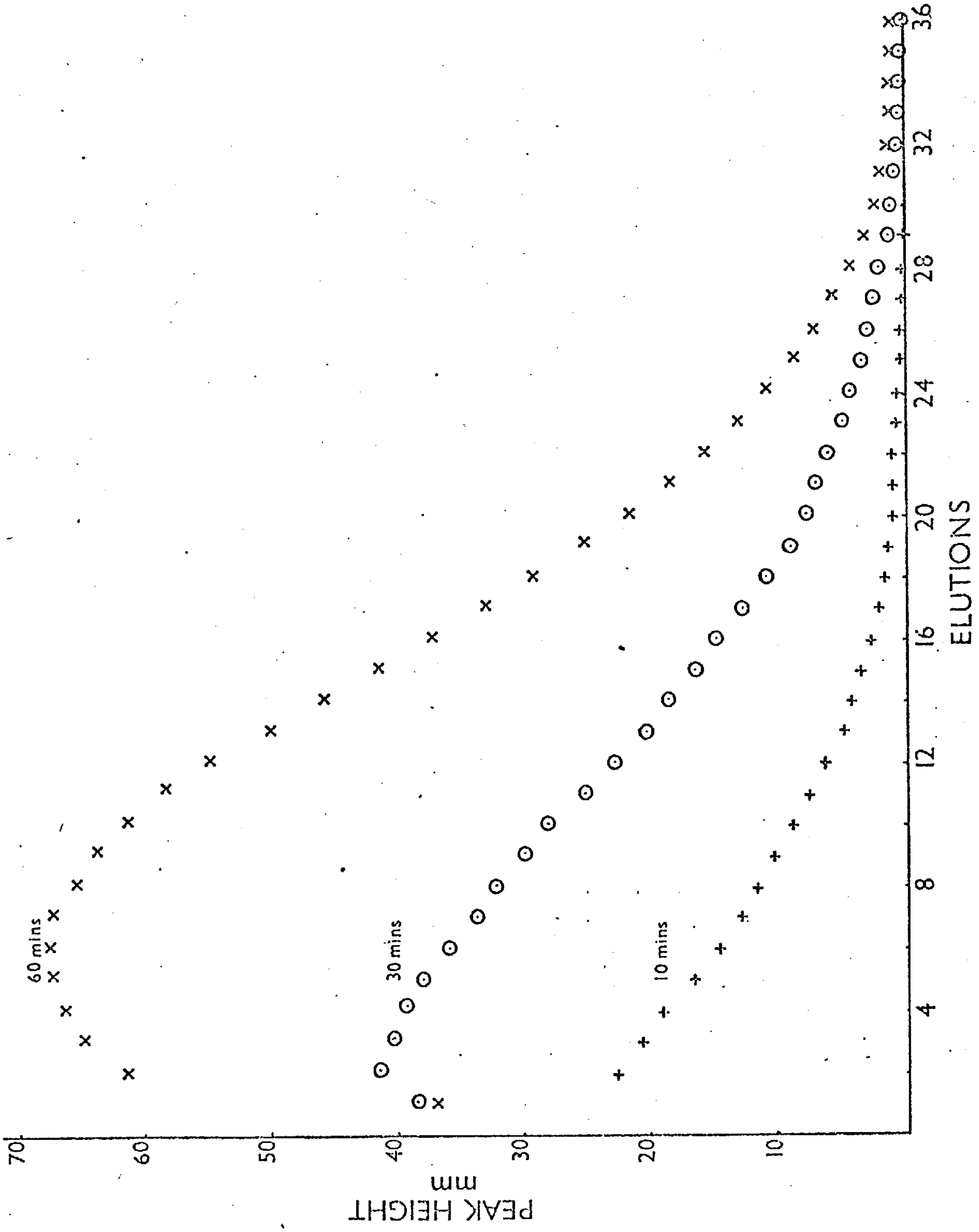


FIGURE 2 Sampling and Elution of an Adsorbent Tube with the Gas Flow in Opposite Directions (sampling periods as indicated)

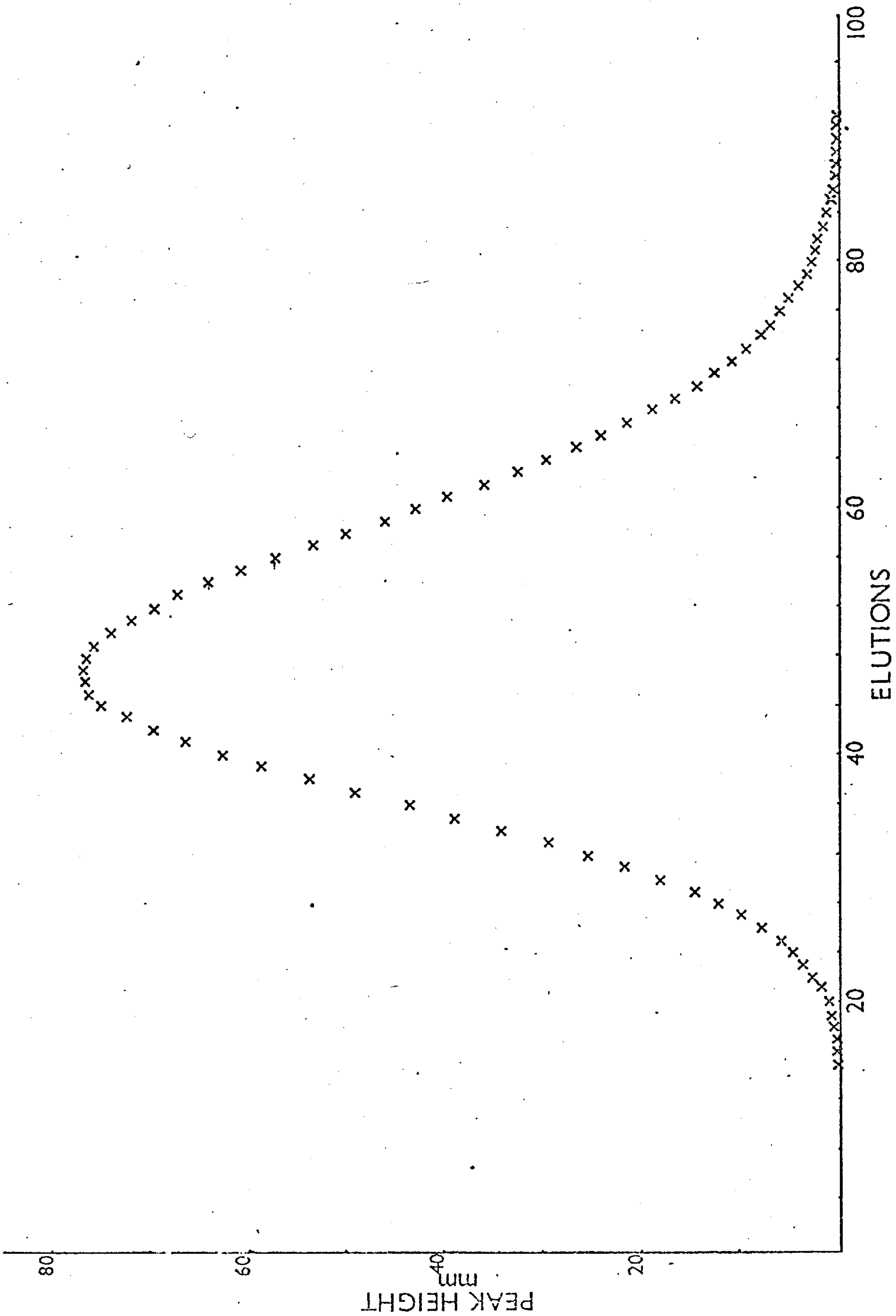


FIGURE 3 Sampling and Elution of an Adsorbent Tube with the Gas Flow in the Same Direction

occurred. In each of the following instances Table 1.11, 16.2 µg of benzene were sampled at a flow rate of 80 ml $\min^{-1}$ over a ten minute time period.

Table 1.11. The effect of flow drop and length of time the tube is left in the oven on the observed retention time

TIME LEFT IN OVEN AT 130°C Min	FLOW DROP $\frac{F_2 - F_1}{F_2}$	NO. OF ELUTIONS TO PEAK MAXIMA	PEAK AREA
10	0.86	65	45
10	0.78	75	45
15	0.85	60	42
15	0.78	67	44
30	0.83	49	42
30	0.74	52	43
30	0.76	54	46
40	0.79	44	46
40	0.78	44	44
50	0.83	43	42
50	0.79	43	46
50	0.79	45	43
60	0.74	37	42

A comparison of peak areas obtained illustrates the reproducibility of the technique, the mean peak area being 44 ± 2. The data also indicates that if the pressure drop across the tube increases then the retention time decreases. The observed retention time is dependent not only upon the pressure drop but also upon the length of time the tube is left in the oven. Therefore for further work where reproducibility is required the pressure drop and the length of time the tube is left in the oven have to be related to standard conditions and preferably should be kept constant.

Benzene was then sampled on to tubes having similar pressure drops, the sampling flow rate being kept constant at 80 ml $\min^{-1}$ and the tubes left in the oven for 30 minutes. The data in the following Table 1.12 gives the mean value from 5 determinations for each quantity of benzene sampled.

Table 1.12. Sampling different quantities of benzene

Weight of Benzene µg	Total Volume of Carrier Gas ml	Number of Elutions to Peak Maximum	Peak Area	Peak Height	Peak Gradient
8.15	400	49	63	4.9	0.38
16.30	800	48	140	10.6	0.80
48.90	2400	46	282	20.6	1.50
97.80	4800	44	813	55.3	3.75
163.00	8000	41	1372	92.4	6.22
250.00	12000	38	2148	135.1	8.80
366.80	18000	35	3087	203.0	13.40

On consideration of this data it can be seen that there is an inverse relationship between the volume of gas sampled and the observed retention time, Figure 4. As would be expected there is a linear relationship between the quantity of benzene sampled and the peak area obtained. From these results it is possible to calculate the breakthrough volume.

Table 1.13. The effect of volume of gas sampled on the position of the leading edge of the benzene peak

Sampled Air Volume ml	No. of Elutions to Peak Maximum	No. of Elutions from the Middle to the Edge of the Peak	Position of Leading Edge of the Peak Calculated	From Trace
400	49	26	23	24
800	48	26	22	23
2400	46	27	19	17
4800	44	29	15	13
8000	41	30	11	10
12000	38	31	7	7
18000	34	32	2	2

The position of the leading edge of the peak can be calculated from the gradient and the position of the peak maxima.

The breakthrough volume is determined by plotting the sampled air volume against the number of elutions to the leading edge of the peak Figure 5. The breakthrough volume is given by the intercept of the line with the x-axis which is ~21 litres. The

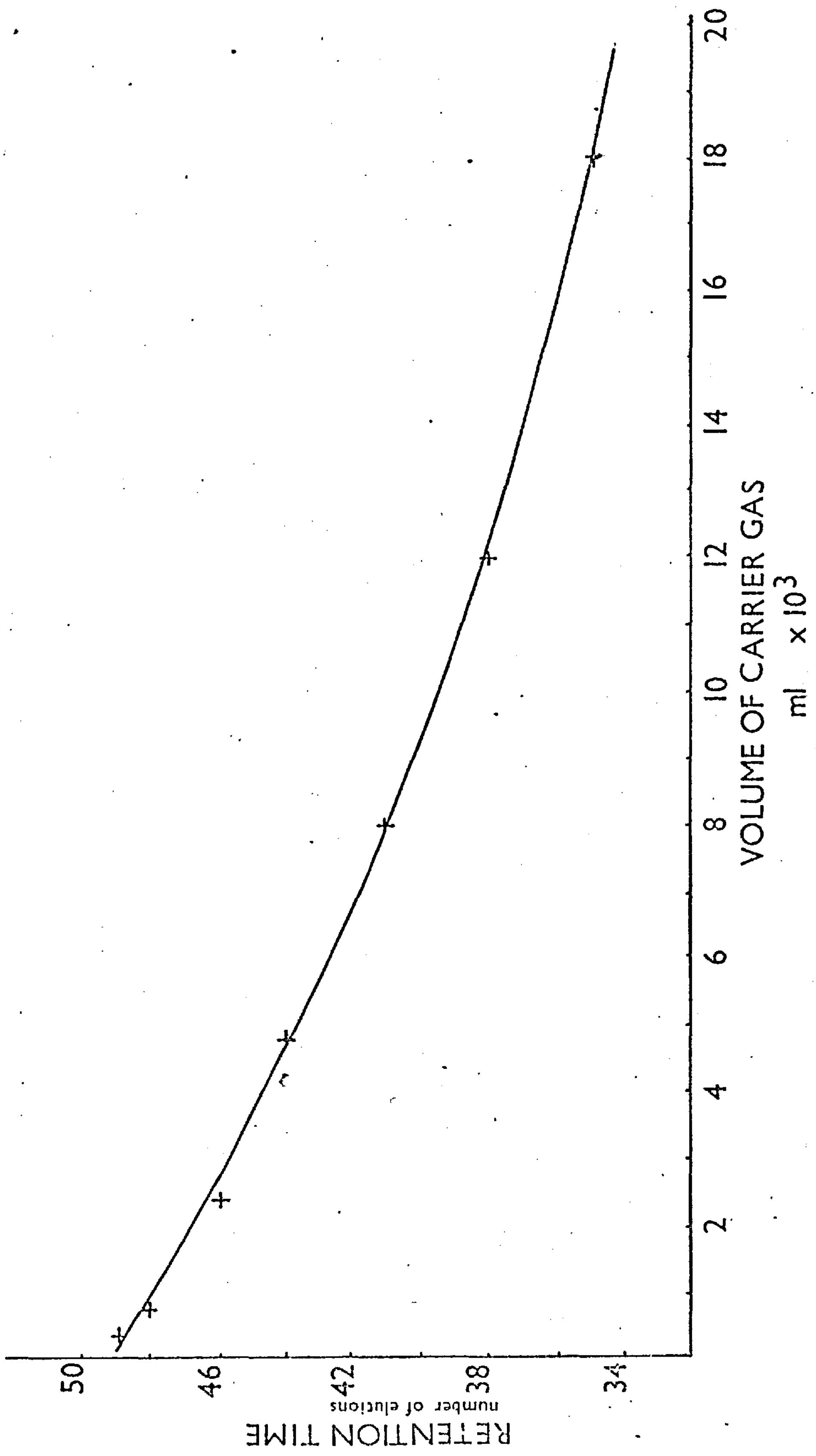


FIGURE 4 Relationship Between Retention Time on a Sampling Tube and the Sampled Air Volume

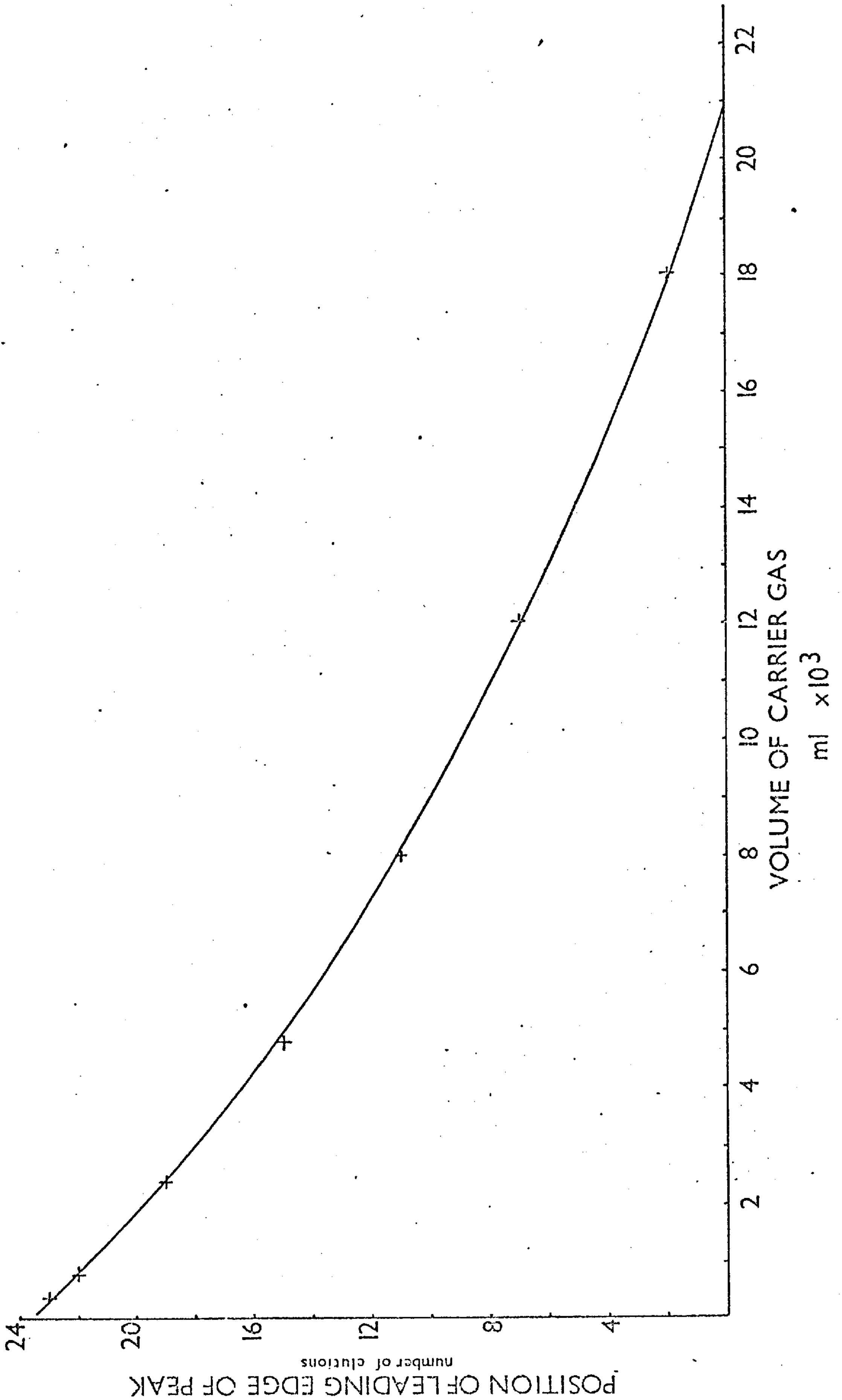


FIGURE 5 Determination of the Breakthrough Volume of Benzene

breakthrough volume will have been exceeded if the calculated position for the start of the peak yields a negative value. The attenuator setting on the gas chromatograph will have some effect on the observed starting position of the peak and for this reason the setting was adjusted so that the maximum peak height was as close to two-thirds full scale deflection as possible. In this way the relative response of the first part of the peak was similar in every case. The attenuator setting has no effect on the calculated value.

The length of time the tube is left in the oven will affect to some extent the breakthrough volume calculated in this manner. The longer the tube is left in the oven the shorter the value for the breakthrough volume will be.

Taking into consideration these limitations and also the variations caused by; differing flow drops across various tubes, slight differences in chromatographic packing, sampling tube packing techniques and sampling conditions, it is advisable to sample only 75 - 85% of the breakthrough volume when taking environmental samples.

Effect of Flow Rate

It was found for the flow rates tested, that the most important consideration was not the flow rate but the volume of gas flowing during the sampling period.

Table 1.14. Effect of flow rate on sampling.

ml min^{-1}	Total Volume of Gas ml	No. of Elutions to Peak Maximum	No. of Elutions to Leading Edge of Peak
80	800	48	23
275	2750	46	19
660	6600	43	13

The positions of the peak maxima lie close to the straight line on the graph Figure 4.

Effect of Benzene Concentration on Sampling

The temperature of the permeation tube oven was altered so that different concentrations of benzene could be produced for the same carrier gas flow rate which was kept at 80 ml min^{-1}, the sampling period being ten minutes.

Table 1.15. The effect of benzene concentration on sampling.

Permeation Temperature	Benzene µg min^{-1}	Observed Position of Peak Maximum	Peak Area
40°C	0.83	49	66
50°C	1.63	48	138
60°C	3.10	48	210
70°C	5.55	47	350

The variation of the concentration in the carrier gas has little effect on the adsorption characteristics as is illustrated by the above data.

The Effect of Carrier Gas Flow

Benzene was sampled for ten minutes at a flow rate of 80 ml min^{-1} and then pure carrier gas was passed through the tube at the same flow rate. This had the effect of moving the adsorbed material down the tube.

Table 1.16. The effect of passing further carrier gas through a sampling tube after having sampled benzene.

Observed Position of Peak Maximum	Volume of Air Sampled ml
48	800
48	1600
47	2400
46	3200
45	4000

These results are also in accord with the conclusion that it is the total amount of sampled air that is the most important consideration. The position of the peak maxima falling on the line obtained in the graph, Figure 4.

Effect of Oven Temperature

The effect of varying the sampling tube oven temperature was investigated briefly. On increasing the oven temperature the retention time decreased and the peak was sharper, and on decreasing the temperature the retention time increased and the peak was broader. The oven temperature has no effect on the breakthrough volume determined in the manner described earlier, it only affects the gradient of the line plotted from the data.

Storage of Sample

Various tubes were stored at ambient temperature wrapped in aluminium foil up to seven days before an analysis was carried out. No decrease in the amount of adsorbed material was observed on subsequent analysis of these tubes.

Breakthrough Volume of Other Compounds

Both toluene and o-xylene were sampled on to the sampling tubes. On analysis the breakthrough volume of o-xylene was found to be greater than that of toluene which was greater than that of benzene, which is as expected.

Moisture Content of the Carrier Gas

When the carrier gas was bubbled through water prior to passing through the sampling tube, no significant alteration in the breakthrough volumes was observed.

Sampling onto Two Tubes Connected in Series

Environmental samples were collected passing the air through two tubes connected in series under differing environmental conditions, i.e. temperature and relative humidity. When only 75-85% of the breakthrough volume was sampled no compounds of interest were ever determined in the second tube although the presence of other more volatile compounds was often observed.

Conclusions

It would appear that satisfactory representative environmental samples can be collected with tubes containing 0.35g Chromosorb 102, if no more than 75-85% of the calculated breakthrough volume for the most volatile compound to be analysed is sampled. Samples collected in this manner can be stored for up to 7 days which is convenient if a sampling programme is being conducted at sites away from the laboratory.

Environmental samples were taken using similar tubes and the results are recorded in Chapter 2.

1.4.6.5. An Evaluation of the Elscint Sampling Device

Using the same criteria as were used for the sampling techniques described previously in Sections 1.4.3. and 1.4.4. a commercially available instrument was evaluated for sampling ppb levels of organics in the atmosphere.

Mode of operation:-

A short column of adsorbent is housed in a Teflon cartridge, Figure 6. After adsorption onto this column desorption is accomplished by the heat generated by a pulse of electricity passing through the platinum coil. The desorption temperature can be set in the range 200-400°C. The instrument contains an automatically controlled pump so that the sampling time and flow rate can be preset.

Although the makers claimed that there was almost total desorption of the adsorbed material with the first elution it was found that significant amounts were eluted on subsequent heat pulses.

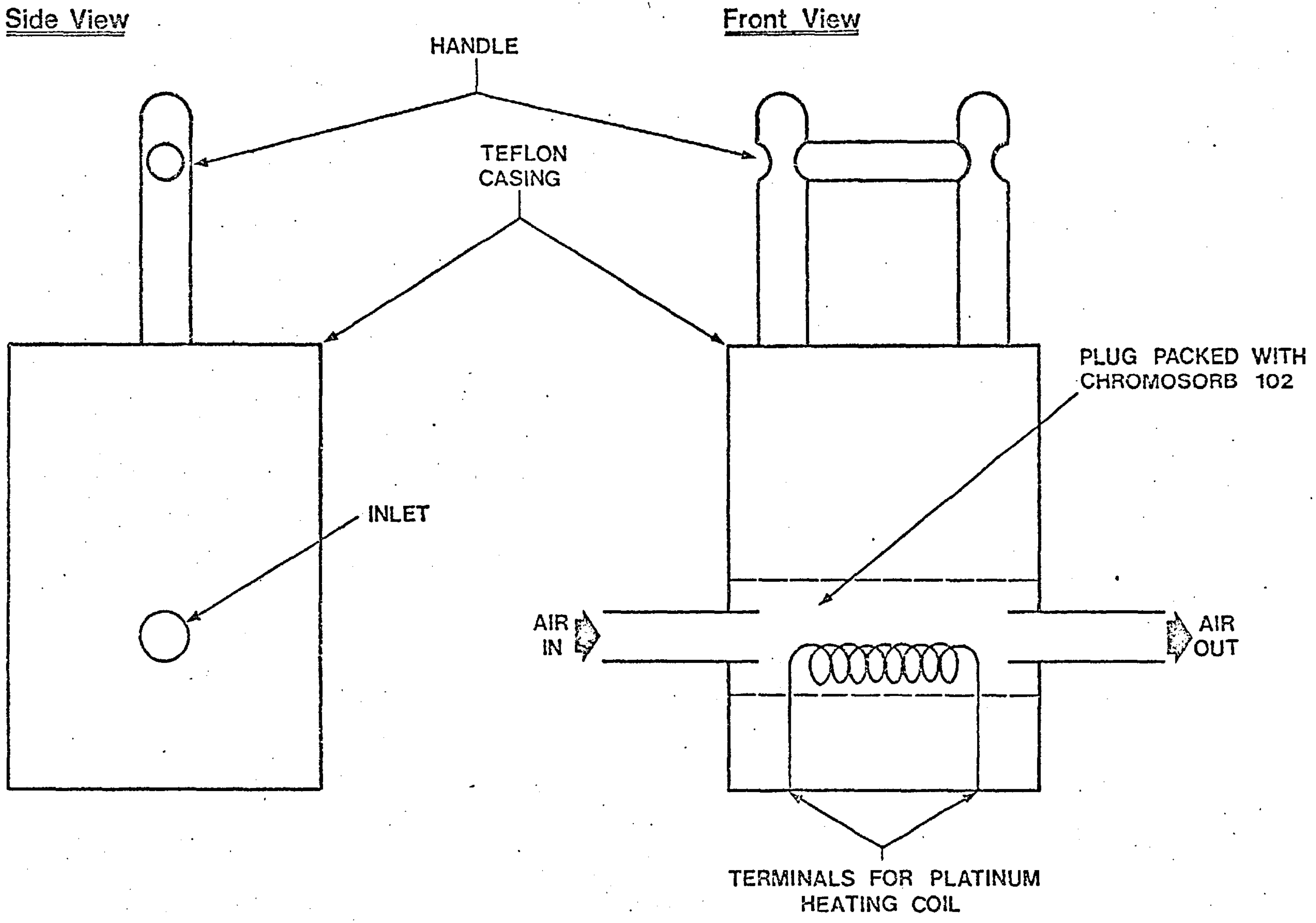


FIGURE 6 Elscint Sampling Plug

Experimental

An investigation into the adsorption/desorption characteristics for two terpenes, α-pinene and β-caryophyllene on Elscint plugs packed with either Chromosorb 102 or activated charcoal was carried out.

Standard atmospheres of these two terpenes were generated using the permeation tube oven. The oven was operated at a constant temperature of 50°C and the permeation rates, determined gravimetrically, were found to be 2.19 $\mu g\ min^{-1}$ for α-pinene and 0.17 $\mu g\ min^{-1}$ for β-caryophyllene. Sampling times of 3 and 30 minutes were employed for α-pinene and β-caryophyllene respectively, and thus sampling plugs were exposed to either 6.57 µg α-pinene or 5.10 µg β-caryophyllene.

In an attempt to increase the efficiency of trapping the terpene species during headspace analysis the method of packing the sampling plugs was modified. In order to increase the surface area of packing material in the plug, and thus increase the contact between the packing and the sample stream drawn through the plug, packing was placed inside the platinum coil and kept in position by glass-wool wadding.

The maximum amount of packing material which can be accommodated by a sampling plug was found to be 0.06g. Typically 0.03g of packing material was used at a sampling flow rate of 80 $ml\ min^{-1}$ and a filament temperature control setting of 10 (an indication of the temperature of desorption).

RESULTS USING THE ELSCINT SAMPLING SYSTEM

The data contained in Table 1.17 illustrate the effect of variation in the quantity of Chromosorb 102 packing material for three nominally similar sampling plugs. The results are expressed as relative peak areas for α-pinene, sampled and eluted under standard conditions using FID.

Table 1.17 α-pinene on Chromosorb 102

Elution	0.03g Chromosorb 102 Plug 1	4	5	mean	0.06g Chromosorb 102 Plug 1	4	5	mean
1st	224	368	308	300	256	1616	497	713
2nd	56	61	70	62	244	553	290	362
3rd	15	41	22	26	93	132	274	166

These data indicate that the type of problems associated with the irreproducibility of such a technique are more evident for a packing of 0.06g. Although an increase of 100% in weight of packing material for plug 4 gave, initially, a 400% increase in α-pinene eluted and detected, the effect for plug 1 was negligible. A standard weight of packing material (0.03g) was, therefore, adopted for all subsequent experiments.

Table 1.18 contains the relative peak areas for α-pinene sampled onto 5 similar sampling plugs packed with Chromosorb 102 under similar conditions.

Table 1.18 α-pinene on Chromosorb 102

Elution	Plug 1	2	3	4	5	mean
1st	585	170	86	160	128	195
2nd	65	172	135	245	110	145
3rd	70	195	90	196	52	120
4th	87	213	57	177	54	118
5th	96	204	75	74	53	100

Tables 1.19 - 1.21 contain relative peak areas for combinations of terpene and packing material as indicated.

Table 1.19 α-pinene on activated charcoal

Elution	Plug							
	1	2	4	5	1	4	5	mean
1st	230	37	50	48	26	165	55	87
2nd	20	8	7	15	8	38	22	17
3rd	13	3	3	7	3	15	8	7

Table 1.20 β-caryophyllene on Chromosorb 102

Elution	Plug			
	1	2	5	Mean
1st	16	72	42	43
2nd	13	27	17	19
3rd	9	17	14	13

Table 1.21 β-caryophyllene on activated charcoal

Elution	Plug				
	1	6	5	1	Mean
1st	17	8	30	12	16
2nd	2	0.7	3	3	2
3rd	*	*	*	*	*

* Not detected

The measured responses for β -caryophyllene recorded in Tables 1.20 and 1.21 were considerably lower than those obtained for ∝ -pinene, Tables 1.18 and 1.19. Tables 1.22 shows a comparison of the mean responses for several plugs adjusted to account for the fact that the original chromatograms were recorded on different recorder attenuations.

Table 1.22 Mean responses

Elution	∝ -pinene		β -caryophyllene	
	Chromosorb	Charcoal	Chromosorb	Charcoal
1st	195	87	10	4
2nd	145	17	4	0.5
3rd	120	7	3	*

*Not detected

The type of scatter in efficiencies observed for different plugs packed in a similar way also occurs for the same plug packed and re-packed under similar conditions. The data presented in Table 1.23 indicate that the characteristics for 2 plugs varied considerably over several packings of Chromosorb.

Table 1.23 Variation of response for similar plugs with change of packing material. ∝ -pinene on Chromosorb 102

Elution	Plug 4			Plug 5		
	0.03g	0.03g	0.06g	0.03g	0.03g	0.06g
1st	368	160	1616	308	128	497
2nd	61	245	553	70	110	290
3rd	41	195	132	22	52	274

It was noted that unpacked plugs 'trapped' the terpene species under study and that the adsorption/desorption characteristics of unpacked plugs vary considerably. Table 1.24 lists data comparing the efficiencies of two different plugs both packed and unpacked.

Table 1.24 α-pinene on packed and unpacked plugs

Elution	Plug 2		Plug 5	
	Packed Chromosorb 102	Unpacked	Packed Chromosorb 102	Unpacked
1st	531	35	304	126
2nd	104	6	240	24
3rd	98	3	160	6

For plug 5 the first elution from the unpacked plug is ~ 40% of the value from the same plug when packed with Chromosorb 102, whereas for plug 2 it is less than 7% of the value for the packed plug. These data clearly indicate that the condition of the filament will have a critical effect on the adsorption/desorption characteristic for a particular plug and will be yet another source of uncertainty in the results obtained for a range of plugs.

A series of experiments was carried out to determine the relationship between the amount eluted (desorption efficiency) and the filament temperature. It is not possible to determine the actual filament temperature, but for reproducible results it would be a requirement that a given filament control setting would generate the same temperature (within narrow limits) over a range of plugs.

Table 1.25 α-pinene on Chromosorb 102, variation of peak area with filament temperature control setting

Elutions	Plug			
Filament setting 1	1	2	5	Mean
1st	2	1	11	5
2nd	2	1	3	2
3rd	2	0.8	2	1
Filament setting 5				
1st	276	41	58	125
2nd	6	8	21	11
3rd	5	4	10	6
Filament setting 10				
1st	920/104	150	192/222	317
2nd	80/34	34	60/90	59
3rd	54/12	12	28/32	27

An investigation into the relationship between sampling flow rate and amount of terpene adsorbed by the support was also carried out. The data obtained are presented in Table 1.26.

Table 1.26 α-pinene on Chromosorb 102

Elution	Plug	
	1	6
Flow 80 ml min^{-1}		
1st	144	60
2nd	52	24
3rd	16	17
Flow 250 ml min^{-1}		
1st	56	68
2nd	20	15
3rd	14	12
Flow 450 ml min^{-1}		
1st	53	64
2nd	21	21
3rd	18	12

In comparison to other operating parameters the sampling flow rate appears to have little effect on the amount of terpene measured - indeed the results for plug 6 are surprisingly consistent over the range of flows examined.

DETERMINATION OF THE EFFICIENCY OF THE ELSCINT SAMPLING SYSTEM BY COMPARISON WITH DIRECT INJECTIONS

Comparison of the gas chromatographic response obtained from direct liquid injection of a known amount of terpene with the response obtained by successive elutions from an Elscint plug, which has been exposed to a gas flow containing the same amount of terpene, enables the calculation of an overall efficiency for the Elscint sampling system. The standard sample sizes used in this project were 6.57 µg of α-pinene and 5.10 µg of β-caryophyllene: Table 1.27 presents a comparison of the peak areas obtained for these standard sample sizes by direct injection with the mean values obtained under standard conditions (0.03g packing material, sampling flow rate 80 ml min^{-1}, filament setting 10) using the Elscint sampling system.

Table 1.27 Relative responses (FID)

Elution	α-pinene			β-caryophyllene		
	Direct	Chrom 102	Charcoal	Direct	Chrom 102	Charcoal
1st	9042	195	87	13974	10	4
2nd		145	17		4	0.5
3rd		120	7		3	*

* Not detected

Table 1.28 Elscint sampling system efficiencies relative to direct injection. Expressed as percentages of peak areas obtained by direct injection.

Elution	α-pinene		β-caryophyllene	
	Chromosorb 102 %	Activated Charcoal %	Chromosorb 102 %	Activated Charcoal %
1st	2.2	0.9	0.08	0.03
1st + 2nd	3.7	1.1	0.1	0.03
1st+2nd+3rd	5.0	1.2	0.1	

CONCLUSIONS

The data presented above clearly demonstrate that the Elscint gas sampling/concentrater system has severe limitations for quantitative measurements. These data also show that the overall efficiency of such a system, for the terpenes under study, was extremely low.

The data in Table 1.27 indicate that the efficiency of the sampling system varies considerably with both the compound under study and the packing material used. Variations in operating parameters such as filament temperature also produce large variations in the adsorption/desorption characteristics for given compounds on specific packings. More significantly, it proved impossible to obtain reproducible results even when all procedures and operating parameters were standardised (Table 1.18).

Such low efficiencies together with the other operating problems would combine to make such a system of no real value for quantitative measurements at the levels likely to be encountered in field samples. Indeed it would not even be possible to determine minimum detectable limits (or ranges of detection) for a given compound on a specific packing without prior collection of a statistically valid number of results under similar conditions.

Many of the problems encountered appear to be the result of the size and design geometry of the sampling plug, which affect both the adsorption and desorption stages of the process.

(a) Adsorption stage:

(i) The amount of packing material which the plugs can accommodate is insuffient.

(ii) Consistency of packing cannot be ensured.

(iii) 'Channelling' of the sample flow can occur through the plug.

(b) Desorption stage:

(i) The thermal characteristics of the plug on elution would appear to depend on packing and are therefore not reproducible.

(ii) Inconsistencies in packing affect the characteristics of flow of the purge gas.

CHAPTER 2

LEVELS OF HYDROCARBONS IN THE ATMOSPHERE

2.1. INTRODUCTION

During the period 1974-1977 the Public Health Engineering Sections mobile laboratory was used to monitor air quality at various sites mainly in the London area although a survey in Teesside was also carried out.

The mobile laboratory is an adapted 3 ton Bedford ambulance and it is possible to power the instrumentation within the vehicle from three alternative sources:

(i) Mains electricity - preferred when available.

(ii) 12 volt batteries linked to an inverter to give a 240 volt supply.

(iii) A generator fitted with a catalytic converter to reduce exhaust emissions.

Air pollution monitoring equipment built into the vehicle included:

(i) A gas chromatograph with appropriate sampling trains for the monitoring of individual hydrocarbons.

(ii) An automatic air quality chromatograph for monitoring carbon monoxide, methane and total hydrocarbons.

(iii) Directional sampling and meteorological equipment.

(iv) A filter system for the collection of particulate matter prior to lead analysis.

2.1.1. Air Quality Chromatograph (AQC)

A Beckman Model 6800 AQC was used to determine total hydrocarbons (THC), methane (CH_4), carbon monoxide (CO) levels and non-methane hydrocarbons (NMHC) by the difference between the THC and CH_4 levels. A continuous stream of air was drawn directly from a sampling duct 3m above ground level. Subsamples of this air stream were analysed at 5 minute intervals. Results were presented as a graphical printout and by comparison of sample peak heights with those obtained using standard calibration gas mixtures the concentration of each component was determined.

2.1.2. Lead Analysis

The particulate inorganic lead level in air was determined by the following procedure:-

(i) Air was subsampled isokinetically from the main air duct at a rate of approximately 5 $1\mathrm{min}^{-1}$ through a 0.22µ Millipore filter. The actual volume being collected was recorded on a gas meter. The filter was then stored prior to analysis by atomic adsorption spectrophotometry.

(ii) Pretreatment was carried out by the immersion of the filter in a solution of hydrogen peroxide (10ml, 6%) and nitric acid (5ml, 10%) for 30 minutes. Subsamples of this solution (50 µl) were then injected into the graphite furnace of a Perkin Elmer 305 AA Spectrophotometer. The concentration of lead in solution was determined by comparing the values obtained from the samples with those of standards which had been previously injected.

2.1.3. Meteorological Data

In an air pollution survey accurate meteorological data is necessary when analysing the data and ascertaining the source of a pollutant. Such variables as windspeed, wind direction and temperature affect the dispersion and generation of pollutants and as they vary they will therefore alter the levels determined at a specific sampling site.

2.2. Survey in the Teesside Area

Seven visits were made to the Teesside area during the period October 1974 - October 1975. Measurements were made at eleven sites all of which lay north of the River Tees, the majority of the sites encompassing two areas:-

(i) The crude oil storage depot at Greatham.

(ii) The refinery at Seal Sands.

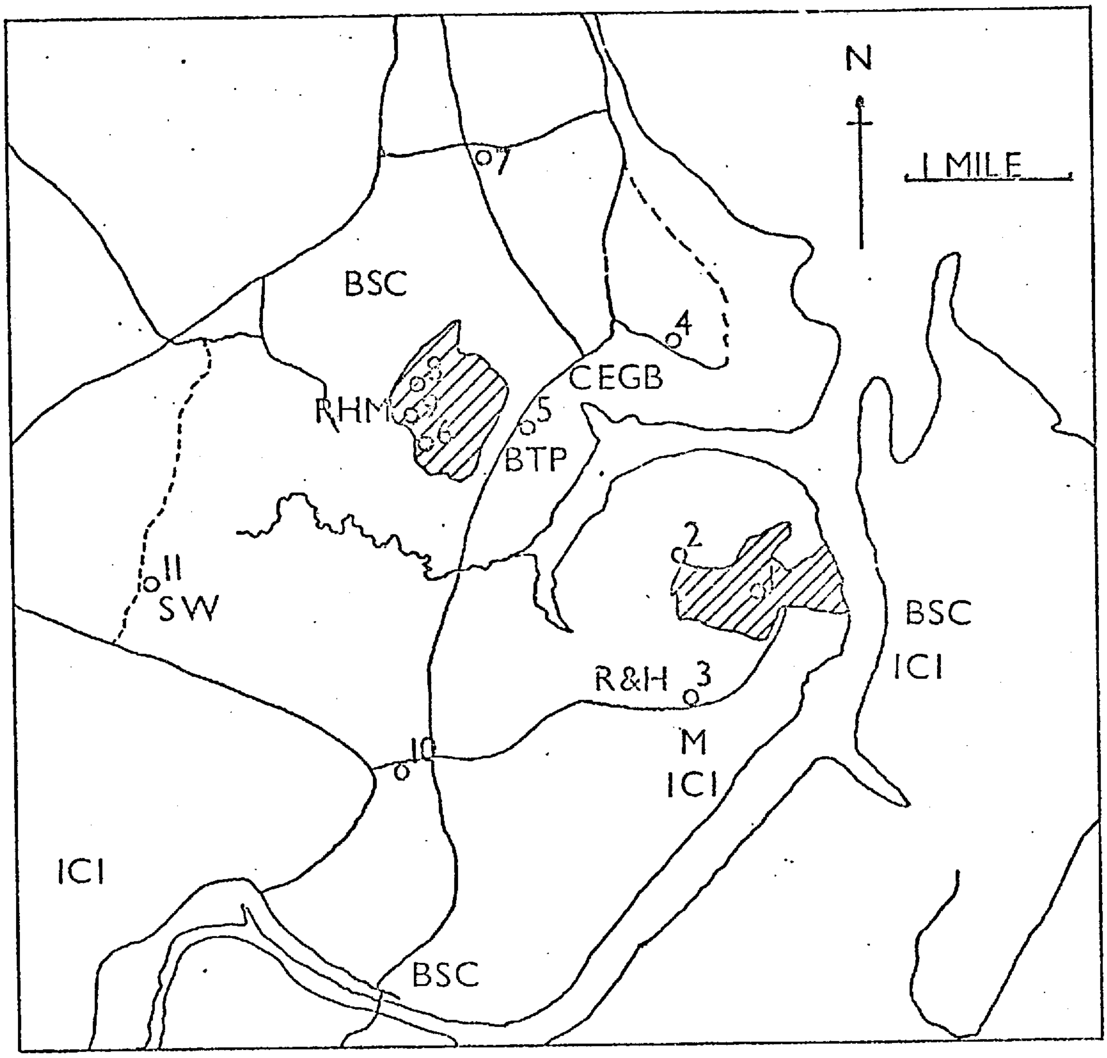
The sites are listed below and their positions can be determined by reference to the map Figure 7.

1. Seal Sands - main carpark
2. Seal Sands - west security gate
3. Approximately 30m from roadside
4. Roadside
5. Approximately 20m from roadside
6. Greatham
7. Carpark at the rear of a hotel approximately 50m from two roads
8. Greatham - close to a road used by vehicles on the construction site
9. Greatham
10. Fire station
11. Sewage works

In Table 2.1. the mean value for each component listed is given for every site over the total survey period.

Table 2.1. Mean and range of levels of THC, CH_4, CO, NMHC and lead determined in the Teesside area

Site	THC ppm	CH_4 ppm	NMHC ppm	CO ppm	Pb $\mu g\ m^{-3}$
1	2.1 1.2 - 7.8	1.4 1.0 - 5.1	0.6 0.0 - 2.6	1.0 0.0 - 12.8	0.6 0.4 - 0.9
2	1.5 1.1 - 2.0	1.4 1.1 - 1.7	0.1 0.0 - 0.4	0.4 0.0 - 2.1	1.3 0.5 - 2.5
3	2.2 1.5 - 3.4	1.4 2.0 - 1.0	0.8 -	0.9 0.1 - 2.2	3.6 -
4	1.8 1.3 - 2.3	1.3 0.8 - 1.9	0.4 -	0.6 0.1 - 0.9	- -
5	1.7 1.3 - 2.7	1.4 1.2 - 2.0	0.3 0.0 - 0.8	0.6 3.2 - 0.1	- -
6	1.6 1.3 - 2.3	1.6 1.2 - 2.1	0.08 0.0 - 0.4	0.3 0.1 - 0.7	0.6 0.3 - 0.9
7	2.0 1.3 - 4.0	1.5 1.2 - 1.8	0.5 -	1.9 0.0 - 15.2	- -
8	2.1 1.4 - 10.3	1.3 1.0 - 1.9	0.7 -	0.6 0.1 - 2.1	0.4 -
9	1.5 1.3 - 1.8	1.5 1.2 - 1.7	0.07 0.0 - 0.2	0.03 0.0 - 0.4	0.8 0.6 - 1.0
10	1.6 1.3 - 2.2	1.4 1.0 - 2.0	0.2 0.0 - 0.6	0.3 0.0 - 1.7	0.6 0.1 - 1.5
11	1.4 1.3 - 1.7	1.3 1.2 - 1.5	0.1 0.0 - 0.8	0.3 0.4 - 0.1	0.4 0.2 - 0.7



KEY: ICI - Imperial Chemical Industries
BSC - British Steel Corporation
CEGB - Central Electricity Generating Board
M - Monsanto
BTP - British Titan Products
R & H - Rohm and Hass
RHM - Rank Hovis McDougall
SW - Sewage Works

FIGURE 7 Map of Teesside Area

On consideration of the levels determined during this survey it would appear that a major contributor to hydrocarbon air pollution in the area under study is vehicle emissions. Readings were consistently higher when the wind blew off the roads towards the sampling site than they were when it blew from any other direction and at site 1. which was a carpark the levels recorded and their variation were consistent with traffic movements. At sites which were remote from any vehicles (sites 6. and 9.) levels were consistently low.

2.3. Heathrow Airport Survey

A brief survey was carried out at Heathrow Airport during June and July 1976 where four sites were used. Their positions can be ascertained by reference to Figure 8.

1. Perry Oaks:-

This site was situated at the eastern end of the TWA Perry Oaks sludge disposal works and lay between the two main east-west runways (nos. 1 and 5) adjacent to the take-off and landing points and 500m westward of the airports main fuel farm.

2. Vanguard Club:-

Situated to the north of the airport and the north perimeter road, this site was close to the taxi-ing and take-off points of the northern (no. 1) runway. Heavy traffic movement occurred on the A4(T) road approximately 50m to the north of the site.

3. Boadicea House:-

Fairly open ground lay between this site and the runway complex. It was situated in the main maintenance area east of the runways and was sheltered from traffic movements in and out of the area by the British Airways computer centre.

4. South Perimeter Road:-

The south perimeter road carrying moderately heavy traffic was

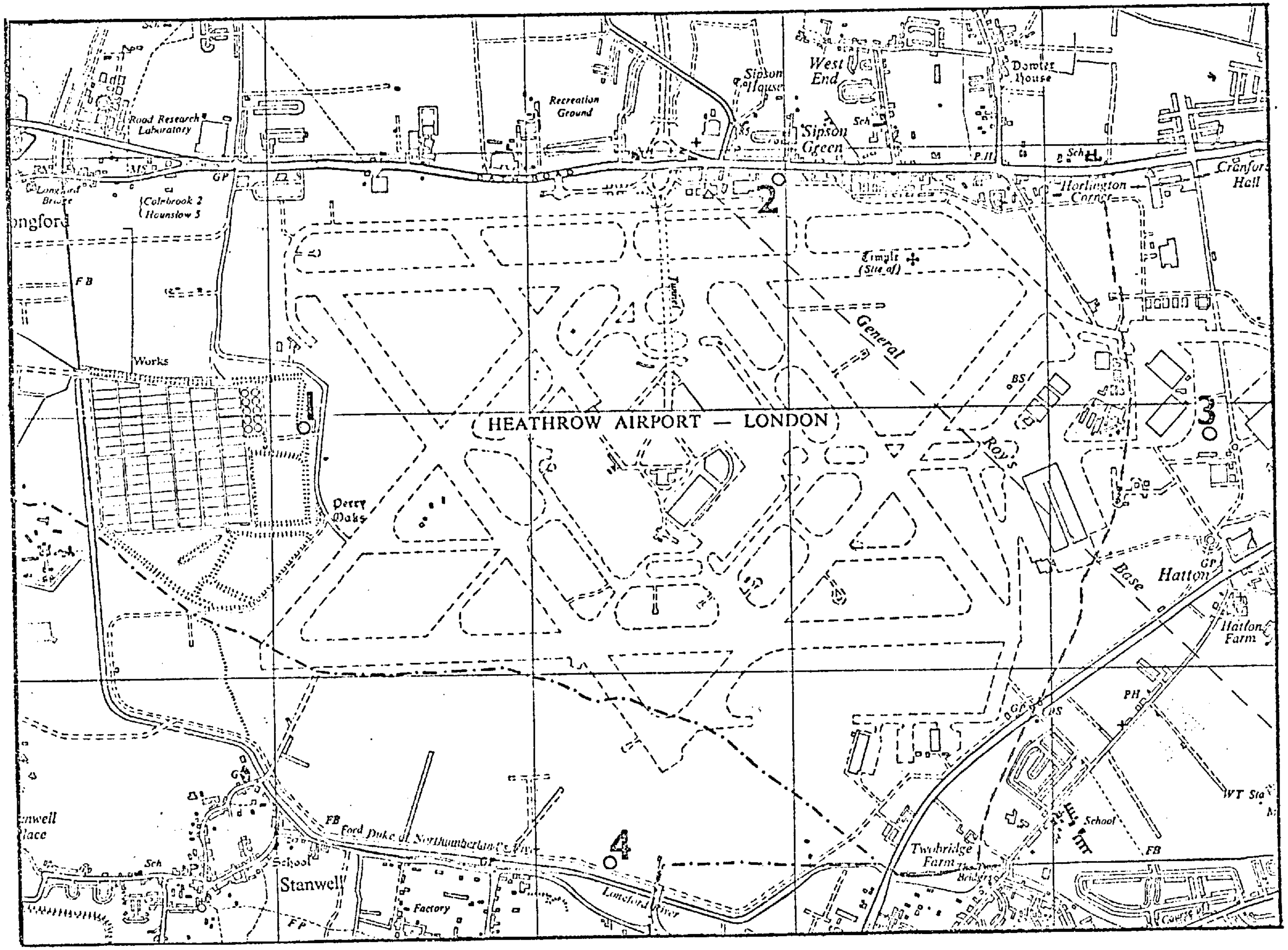


FIGURE 8 Map of Heathrow Airport

about 10m from the site. Open ground lay between the site and the main southern (no. 5) runway 500m away.

In Table 2.2. the mean result and the range of values determined at each site are given for the total survey period.

Table 2.2. Levels of THC, CH_4, CO, NMHC and lead determined in the vicinity of Heathrow Airport

Site	THC ppm	CH_4 ppm	NMHC ppm	CO ppm	Lead $\mu g\ m^{-3}$
1	2.9 1.6 - 6.0	2.5 1.4 - 6.0	0.4 0.0 - 3.7	0.2 0.0 - 0.7	0.9 0.0 - 2.0
2	1.8 1.4 - 3.0	1.5 1.2 - 2.1	0.3 0.01 - 1.4	0.5 0.0 - 1.6	0.9 0.1 - 2.1
3	1.8 1.3 - 8.9	1.4 1.2 - 1.6	0.3 0.0 - 7.5	0.3 0.0 - 1.1	0.9 0.3 - 2.2
4	1.6 1.3 - 2.1	1.4 1.1 - 1.6	0.1 0.0 - 0.6	0.6 0.1 - 1.9	1.1 0.3 - 2.0

From the results obtained at each site various observations can be made.

Perry Oaks: When the wind blew from the direction of the airport all pollutant levels were appreciably higher and mean non-methane hydrocarbon levels of approximately 0.5 ppm were experienced. The high methane levels at this site were due to the proximity of the sampling site to the sludge lagoons. A maximum level of 3.78 ppm for non-methane hydrocarbons was recorded with the wind blowing from the direction of the 'holding area' on runway no. 1. There was however, no appreciable difference in overall levels when different runways were in use. Carbon monoxide levels were low, as might be expected for a site remote from motor vehicle traffic.

Vanguard: Mean total hydrocarbon levels did not vary much with changing wind direction. When the wind blew from the A4(T) road levels followed fluctuations in traffic density (up to 2000 vehicles per hour). Lead levels rose noticeably when the wind blew from this direction (max. 2.18 $\mu g\ m^{-3}$). When the wind blew from the airport there was no significant rise in pollutant levels even when the runway (no. 1) closest to the site was used.

Boadicea House: High pollutant levels were measured (up to 7.5 ppm total hydrocarbons) when the wind blew from the direction of the maintenance area and engine test beds. It was also observed that non-methane hydrocarbon levels were appreciably higher when runway no. 6 was in use (taking off to the east) than when runway no. 1 was used. Carbon monoxide levels were low as expected from an area with few vehicles.

South Perimeter: At this site there was heavy traffic movement, approximately 1,200 cars and 250 heavy vehicles per hour. Lead and carbon monoxide levels were higher when the wind blew off the road. High non-methane hydrocarbon levels were also recorded under such conditions and were due to road traffic and not to aircraft emissions.

2.4. Measurements at various sites in London

The levels of total hydrocarbons, methane, carbon monoxide, non-methane hydrocarbons and inorganic lead were determined at several sites around London and a description of these sites is given below.

Exhibition Road: This is a wide dual carriageway carrying approximately 1,500 vehicles per hour. Many cars park along the sides of the road and either side of the central reservation. Depending on the exact location of the site factors affecting levels determined include: traffic lights, high buildings altering dispersion characteristics, the exit from Imperial College carpark, icecream vans and a Post Office van park.

Croydon: This site was situated underneath a flyover bounded by Croydon High Street approximately 30m away on one side and by a multi-storey carpark on the other. When conditions were still there was a noticeable buildup of pollutants because of the sheltered position of the site.

Olympia Carpark: The mobile laboratory was parked close to the exit of this multi-storey carpark inside a fairly enclosed area with a ceiling height of 5m.

Heathrow Airport Tunnel: This site was situated close to the roundabout at the airport end of the M4 tunnel. There were approximately 2,700 vehicles per hour into and out of the airport. Sampling was conducted 5m from the mouth of the tunnel.

2.4.1. Diurnal Variation

The diurnal variation of the compounds of interest was monitored both at the Exhibition Road site and at Croydon. A typical example of the fluctuations in levels observed is given in Figure 9. From this it can be seen that a peak in pollutant levels occurs during the afternoon rush hours 16.00 - 18.30 and the levels of non-methane hydrocarbons then gradually fall off with a slight increase again around 23.00 hours. The carbon monoxide variation is more spasmodic.

The levels then fall again and from 24.00 they are negligible until approximately 07.30 when the levels start to rise. Between 08.00 and 10.00 a peak in levels can be attributed to the morning rush hour, and after this there is a slight decrease until between 12.00 - 15.00 when there is another peak.

It is obvious that the carbon monoxide and non-methane hydrocarbon levels in the vicinity of these sites are directly related to the traffic density, and that other contributions to these levels are insignificant.

In Table 2.3. the range of values and the mean levels observed at each of the sampling sites in London is given as are results obtained at Heathrow Airport and Teesside.

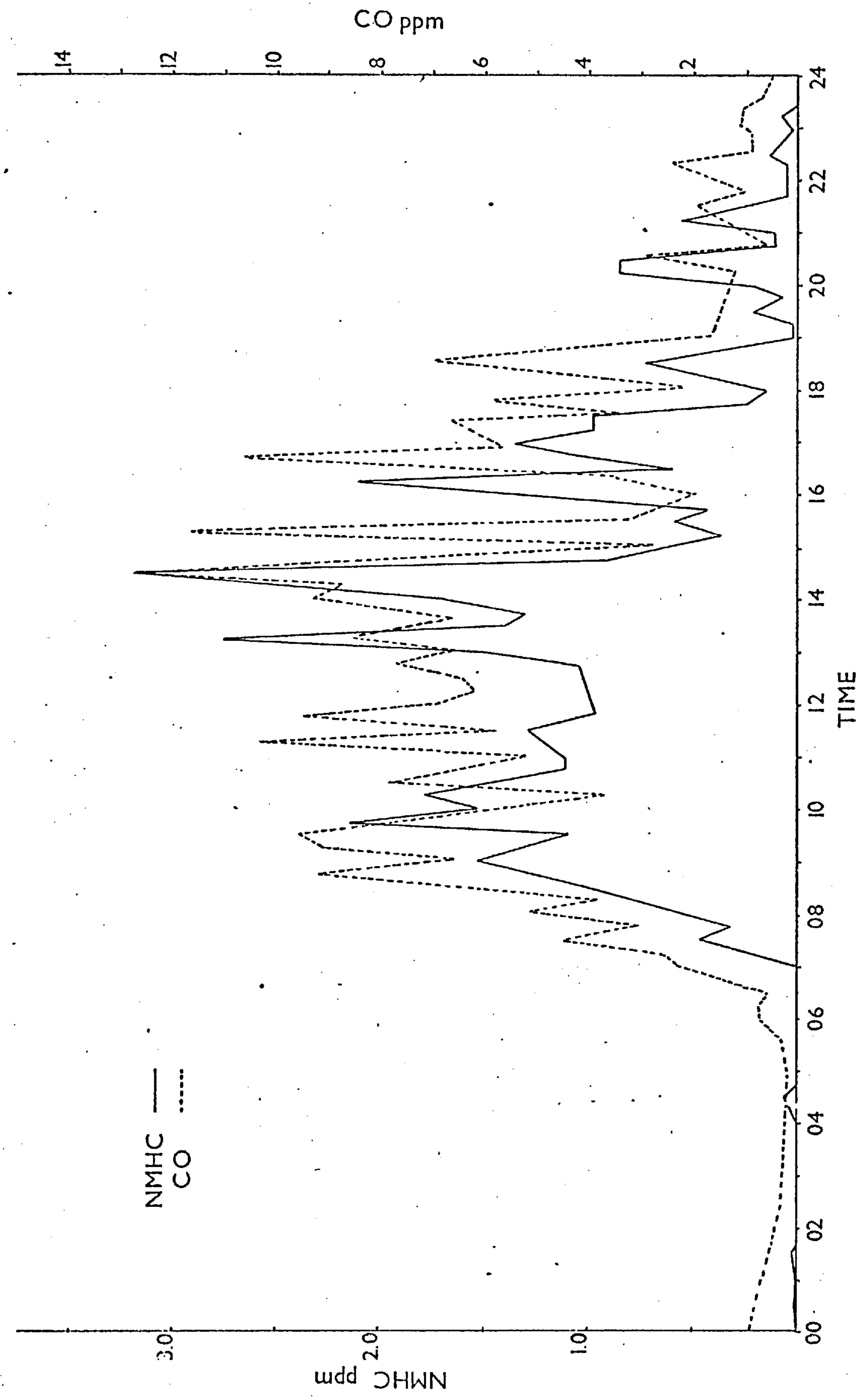


FIGURE 9 Diurnal Variation of CO and NMHC on Exhibition Road

Table 2.3 Mean and range of levels of THC, CH_4, CO, NMHC and lead determined from 1974 - 1976

SITE, DATE AND TIME	THC ppm	CH_4 ppm	CO ppm	NMHC ppm	Lead $\mu g\ m^{-3}$
Exhibition Road					
19th June 1975 1200 - 1850	1.4 - 2.8 2.0	1.3 - 1.8 1.5	1.5 - 7.4 3.5	0.1 - 1.0 0.5	2.4 - 10.7 3.7
23rd June 1975 1400 - 1800	1.3 - 2.5 1.7	1.2 - 1.3 1.3	0.9 - 3.5 1.6	0.05 - 1.2 0.4	1.4 - 50.6 10.7
5th July 1976 1500 - 1900	1.5 - 5.3 2.8	1.4 - 2.5 1.8	0.4 - 12.4 3.1	0.01 - 3.6 0.9	
6th July 1976 0800 - 1600	1.5 - 8.6 2.6	1.3 - 2.2 1.7	0.2 - 13.3 3.1	0.08 - 7.0 0.8	-
29th November 1976 1250 - 2000	1.7 - 5.0 2.4	1.6 - 2.2 1.8	0.5 - 8.3 2.7	0.01 - 2.8 0.5	-
30th November 1976 0800 - 2000	2.0 - 5.8 3.0	1.6 - 2.9 2.0	1.2 - 13.9 5.9	0.01 - 3.5 1.0	-
1st December 1976 0800 - 2000	2.0 - 8.2 2.9	1.6 - 2.3 1.8	1.2 - 14.2 4.4	0.2 - 6.0 1.0	-
2nd December 1976 0800 - 1730	1.7 - 6.5 2.4	1.5 - 2.3 1.8	0.6 - 12.0 2.7	0.03 - 4.2 0.5	-
3rd December 1976 0900 - 1730	2.3 - 5.1 3.5	1.9 - 2.7 2.2	2.1 - 18.7 6.5	0.3 - 3.0 1.3	-
Olympia Carpark					
22nd October 1975 1300 - 1900	4.0 - 8.5 5.3	2.1 - 2.9 2.4	6.3 - 26.7 11.0	1.2 - 5.6 2.6	4.4 - 11.2 5.9
Croydon					
7th December 1400 - 2000	1.4 - 7.6 2.8	1.4 - 1.8 1.5	1.4 - 14.6 4.4	0.2 - 5.0 1.2	-
8th December 0800 - 2000	2.1 - 11.3 5.2	1.4 - 2.2 1.8	1.3 - 24.0 12.0	0.6 - 10.0 3.3	-
9th December 0700 - 2000	3.3 - 9.5 5.5	1.9 - 4.1 2.5	4.4 - 33.7 12.6	0.6 - 5.8 3.0	5.8 - 18.1 12.5
Heathrow Airport June - July 1976	1.3 - 8.9 2.0	1.1 - 6.0 1.7	0.01 - 1.9 0.4	0.0 - 7.5 0.3	0.0 - 2.2 1.0
Heathrow Tunnel June	6.2 - 8.9 7.2	1.6 - 2.2 1.8	12.9 - 39.6 27.0	4.4 - 7.1 5.3	-
Teesside 1974 - 1975	1.4 - 2.2 1.8	1.3 - 1.6 1.4	0.0 - 1.9 0.6	0.07 - 0.8 0.3	0.4 - 1.3 0.7

2.5. Measurement and Analysis of Individual Hydrocarbons

At certain of the sites described previously and at others air samples were taken so that subsequent gas chromatographic-mass spectrometric analysis could be performed.

The sampling systems described in Chapter 1 were used to determine levels of hydrocarbons (with 6 carbon atoms or more) in the atmosphere. The adsorbent technique was used for routine analysis and the cryostat for obtaining samples prior to mass spectral analysis.

2.5.1 Sampling Procedures

Adsorbent technique:- The sampling tube was connected between a glass fibre inlet filter and a Du Pont constant flow sampling pump. Using this pump a known volume of air could be sampled with confidence. The sample collection rate was automatically regulated to ensure that a preset flow rate in the range 50-200 ml $\cdot$ min^{-1} was maintained within 5%. The flow rate setting was independent of the collector media pressure drop characteristics which was essential in field use where a variety of tubes were used each with a different pressure drop.

Cryostat:- When using the cryostat for sampling a potassium carbonate drying tube was inserted between the inlet filter and the sample tube.

2.5.2 Gas Chromatographic Operating Conditions

Separation of the eluted material was carried out using a 20 ft x 1/8 in o.d. stainless steel column packed with 3% OV7 on Gas Chrom W AWDMCS. The carrier gas flow rate was 30ml min^{-1} and the column temperature programmed between 30^{o}and 150^{o}C at 4^{o} C min^{-1}.

2.5.3 Mass Spectral Analysis

After the separation in a gas chromatograph the compounds were introduced into the mass spectrometer via a membrane separator. The mass spectrometer used was a Hewlett Packard 5930A dodecapole with an on-line 5932A data system. The computer was used to initiate scans recording at 4s intervals. Up to 300 scans can be obtained in this manner and if required the interval between scans can be increased to 6s or 8s. Owing to the low molecular weight of the species being studied the mass range scanned was between $\frac{m}{e}$ 1 and 200. The data collected was used off line to produce reconstructed chromatographs involving either ions of a specified mass range or single ions.

For the purpose of positive identification of the eluted materials, mass spectra corresponding to gas chromatographic peak maxima were stripped of the background mass spectra obtained immediately before or after the elution of the peak under consideration. These stripped spectra (corresponding to as little as 20 ng) were then used in a library search routine enabling the identities of the materials to be confirmed.

Typical chromatograms obtained during this study are given in Figures 10-12 and peaks can be identified by reference to Table 2.4.

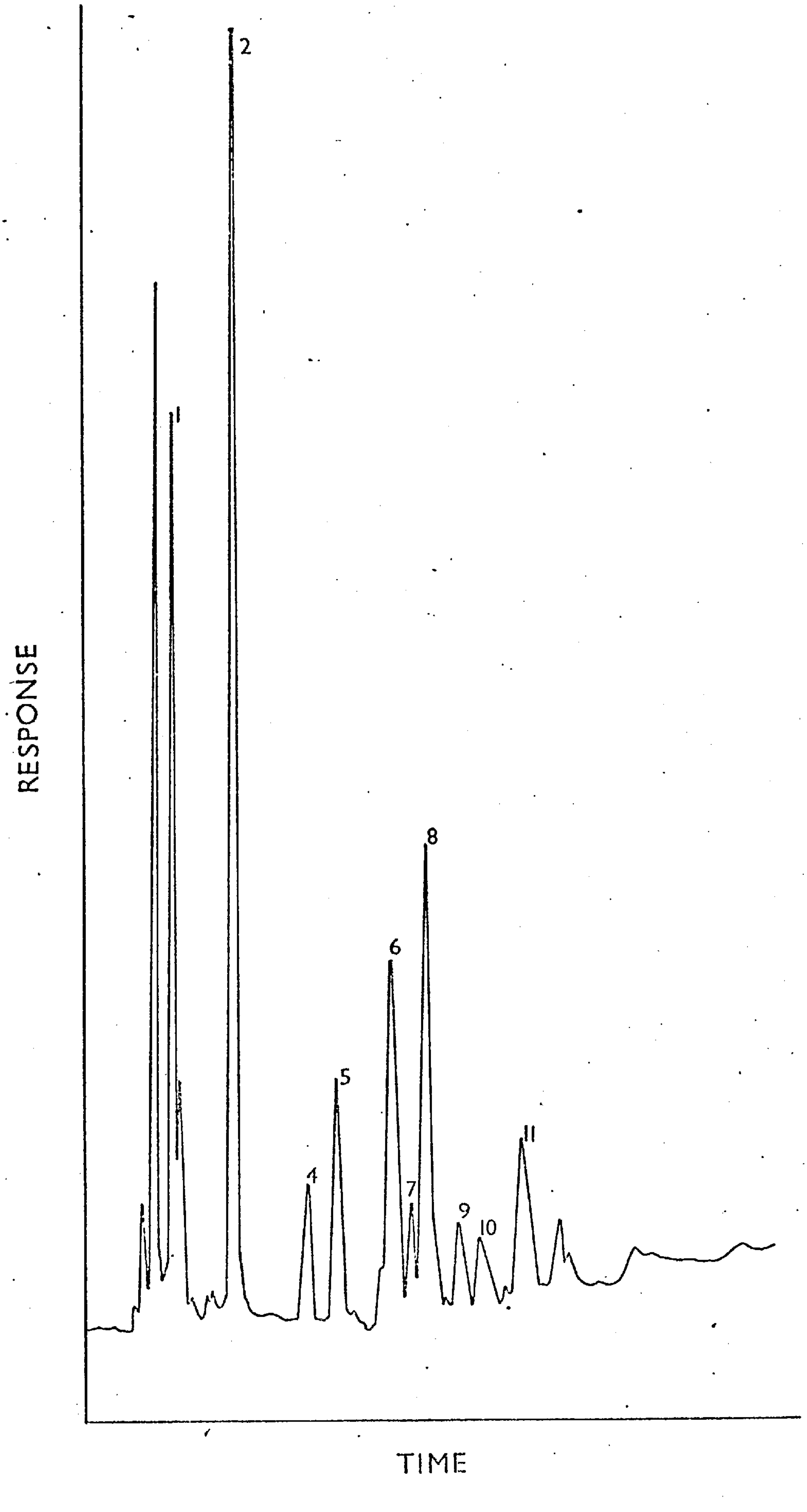


FIGURE 10 Hydrocarbons in Teesside Air

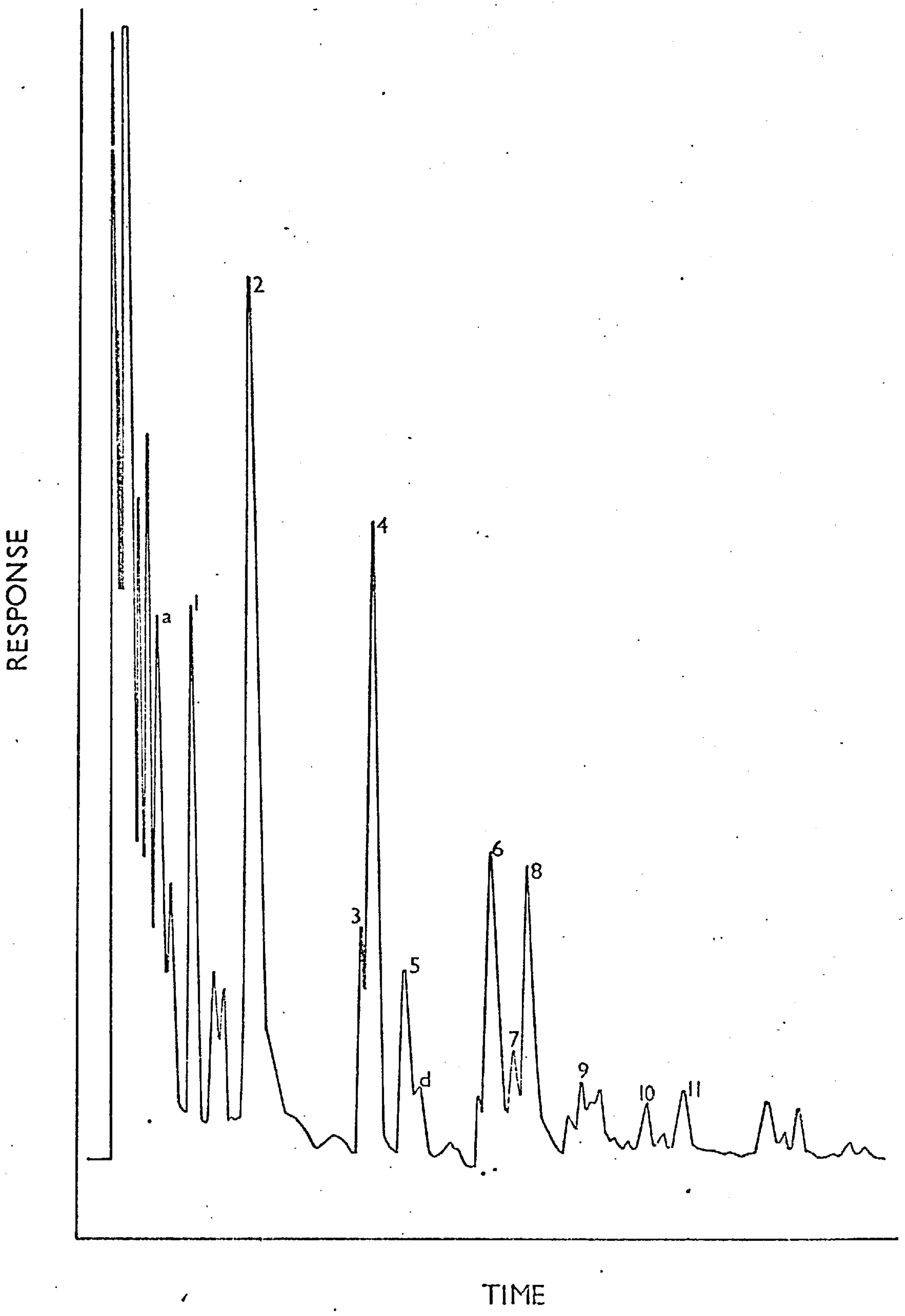


FIGURE 11 Hydrocarbons in Exhibition Road Air

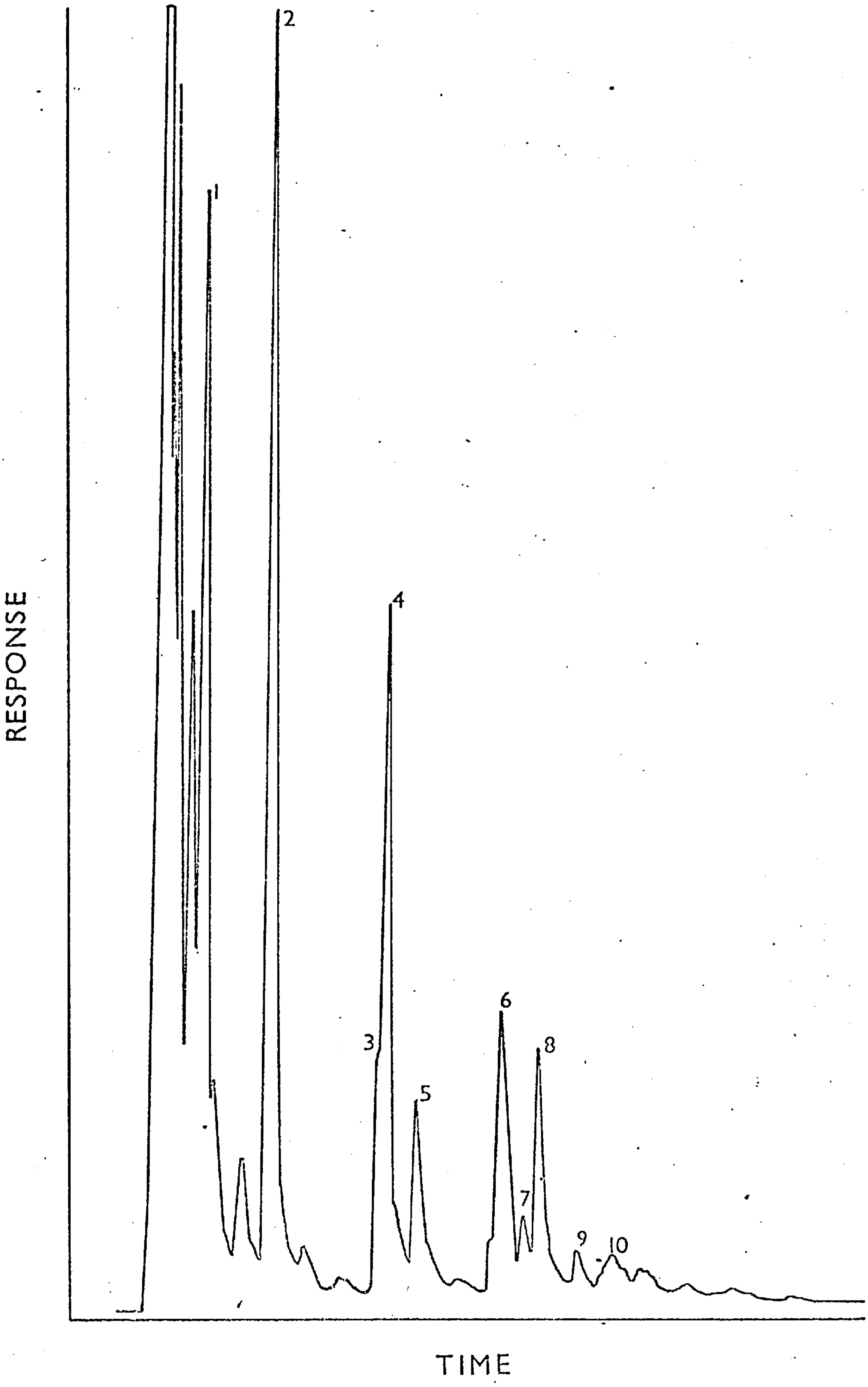


FIGURE 12 Hydrocarbons in Air from a Garage Forecourt

Table 2.4 Peak assignments

Peak Number	Assignment	
1	Benzene	(C_6H_6)
2	Toluene	(C_7H_8)
3	Ethyl-benzene	(C_8H_{10})
4	m-and p-Xylene	(C_8H_{10})
5	o-Xylene	(C_8H_{10})
6	Ethyl-toluene	(C_9H_{12})
7	Isopropyl-benzene or trimethyl-benzene	(C_9H_{12})
8	Trimethyl-benzene	(C_9H_{12})
9	Tert.-butyl-benzene	($C_{10}H_{14}$)
10	Diethyl-benzene	($C_{10}H_{14}$)
11	Dimethyl-ethyl-benzene	($C_{10}H_{14}$)

It is very difficult to positively identify the substituted aromatic hydrocarbons and the assignments given above are somewhat tentative but their carbon number and the fact that they are aromatic compounds is more certain.

The other smaller peaks that can be observed on the chromatograms are either aliphatic hydrocarbons many of which are substituted or aromatic compounds.

2.5.4 Levels of Individual Hydrocarbons in the Atmosphere

In Tables 2.5 - 2.10 levels of aromatic hydrocarbons determined at various sites are recorded. The detection limit for the technique used when sampling 6 l of air was taken to be 0.1 µg m^{-3} for each compound.

Teesside

Table 2.5 Levels of Aromatic Hydrocarbons in the Teesside Area

The site positions can be determined by reference to Figure 7.

Date	Site No.	Benzene	Toluene	m-& p-Xylene	o-Xylene $\mu g\ m^{-3}$	Ethyltoluene	Trimethylbenzene or isopropylbenzene	Trimethylbenzene
9.7.75	1	1.0	4.3	1.9	0.2	5.3		0.8
	2	0.5	1.1	5.6	2.1	19.7		11.2
	2	2.0	3.2	1.9	9.7	10.9		2.6
	10	ALL LESS THAN 0.1						
10.7.75	9	2.0	4.3	1.9				1.9
	9	0.7	2.3	3.7	1.7	9.8		10.7
	1	0.2	0.6	0.9	1.5	3.3		0.8
11.7.75	2	1.1	2.2	1.7	2.2	2.9		1.2
	11	ALL LESS THAN 0.1						
	11	0.2	0.9	1.8	0.7			0.2
	11	0.3	0.9	0.5	0.9	2.7		0.6
	11	0.2	0.9	0.4	0.8	1.5		0.6
17.9.75	1	ALL LESS THAN 0.1						
	2	ALL LESS THAN 0.1						
18.9.75	1	ALL LESS THAN 0.1						
	10	ALL LESS THAN 0.1						
19.9.75	6	ALL LESS THAN 0.1						
7.10.75	2	4.8	9.1	1.2	1.6	2.0		2.6
8.10.75	9	6.5	13.6	2.1	3.2	9.8	1.0	8.4
9.10.75	2	1.2	2.3	0.6	1.8	0.6	0.2	0.9
	6	3.8	4.9	1.0	1.7	1.8	0.3	2.6

Table 2.6. Levels of Aromatic Hydrocarbons Determined in Exhibition Road

Date and Time	Benzene	Toluene	m-& p-Xylene	o-Xylene	Ethyl-toluene	Trimethyl- or isopropyl-benzene	Trimethyl-benzene
				µg m^{-3}			
30.11.76 Temp 9°C W.S. 0-20 km hr^{-1}							
12.05	367	771	674	63	191	18	100
13.05	489	1124	1192	63	154	13	154
14.05	328	886	1085	66	197	22	106
14.35	276	657	663	43	162	17	80
15.05	157	310	373	23	113	10	37
15.35	217	660	619	80	203	17	97
9.12.76 Temp 6.5°C W.S. 0-20 km hr^{-1}							
09.30	174	457	434	29	108	9	51
10.30	230	481	410	24	137	14	74
11.00	100	311	333	25	97	10	56
11.30	149	327	367	26	97	11	41
12.30	140	404	399	33	131	12	73
13.30	132	360	405	20	108	10	48
14.30	355	786	844	41	229	22	103
15.30	300	705					
16.30	409	1044	1320	84	216	20	116
20.2.77							
12.30	59	161	181	32	53	4	48
22.2.77							
12.30	122	306	220	83	180	11	92

Table 2.6., Exhibiticn Road, continued

Date	Benzene	Toluene	m-& p-Xylene	o-Xylene	Ethyl-toluene	Trimethyl- or isopropyl-benzene	Trimethyl-benzene
				µg m^{-3}			
3.3.77	150	310	156	33	70	8	63
9.3.77	42	110	94	10	21	1	18
17.3.77	230	540	562	26	140	10	68
25.3.77	128	310	312	18	110	9	49
5.4.77	147	352	368	27	92	8	87
19.4.77	168	389	380	29	98	8	79
26.4.77	218	540	567	35	118	18	94
3.5.77	236	581	592	25	137	14	128
10.5.77	168	410	442	28	115	16	113
17.5.77	142	331	328	30	127	13	105

Table 2.7. Levels of Aromatic Hydrocarbons Determined on a Garage Forecourt

Date	Benzene	Toluene	*m*-& *p*-Xylene	*o* Xylene	Ethyl-toluene	Trimethyl- or isopropyl-benzene	Trimethyl-benzene
				$\mu g\ m^{-3}$			
3.3.77	1577	3030	1538	32	50	4	42
9.3.77	41	71	35	7	6	1	5
9.3.77	159	300	148	15	71	7	69
17.3.77	128	248	75	13	7	0.8	4
25.3.77	80	141	108	27	46	3	38
5.4.77	527	1227	682	129	276	23	205
19.4.77	770	1422	829	178	385	30	296
26.4.77	224	440	250	56	108	13	94
3.5.77	856	1570	806	21	42	5	37
10.5.77	357	714	350	90	175	23	142
17.5.77	638	1322	651	149	251	32	221

Table 2.8. Levels of Benzene and Toluene Determined at Croydon μg m^{-3}

Date and Time	4.0 - 6.5°C; Still	
	Benzene	Toluene
8.12.76		
8.50	353	723
9.50	324	700
9.12.76		
9.35	260	655
10.35	263	690
11.35	324	710
12.35	381	760

Table 2.9. Levels of Aromatic Hydrocarbons Determined at the M1 Motorway Site $\mu g\ m^{-3}$

Date	Benzene	Toluene	m-& p-Xylene	o-Xylene	Ethyl-toluene
21.2.77	3.6	8.0	7.1	0.8	1.4
22.2.77	3.3	7.5	6.4	0.8	1.4
8.3.77	4.0	8.0	7.6	0.9	2.2
8.3.77	2.8	5.2	5.4	0.4	1.1
26.3.77	3.2	7.4	6.4	0.6	1.4
26.3.77	3.8	8.2	7.5	0.4	0.9
19.4.77	3.4	7.2	7.6	0.6	1.6
19.4.77	3.2	6.8	6.4	0.6	1.6
3.5.77	2.0	3.6	3.1	0.4	1.1
3.5.77	1.8	4.0	3.1	0.2	0.7
17.5.77	3.6	7.9	7.9	0.8	1.6
17.5.77	3.1	7.4	7.2	0.5	1.2
17.6.77	2.9	6.2	6.3	0.3	0.8
17.6.77	2.1	5.8	5.7	0.5	0.9

Table 2.10. Levels of Aromatic Hydrocarbons Determined inside a Moving Vehicle

Date	Benzene	Toluene	m-& p-Xylene	o-Xylene	Ethyl-toluene	Trimethyl- or isopropyl-benzene	Trimethyl-benzene
				$\mu g\ m^{-3}$			
18.2.77	28	68	47	23	23	4	17
20.2.77	20	48	45	27	24	7	20
3.3.77	23	43	34	15	14	8	4
4.3.77	32	67	47	29	27	4	24
9.4.77	14	29	19	12	10	1	9
12.4.77	22	48	32	21	18	2	15
17.4.77	16	35	28	14	12	2	10

From these results certain observations can be made. It would appear that the levels of hydrocarbons are dependent upon the dispersion characteristics of the individual sites.

Levels at the motorway site were low; the assumption is that the heavy vehicles passing the site cause a considerable amount of turbulence which aids the dispersion of the hydrocarbons.

The Teesside area is a flat, windswept region much of which has been reclaimed from sea marshes. Dispersion under these conditions is rapid and as can be seen, levels of hydrocarbons away from roads were extremely low.

There were great fluctuations in levels at the garage site. The levels recorded will be affected by petrol spillages, wind conditions and also the positions cars are parked or left running in relation to the sampling position.

Levels determined at Croydon were slightly higher on average than those in Exhibition Road. This might be expected as the Croydon site was enclosed and still conditions prevailed during the sampling period.

2.6. Fuels Used in Mobile Internal Combustion Engines

Figures 13 - 15 show chromatograms obtained by injecting typical fuels used in mobile internal combustion engines. Striking differences in the range of compounds in each can be observed and those present can be identified by reference to Table 2.11.

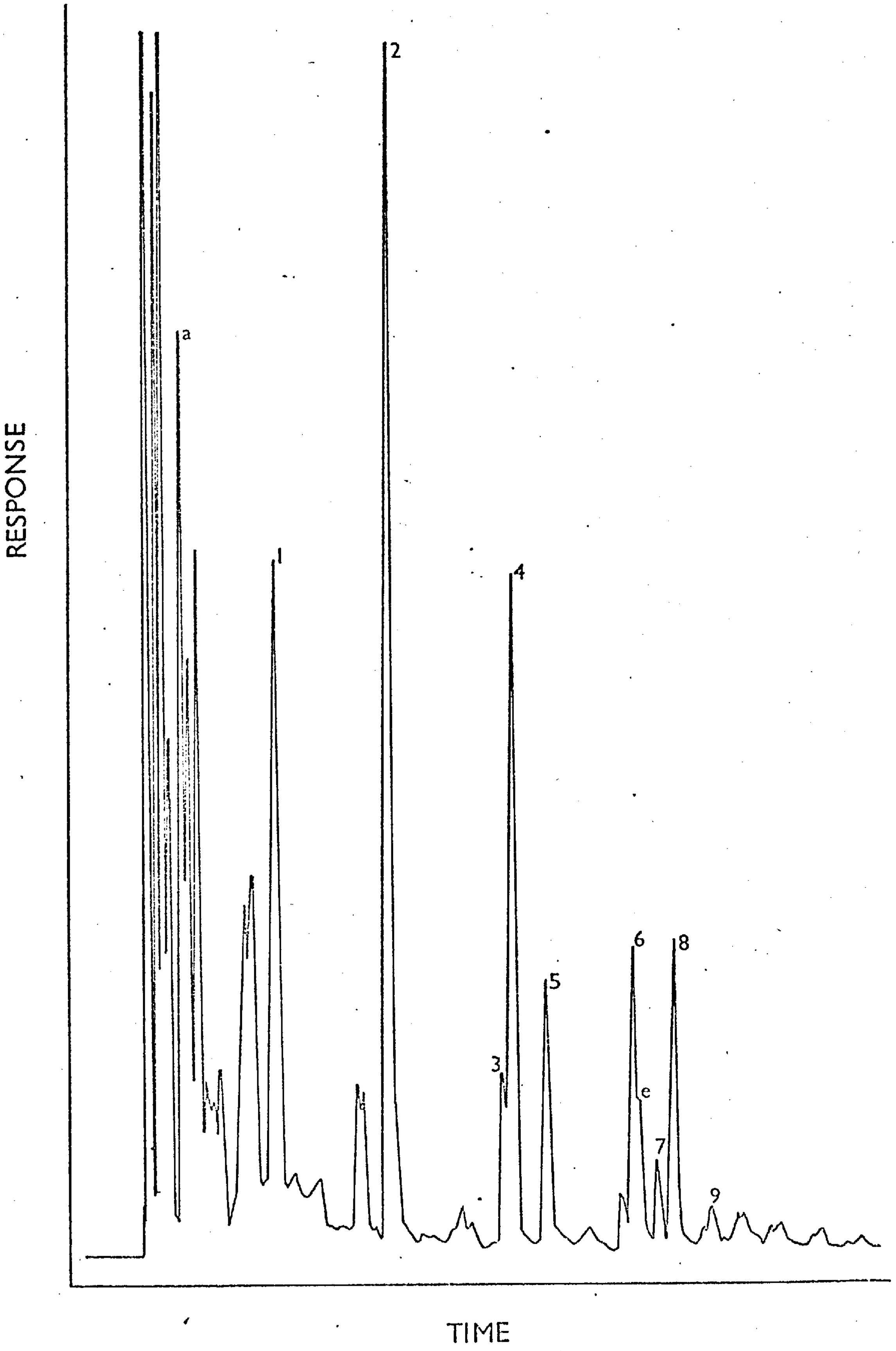


FIGURE 13 Petrol

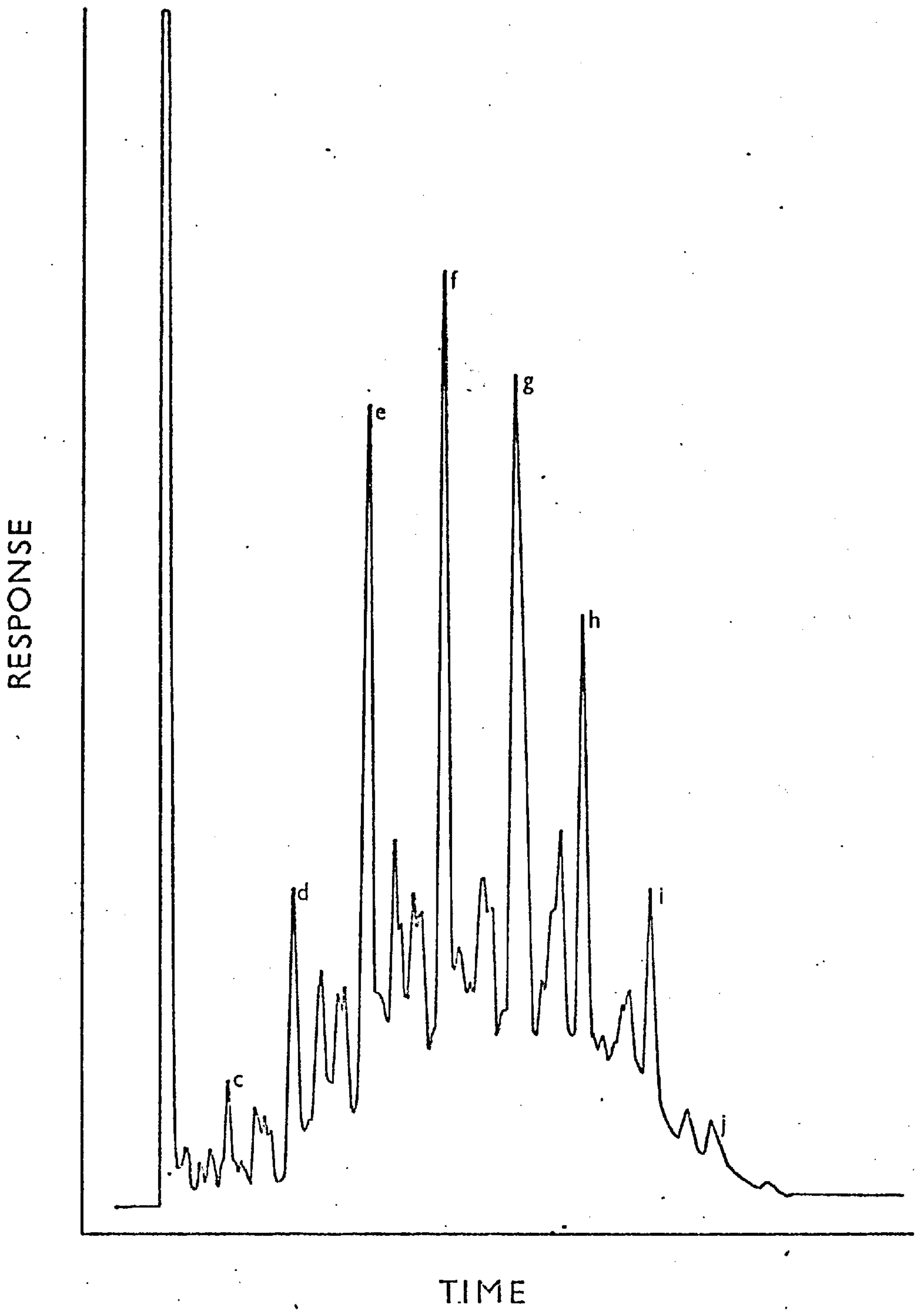


FIGURE 14 Aircraft Fuel

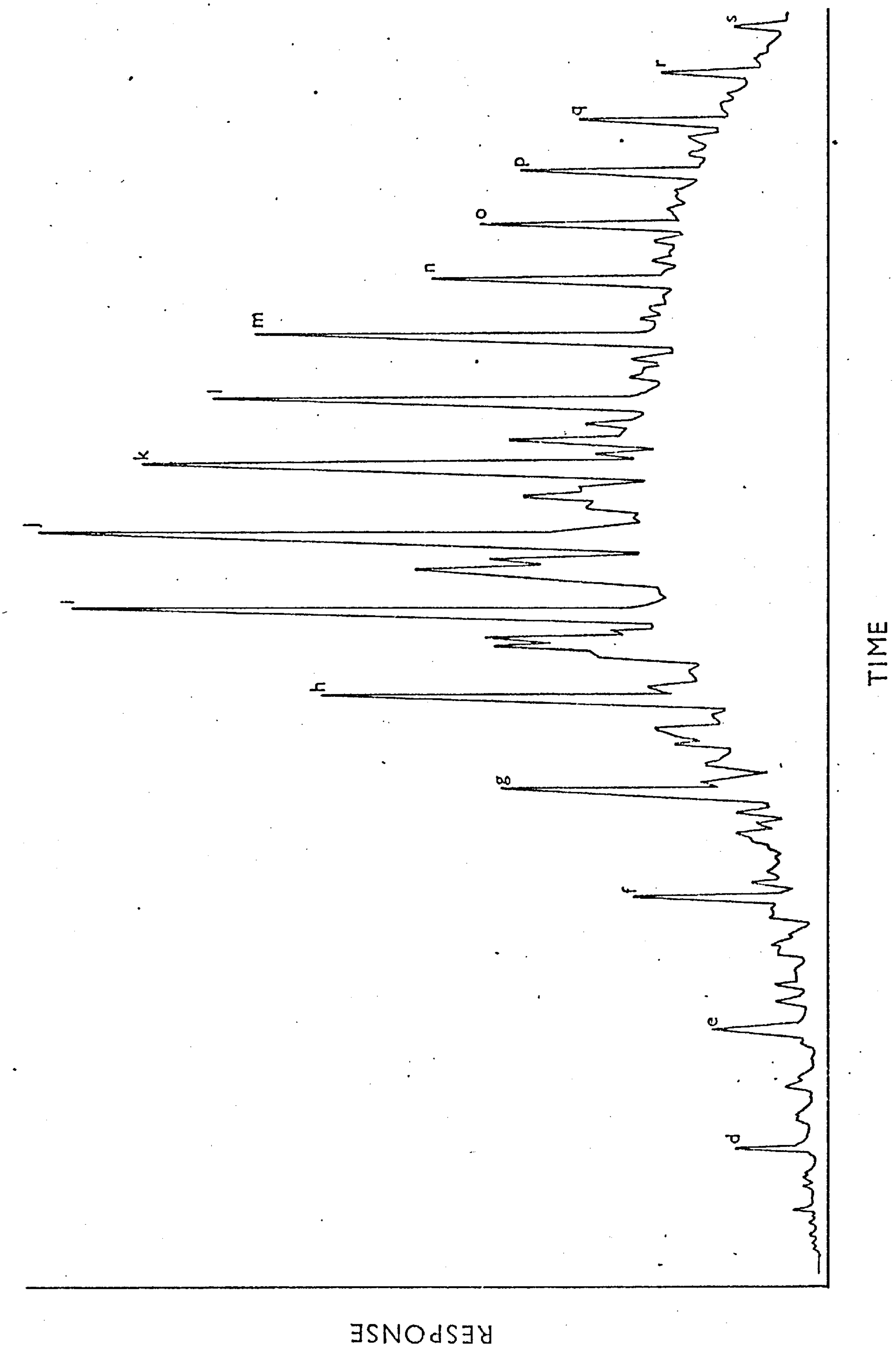


FIGURE 15 Diesel

Table 2.11. Peak Assignments

1	Benzene	a	Hexane
2	Toluene	b	Heptane
3	Ethyl-benzene	c	Octane
4	m-& p-Xylene	d	Nonane
5	o-Xylene	e	Decane
6	Ethyl-toluene	f	Undecane
7	Isopropyl-or trimethyl-benzene	g	Dodecane
8	Trimethyl-benzene	h	Tridecane
9	Tert-butyl-benzene	i	Tetradecane
10	Diethyl-benzene	j	Pentadecane
11	Dimethyl-ethyl-benzene	k	Hexadecane
		l	Heptadecane
		m	Octadecane
		n	Nonadecane
		o	Eicosane
		p	Heneicosane
		q	Docosane
		r	Tricosane
		s	Tetracosane

As the fuels used are so different, then it would be expected that the vehicle emissions would also vary and it would be possible under certain conditions to attribute the source of the pollutants by the levels of specific compounds present in an analysis. Further work will have to be done to determine whether this is a feasible technique or whether the levels of the hydrocarbons with more than 11 carbon atoms are too low to give significant meaning to such a procedure.

2.7. Levels of Aromatic Hydrocarbons in Car Exhaust

Some work was carried out to determine levels of C_6- C_{10} hydrocarbons in car exhaust. A typical chromatogram of car exhaust is shown in Figure 16.

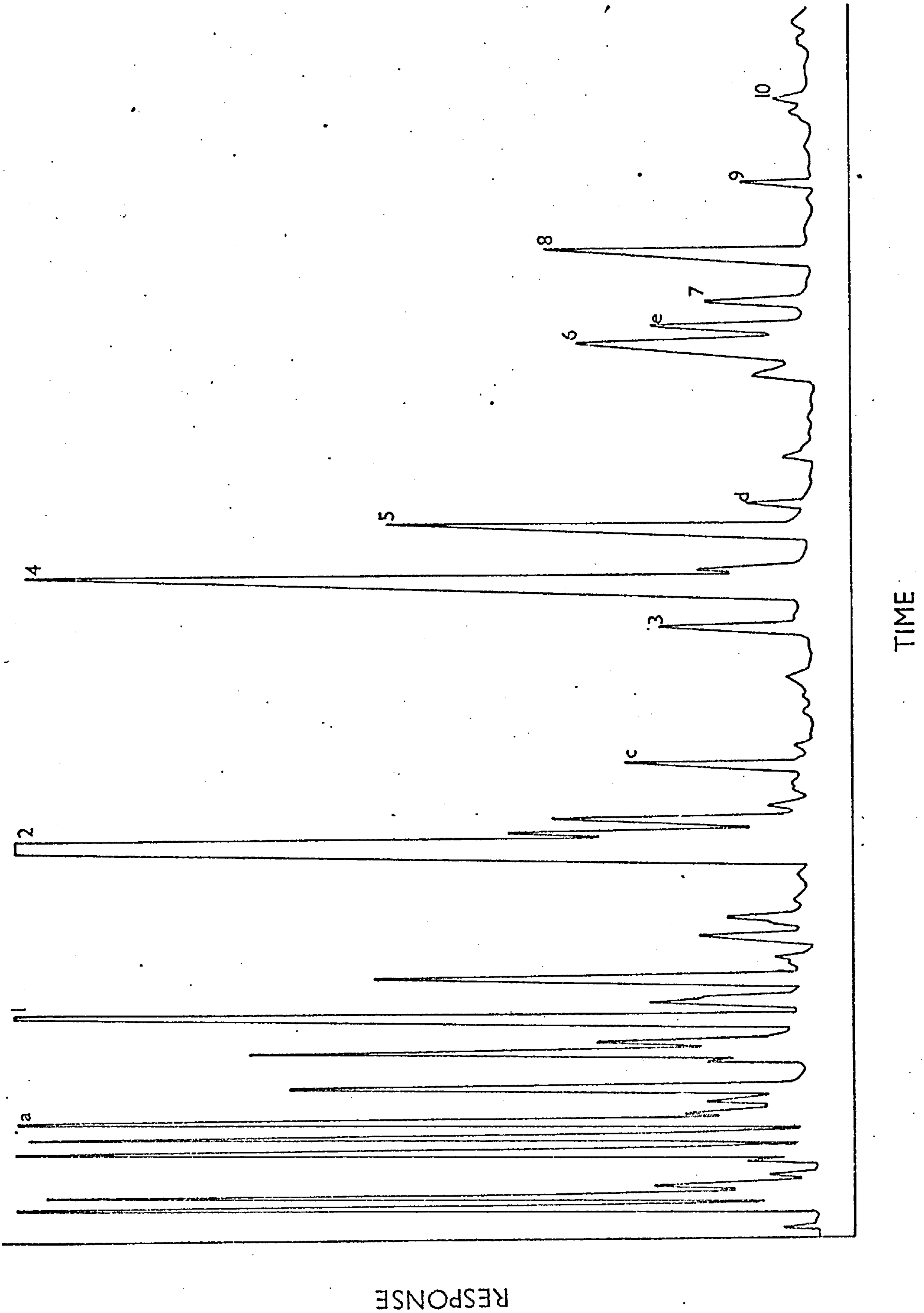


FIGURE 16 Car Exhaust

Using a Clayton Dynamometer a Ford Cortina 1600cc was driven under standard conditions and the exhaust analysed for various components. Both the ECE driving test cycle and constant speed tests were used.

The ECE driving cycle is a repetitive test comprising of four cycles from a cold start. It has been devised to represent typical driving patterns in European towns using European cars. The total raw exhaust gas from the four cycles is passed through a heat exchanger to remove most of the water vapour and then into four large plastic bags, cycles 1 and 2 into one bag and cycles 3 and 4 into the other.

For each bag the following parameters were determined: total hydrocarbons, carbon monoxide, carbon dioxide, oxides of nitrogen, C_6-C_{10} individual hydrocarbons.

Table 2.12. Various Species produced under ECE Driving Test Cycle Conditions

		THC (ppm)	CO (% v/v)	CO_2 (% v/v)	NO_x (ppm)
COLD START					
(1)	Bag 1	390	4.2	9.8	720
	Bag 2	300	3.1	10.2	760
(2)	Bag 1	410	4.7	10.2	760
	Bag 2	330	3.8	10.9	780
HOT START					
	Bag 1	290	3.0	11.4	840
	Bag 2	272	3.1	11.0	230

			HYDROCARBONS (ppm)						
			THC	Benzene	Toluene	m-& p-Xylene	o-Xylene	Ethyl-toluene	Trimethyl-benzene
CS	(1)	(i)	390	4.2	12.6	11.0	2.7	2.6	1.3
		(ii)	300						
	(2)	(i)	410	5.3	14.2	11.6	2.8	2.8	1.5
		(ii)	330	4.0	11.1	8.0	2.6	2.4	1.1
HS	(1)	(i)	290	2.7	9.1	5.6	2.3	1.8	0.9
		(ii)	272	2.4	7.6	5.3	2.2	1.6	0.8

Table 2.13. Various Species Produced Under Constant Speed Test Conditions

Speed	THC (ppm)	CO (% v/v)	CO_2 (% v/v)	NO_x (ppm)
I	183	1.1	11.1	80
10	231	4.4	10.0	200
20	272	3.7	10.9	320
30	282	2.0	13.0	920
	295	2.6	12.3	1100
40	213	1.1	13.0	1820
50	172	1.0	13.0	2150
	202	1.3	12.3	2200

Speed	HYDROCARBONS (ppm)						
	Total	Benzene	Toluene	*m*-& *p*-Xylene	*o*-Xylene	Ethyl-toluene	Trimethyl-benzene
I	183	3.8	6.4	4.7	1.9	1.7	1.4
10	231	4.4	8.3	6.2	2.1	2.1	1.5
20	272	5.0	10.2	7.9	2.6	2.3	1.6
30	282	5.3	11.9	8.8	3.1	2.7	1.5
	295	5.9	12.0	10.0	3.7	3.2	1.6
40	213	4.7	9.8	7.7	2.7	2.5	1.5
50	202	4.1	8.6	5.5	2.3	1.5	1.2

2.8. Conclusion

From the results obtained in these studies it would appear that at the sites where levels were determined a significant contribution to hydrocarbon pollution was from motor vehicles. Levels determined using the adsorbent technique and those obtained using the cryostat agreed to within 10% at any given site. The levels of individual hydrocarbons from the Teesside survey should only be taken as a guide to the order of magnitude at which they were present, because at the time they were taken the factors affecting the sampling techniques were not fully understood.

Ambient levels of hydrocarbons would not appear to pose any threat to health although it is interesting to note that at all times between 0800 - 2000 the average concentration of non-methane hydrocarbons exceeded the EPA standard.

It has been suggested that the toluene to benzene ratio is an indicator of the degree of contribution of automobiles to the total atmospheric hydrocarbon level. The ratio has been determined in Toronto where a value of 2.5:1 was obtained (18). This is in good agreement with the work presented in this thesis for levels determined by the road side which was 2.4:1. However, when taking measurements at a site where the main sources of hydrocarbons are evaporative losses e.g. the garage, then the ratio changes and it was found to be 1.9:1. It might be expected therefore that in the summer the ratio will be lower than in the winter as evaporative emissions will be more significant at that time because of the higher ambient temperature.

The measurements recorded were all from point sources and when considering the results it is not valid to extrapolate and predict levels for hydrocarbons at other places in London from the results already obtained. They may give an indication of what to expect but the local topography of an area and the prevailing meteorological conditions can affect the results drastically.

CHAPTER 3

ETHYLENE DIBROMIDE IN THE ATMOSPHERE

3.1. Introduction

Ethylene dibromide (EDB) and ethylene dichloride (EDC) are used mostly as petroleum additives. In this application these compounds should more correctly be known as 1,2-dibromoethane and 1,2-dichloroethane; and their function in lead alkyl containing petrols is to act as scavengers for the lead oxide released in the combustion process.

For quite some time there has been concern about the potential toxic hazards of chlorinated organic compounds used as insecticides. More recently some degree of attention has been transferred to the lower molecular weight organohalogen species which are produced and used industrially on a vast scale. In a recent publication (130) the authors have considered the problems associated with the chloroderivatives of methane, ethane and ethylene which were found to be widely distributed in the atmosphere at a background level in the ppb range.

In the report of a workshop held in America (131) it was concluded that there are currently four practical methods for the measurements of environmental concentrations of the halogenated hydrocarbons. These are:-

1. Gas chromatography with an electron capture detector (132-147). This is the most widely used technique, its major disadvantage being that it is compound dependent in its sensitivity, so although it can detect 1 ppt of CCl_4, for CH_3Cl the detection limit is 0.1-1.0 ppb.
2. Gas chromatography coupled with mass spectrometry (50,55,148-151). This has a maximum sensitivity of 5 ppt v/v which is equivalent to 0.5 picogrammes in a 20ml sample. The advantage of this system is that it has equal sensitivity for all compounds.
3. Long path length infra-red adsorption spectroscopy (108, 153,154). The detection limit of this technique is 10 ppb. For use at ambient levels, therefore, a preconcentration step is required. The compounds after separation on a GC column have to be collected and

introduced into an infra-red cell before measurements can be taken.

4. Infra-red solar spectroscopy (155).

   This utilises the solar spectrum at large zenith angles to obtain great path lengths through the atmosphere. The results obtained require detailed computer analysis and the technique is not sufficiently sensitive to detect some of the compounds of interest at ambient levels.

Investigations into the levels of low molecular weight brominated compounds in the atmosphere have been limited; bromoform (55), methyl bromide (148) and 1,2-dibromoethane (146,147) being the only compounds detected.

It is apparent that the distribution and character of potential sources of EDB and EDC are very different to those for other halogenated compounds. Particularly in urban areas the potential for localised concentrations well above background levels resulting from the accumulation of vehicles or proximity to garages cannot be ignored. The concentration of EDB in petrol is variable but the sum of EDB and EDC added is on a mole to mole basis with organic lead. A typical fuel contains 0.5g Pb l^{-1} with an atom ratio of Pb:Cl:Br of 1:2:1.

In October 1974 the National Cancer Institute, USA, issued a memorandum of alert on EDB having previously reported (155) experiments to determine the carcinogenicity of EDB to rats and mice. A preliminary study has been conducted by the EPA (146) in the USA to determine the levels of EDB in both urban air and in the vicinity of manufacturing plants. The levels reported in this and a more extensive subsequent EPA report (156) were several orders of magnitude below the threshold limit value of 25 ppm currently applied by the American Conference of Governmental Industrial Hygenists.

Although EDB does not appear to be a substance posing immediate environmental hazards, there is available only limited information, upon which assessments may be based of the potential consequences of long-term low-level exposures or possible synergistic effects. Thus the chemical cannot be considered environmentally safe.

When heated with water EDB hydrolyses to ethylene glycol and bromoethanol. Under neutral conditions and ambient temperature the half-life of this reaction is 5-10 days. EDB is resistant to atmospheric oxidation by peroxides and ozone, typically the half-life for these reactions is in excess of 100 days.

There are several differences between the USA and UK situations which make it desirable that levels of EDB should be determined in this country:-

I) There are no evaporative or combustion emission controls in the UK.

II) The structure of the vehicle population is different as are driving conditions and modes of operation.

Furthermore workers in the USA stated that: "EDB is not expected to be emitted in the exhaust because it is not expected to survive the combustion process." Preliminary studies in this laboratory have shown this assumption to be invalid.

3.2. Experimental

EDB was determined in the atmosphere by adsorption of the compound onto a short column of Chromosorb 102 as described in Section 1.4.4. The adsorbed material was subsequently heat desorbed and analysed by gas chromatography using electron capture detection.

3.2.1. Sampling Tubes

Chromosorb 102 (0.35g) was packed into 4 x $\frac{1}{4}$ in o.d. stainless steel tubes which were purged with helium at 220°C and a flow rate of 20 ml min^{-1} for 24 hours. After this time the Chromosorb was repacked, to overcome problems of preferential gas channelling resulting from polymer shrinkage and purged for a further 12 hours.

3.2.2. Sampling Prodcedure

The sampling tube was connected between a glass fibre inlet filter and a Du Pont constant flow sampling pump. Using this pump a known volume of air could be sampled with confidence. The sample collection rate was automatically regulated to ensure that a preset flow rate in the range 50-200ml min^{-1} was maintained to within 5%. The flow rate setting was independent of the collector media pressure drop characteristics which was essential in field use where a variety of tubes were used, each with a different pressure drop.

Air was sampled at 100ml min^{-1} for one hour. Desorption and analysis were carried out by connecting sample tubes via a Carle valve into the carrier gas line of the gas chromatograph just prior to the injection port. The valve was contained in a thermostatically controlled oven capable of being heated to 300°C. Following the connection of the tube to the valve the whole system was warmed to 200°C whilst carrier gas flowed through a closed trap on the valve. When this temperature had been reached the carrier gas was diverted to flow through the tube. The carrier gas was allowed to flow continuously through the tube to achieve complete desorption of the adsorbed material.

3.2.3. Calibration

This technique was calibrated for EDB using a permeation tube oven. The results obtained from this were compared to those obtained by direct injection of similar quantities of EDB onto the GC column. To determine whether there was any 'breakthrough' of EDB from the sampling plug two tubes were sampled in series. At the flow rate used (100ml min^{-1}) and for a sampling time of 60 minutes no EDB was ever found on the second tube. Comparison of the results obtained from the permeation tube with those for direct injection indicated that the accuracy and reproducibility of the sampling technique were within 5%.

3.2.4. Gas Chromatographic Operating Conditions

Separation of the eluted material was carried out using a Hewlett Packard 5750 gas chromatograph fitted with a Ni 63 electron capture detector. The column used for routine analysis was 8 ft x 1/8 in o.d. stainless steel packed with 5% Carbowax 20M on Gas Chrom W AWDMCS, the argon 5% methane carrier gas flow being 30ml min^{-1} with the column operated isothermally at 70°C. EDB was identified by comparing retention time data obtained on five different columns: Carbowax 20M, NGS, OV101, OV7 and OV17.

3.3. Results

Ambient concentrations were determined at three sites. Typical results of hourly mean concentration are tabulated in Table 3.1. The sampling sites were:

1) Exhibition Road, London SW7. This is a wide dual carriageway carrying approximately 1500 vehicles per hour. The sampling site was 5m from the roadside at a height of 1m above ground level.
2) Car Park. This is an open air car park in the centre of the campus. There was little traffic movement during the sampling period.
3) Garage Forecourt. The sampling point was 5m downwind of the petrol pumps at a height of 1m.

Table 3.1. Ethylene Dibromide in Ambient Air

Sampling Site Date (Wind)	EDB ($\mu g\ m^{-3}$)	Temperature (^{o}C)	Time
Exhibition Road	0.09		11.00-12.00
August 1976	0.08	28-30	12.00-13.00
	0.09		13.00-14.00
Exhibition Road	0.001		10.00-11.00
2nd December 1976	0.001		11.00-12.00
Wind SW 0-40 km hr^{-1}	0.001		12.00-13.00
	0.001	4-9	13.00-14.00
	0.03		14.00-15.00
	0.02		15.00-16.00
	0.01		16.00-17.00
Exhibition Road	0.01		10.00-11.00
3rd December 1976	0.04		11.00-12.00
Wind 0-10 km hr^{-1}	0.10		12.00-13.00
	0.04	4-8	13.00-14.00
	0.02		14.00-15.00
	0.17		15.00-16.00
	0.01		16.00-17.00
Garage Forecourt	1.8	30	14.00-15.00
August 1976	1.2		15.00-16.00
Car Park	0.02	30	15.00-16.00
August 1976	0.05		14.00-15.00

3.4. Dynamometer Studies

Using a Clayton Dynamometer a Ford Cortina 1600cc was driven under standard conditions and the exhaust analysed for various components. Both the ECE driving test cycle, and constant speed tests were used, and the results are tabulated in Tables 3.2 and 3.3 respectively.

The ECE driving test cycle is a repetitive test comprising four cycles from a cold start. It has been devised to represent typical driving patterns in European towns using European cars. The total raw exhaust gas from the four cycles is passed through a heat exchanger to remove most of the moisture and then into two large plastic bags, cycles 1 and 2 into one bag and cycles 3 and 4 into the other.

For each bag the following parameters were determined: total hydrocarbons, carbon monoxide, carbon dioxide, oxides of nitrogen and EDB.

Table 3.2. Ethylene Dibromide and Other Species Produced Under ECE Driving Test Cycle Conditions

		THC (ppm)	CO (% v/v)	CO_2 (% v/v)	NO_x (ppm)	EDB (ppb)
COLD START						
(1)	Bag 1	390	4.2	9.8	720	17.2
	Bag 2	300	3.1	10.2	760	11.6
(2)	Bag 1	410	4.7	10.2	760	19.8
	Bag 2	330	3.8	10.9	780	13.0
HOT START						
	Bag 1	290	3.0	11.4	840	10.9
	Bag 2	272	3.1	11.0	230	10.2

Table 3.3. Ethylene Dibromide and Other Species Produced Under Constant Speed Test Conditions

Vehicle Speed	THC (ppm)	CO (% v/v)	CO_2 (% v/v)	NO_x (ppm)	EDB (ppb)
IDLE	183	1.1	11.1	80	9
10	231	4.4	10.0	200	10
30	282 295	2.1 2.6	13.0 12.3	920 1100	8 9
40	213	1.1	13.0	1820	5
50	172 202	1.1 1.3	13.0 12.3	2150 2200	0.3

* 1 ppb EDB ≅ 4.05 $\mu g\ m^{-3}$

3.5. Dibromoethane/Organic Lead in Air

It was assumed that Premium grade petrol contained 0.51g l^{-1} of lead, was of molecular formula $C_8H_{15.4}$, specific gravity 0.75, and that additives were present in the following concentrations (mole l^{-1}): TEL (tetraethyl lead) 0.57 x 10^{-3}; TML (tetramethyl lead) 1.89 x 10^{-3}; EDB 1.23 x 10^{-3}; and EDC 2.46 x 10^{-3}. Similarly Regular grade petrol was considered to be of composition $C_8H_{15.4}$, specific gravity 0.73, and to contain: lead 0.40 g l^{-1} and TEL 1.95 x 10^{-3} mole l^{-1}, TML 0.02 x 10^{-3} mole l^{-1}, EDB 1.09 x 10^{-3} mole l^{-1} and EDC 2.18 x 10^{-3} mole l^{-1}. The bulk usage of petrol in the UK was taken to be 70% Premium and 30% Regular. The petrol in circulation was assumed to be a mixture of 70% Premium to 30% Regular and the mole fractions of additives in such a mixture calculated:

MOLE FRACTIONS	PREMIUM	REGULAR	MIXTURE
TEL	0.85×10^{-4}	2.98×10^{-4}	1.47×10^{-4}
TML	2.81×10^{-4}	0.03×10^{-4}	1.99×10^{-4}
EDB	1.83×10^{-4}	1.66×10^{-4}	1.77×10^{-4}

The vapour pressures of pure TEL, TML and EDB may be derived from the expression:

$$\log_{10} P = \frac{0.2185a}{T} + b$$

Where T is the temperature in degrees absolute and a and b are constants, the values of which were taken to be as reported in the 54th Edn. of the Handbook of Physics and Chemistry. It was assumed that the vapour pressures exerted by the TEL, TML and EDB fractions in petrol would obey Raoult's Law and theoretical values were determined for the mole fractions obtained above at an assumed temperature of 293°K:

VAPOUR PRESSURE	PREMIUM	REGULAR	MIXTURE
TEL	0.25×10^{-4}	0.86×10^{-4}	0.43×10^{-4}
TML	64.07×10^{-4}	0.68×10^{-4}	45.37×10^{-4}
EDB	20.68×10^{-4}	18.76×10^{-4}	20.00×10^{-4}

These vapour pressures were readily converted to concentrations in the vapour phase and calculated values are recorded below. The values for TEL and TML are recorded as lead concentrations in the vapour phase to enable comparison with experimentally determined levels of organic lead:

CONCENTRATION ($mg\ m^{-3}$)		PREMIUM	REGULAR	MIXTURE
TEL	lead equivalents	0.28	0.97	0.48
TML		72.59	0.77	51.35
EDB		21.26	19.29	20.56

Thus at 293°K evaporative losses of EDB, TEL and TML from the 70% Premium to 30% Regular petrol mixture assumed to be in circulation, would be expected to generate an EDB:organic lead ratio of 0.40 w/w.

3.6. Discussion and Conclusions

The levels of EDB determined in London were in the same range 0.01-1.0 $\mu g\ m^{-3}$ but were generally lower than those reported by the EPA for several cities in the USA, (146,147).

Previous work in this laboratory (157) has included the measurement of organic lead levels at sampling sites close to those used here for the determination of EDB (Exhibition Road). The level of organic lead on hot days was found to be 0.11 $\mu g\ m^{-3}$. Application of the EDB to organic lead ratio derived above (0.40 w/w) would give a predicted EDB concentration of 0.04-0.05 $\mu g\ m^{-3}$. Experimentally determined levels of EDB on a hot day were 0.08-0.09 $\mu g\ m^{-3}$; this difference may be partially accounted for by a contribution to the EDB levels from exhaust emissions. The proximity of the measured and predicted levels generates confidence in the experimental methods used; and although it would be unwise to place undue significance on variations in the few data available, features, which would require statistical verification, are discernible.

In general the levels of EDB determined on Exhibition Road on winter days (temperature 4-9°C) were considerably lower than in summer with a mean on a relatively still day of 0.05-0.06 µg m^{-3}. (This figure contains two high levels of 0.17 and 0.10 µg m^{-3} obtained when vehicles were started up under choke close to the sampling point). The lower winter levels are the result of a reduction in evaporative losses particularly from standing vehicles (the calculated evaporation rate for EDB at 5°C is less than a third of that at 30°C). An indication of the magnitude of evaporative losses from standing vehicles is given by the levels measured in the Car Park (0.02-0.05 µg m^{-3}). It is also probable, however, that an opposing trend will be produced by the change in driving conditions in winter (e.g. cold starts), which will cause an increase in the EDB content of exhaust emissions (Table 3.2). Thus, if the levels of EDB reaching the atmosphere are considered to be produced by unburnt fuel, the relative contributions of evaporative and exhaust sources to this total will vary with weather and traffic conditions. In summer (high temperatures) evaporative losses will be the most significant contribution to the levels of EDB in the environment, whilst the change in mode of operation generated by the lower winter temperatures will cause an increase in the significance of exhaust emissions. The study has shown that using this technique it is possible to obtain rapid reproducible results for levels of EDB. Sampling periods as short as 15 minutes could be used but if desired the sampling time could be extended to many hours. The levels of EDB so far determined in ambient air do not appear to constitute a significant risk to health.

CHAPTER 4

THE DETERMINATION OF TERPENOID COMPOUNDS IN THE HEADSPACE VAPOURS OF CANNABIS

4.1. Introduction

By utilising the experience gained in the analysis of trace organics in the atmosphere it was possible to devise methods for the analysis of headspace vapours. In this section these methods are described together with the identification of certain terpenoid compounds found in the headspace vapours of cannabis. Earlier investigations (158 - 161) have shown the presence of monoterpenes, monoterpene alcohols, sesquiterpenes and a sesquiterpene oxide in cannabis resin.

4.2. Production of a Standard Library Tape

The library tape for the data system was compiled using samples of known terpenes obtained from various sources. Samples were introduced into the mass spectrometer via the heated expansion volume facility, which was operated at 100°C.

Several replicate spectra were recorded for each compound, as slight variations in the spectral detail were apparent between scans.

The terpene standards were obtained from three sources. Samples supplied by the Home Office varied greatly in purity (60-98%). Secondary sources were Imperial College Chemistry Department and Firmenich, Geneva. All samples obtained from these sources were $\geqslant$90% pure.

4.3. Headspace Sampling Techniques

Four techniques in all were used to sample the headspace vapours:

4.3.1. Gas Tight Syringe:- A quantity of cannabis was placed in a glass vial fitted with a septum. If required the vial was then warmed and the headspace vapours were allowed to equilibrate. Samples of this headspace were then withdrawn by means of the syringe and injected into the gas chromatograph.

4.3.2. Elscint Gas Sampler:- This system was useful as a method of concentrating sufficient material for a gas chromatographic/mass spectral analysis. Its value for quantitative work was, however, limited, as has been discussed in Chapter 1. The headspace was sampled by placing some cannabis in a glass vessel and drawing air across it. The incoming air was purified by passing it through a 'U' tube packed with a solid adsorbent, cooled in liquid nitrogen.

4.3.3. Chromosorb 102 Sampling Tubes:- The adsorption technique devised to analyse organics in the atmosphere was used successfully to analyse cannabis headspace, the sampling protocol being the same as that used with the Elscint.

4.3.4. Solvent Technique:- A sample of cannabis was placed in the bottom of a vacuum desiccator. A viscous liquid e.g. Dinonyl Phthalate was suspended above this either in a stainless steel loop or between two fine stainless steel meshes. The desiccator was then evacuated and left for 12 hours. The phthalate was collected in a piece of narrow bore glass tubing and subsamples of this were injected into the gas chromatograph.

The solvent technique and direct injection of the headspace vapours using a syringe yielded comparable results. When sampling onto the solid adsorbents however, there was a greater abundance of the more volatile compounds because these were stripped more readily from the cannabis in the vessel during the sampling period. This effect was more pronounced with the Elscint Sampler. With this system desorption of the higher molecular weight compounds was more difficult than that of the more volatile compounds whereas with the other adsorption technique there was complete desorption of all the terpenes present. This accounts for the difference between the two adsorption techniques and between them and the other sampling methods where the headspace vapours were in equilibrium.

4.4. Gas Chromatographic Operating Conditions

The column was 20 ft x 1/8 in o.d. stainless steel packed with Chromosorb W coated with 3% OV17. The column was programmed between 50 and 150°C at a rate of 4°C min^{-1}, the final temperature being maintained until all compounds had been eluted from the column. The nitrogen carrier gas flow rate was 25 ml min^{-1}.

Under these conditions retention times for terpenes were determined relative to that of limonene, and are recorded in Table 4.1. Several mixtures of terpenes in diethyl ether solution were used for this procedure, limonene always being present as an internal standard.

Table 4.1. Retention Times for Terpenes Relative to Limonene. Response Factors for 1 μg of Terpene Measured on the Gas Chromatograph Relative to 1 μg Limonene.

Compound	Relative Retention Time	Response Factor
α-Pinene	0.6	0.5
Camphene	0.7	
β-Pinene	0.8	0.7
Myrcene	0.8	0.5
Δ-3-Carene	0.9	0.6
2-Methyl-6-heptene-one	0.9	0.6
Limonene	1.0	1.0
Phellandrene	1.0	0.6
p-Cymene	1.0	0.9
Ocimene	1.0	0.7
Terpinolene	1.2	0.2
Linalool	1.3	0.9
d-Fenchyl alcohol	1.3	1.2
Borneol	1.5	
Terpineol	1.6	1.1
Trans-α-bergatomene	2.2	
Caryophyllene	2.2	1.1
Bisabolene	2.3/2.6*	0.1
Humulene	2.3	0.6
α-Selinene		0.8
β-Selinene	2.5	1.1
Caryophyllene oxide		0.5

* It would appear probable that the relative retention time of bisabolene is 2.6 and that the peak at 2.3 is a major impurity in the sample.

4.5. Quantities Required for Analysis

The detection limit for any individual terpene by this technique is effectively determined by the minimum amount required for definitive mass spectral identification. The quantity of compound reaching the mass spectrometer is critically dependent on the efficiency of the gas chromatograph/mass spectrometer interface mechanism.

The gas chromatograph is linked to the mass spectrometer via a silicone membrane separator, which has a relatively low transfer efficiency. Thus the quantities of terpenes required for positive mass spectral identification using this system are relatively large.

A diethyl-ether solution of known amounts of three terpenes (α-pinene, limonene and caryophyllene, 1.06 : 1.00 : 0.39 by weight) was prepared and used to investigate the efficiency of the separator system. The actual amounts of each component contained in the sample injections were 13.8, 12.9 and 5.0 µg for α-pinene, limonene and caryophyllene respectively. The relative response factors for the terpenes were determined by comparison of peak areas from both flame ionisation detector and 'reconstructed' chromatograms, the latter represent the use of the mass spectrometer as a total ion detector. The results obtained are presented in Table 4.2.

The data quoted in Table 4.2. indicate that although the relative responses of the gas chromatograph/flame ionisation detector and the gas chromatograph/separator/mass spectrometer are in reasonable agreement for α-pinene and limonene, this is not the case for limonene and caryophyllene.

Table 4.2. Relative Response Factors for Terpene Mixture on Gas Chromatograph/Flame Ionisation Detector and Gas Chromatograph/Separator/Mass Spectrometer Systems

Compound	Gas Chromatograph/ Flame Ionisation Detector Response	Gas Chromatograph/ Separator/ Mass Spectrometer Response	Amount Required for +ve Identification
α-Pinene	0.57	0.45	6µg
Limonene	1.00	1.00	6µg
Caryophyllene	1.14	3.19	2µg

The separator is apparently three times more efficient towards caryophyllene then limonene. These data clearly demonstrate that a major problem in the determination of detection limits for individual compounds is introduced by the differences in transfer efficiency of the separator towards specific components of a mixture. Thus determination of an absolute amount of any compound required for positive identification by such a system is intimately related to the transfer efficiency of the separator for that compound under a given set of operating conditions. As shown in Table 4.2. the required amount of compound will probably lie in the 1-10 µg range. It is probable that the use of a capillary column interfaced directly to the mass spectrometer and avoiding the use of a separator would considerably increase the sensitivity of the system.

4.6. Identification of some Terpenes In Cannabis Headspace

Figures 17, 18 are the reconstructed chromatograms of typical headspace samples (samples 11 and 12). These were taken above a resin at

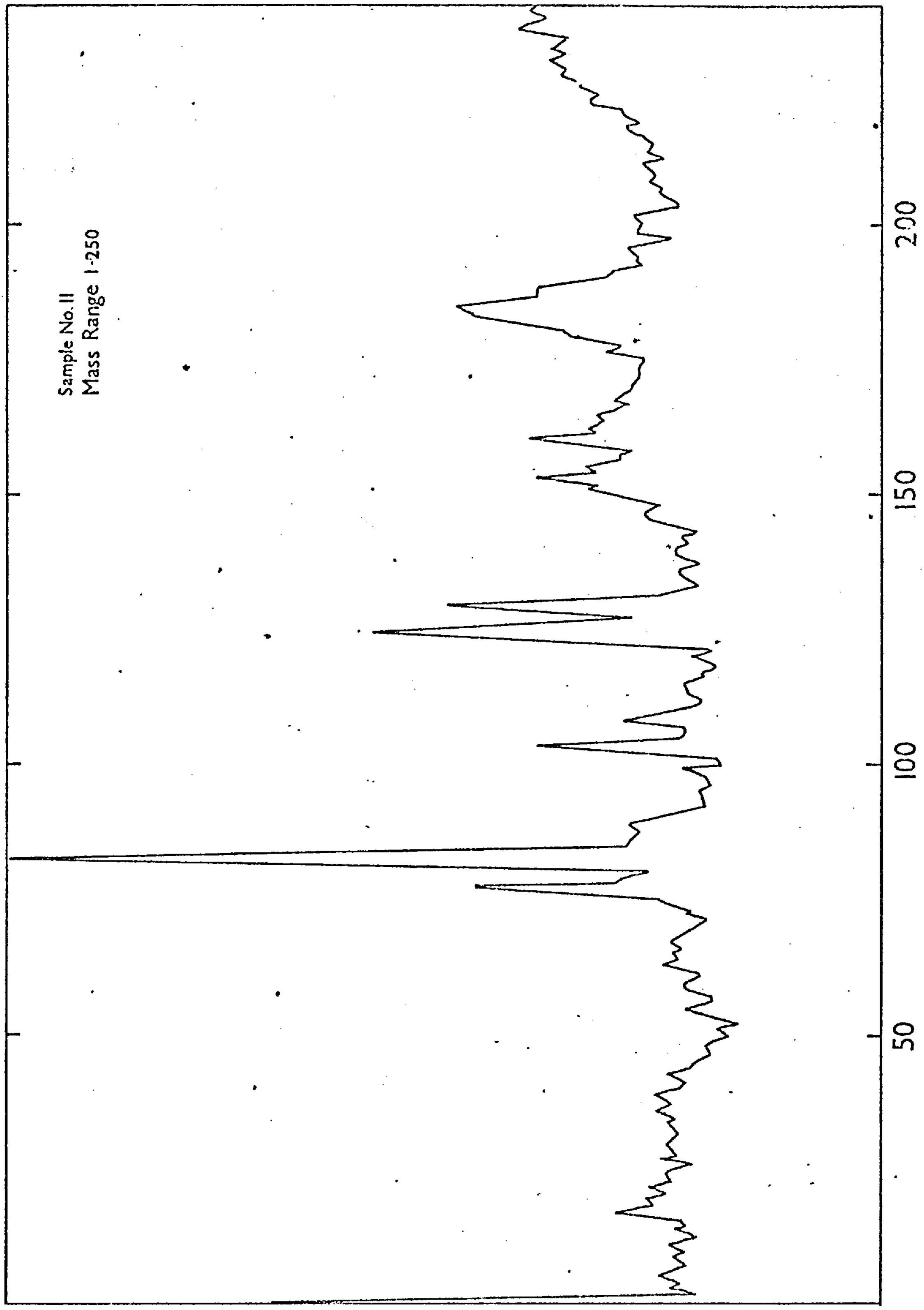


FIGURE 17 Reconstructed Chromatogram of Headspace Above Cannabis Resin

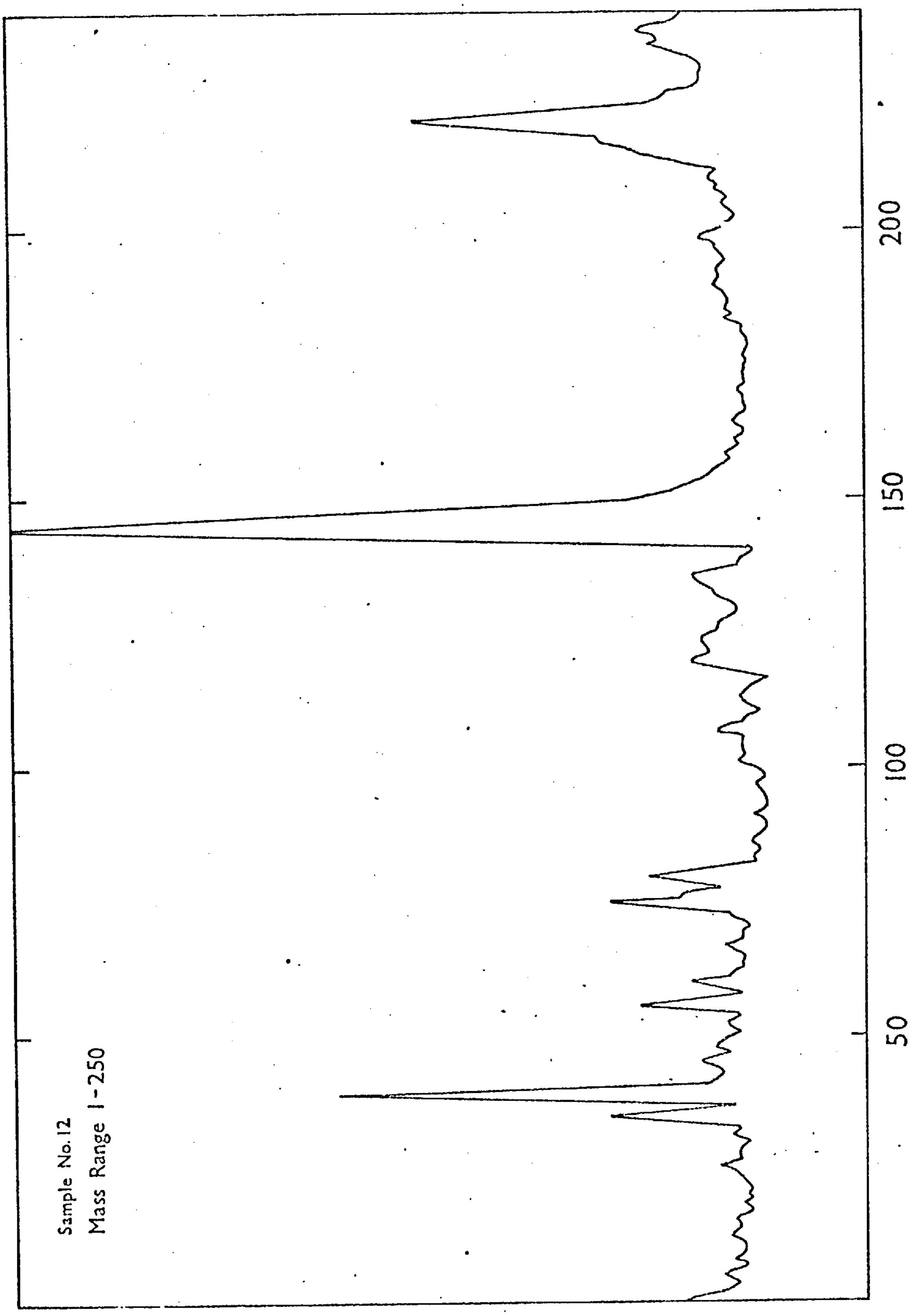


FIGURE 18 Reconstructed Chromatogram of Headspace Above Cannabis Resin

elevated temperature (typically 60°C). They were analysed on the gas chromatograph/membrane separator/mass spectrometer system and the reconstructed chromatograms were produced using a standard Hewlett Packard programme on the data system. Figure 19 is the reconstructed chromatogram of a standard solution (sample 14) of known terpenes generated under the same operating conditions as used for the analysis of the resin headspace samples.

Table 4.3. lists the compounds identified in these samples and indicates the spectrum numbers in the reconstructed chromatograms corresponding to each compound.

Table 4.3. Reconstructed Chromatograms (Figures 17-19) are listed showing Correlations between Spectrum Numbers and Compounds Present

Compound	Sample 11 Spectrum Number (Figure 17)	Sample 12 Spectrum Number (Figure 18)	Sample 14 Spectrum Number (Figure 19)
Thujene	78	35	-
α-Pinene	83	39	41 - 42
Camphene	89	-	-
β-Pinene	104	55	59 - 60
Myrcene	109	59 - 60	63 - 64
2-Methyl-6-heptene-one	-	-	75
Limonene	124	74	79 - 80
Ocimene or phellandrene	129 - 131	79 - 80	-
Terpineol	-	144 - 146	154 - 155
Caryophyllene	184 - 188	220	235 - 237
Humulene	-	237 - 238	-

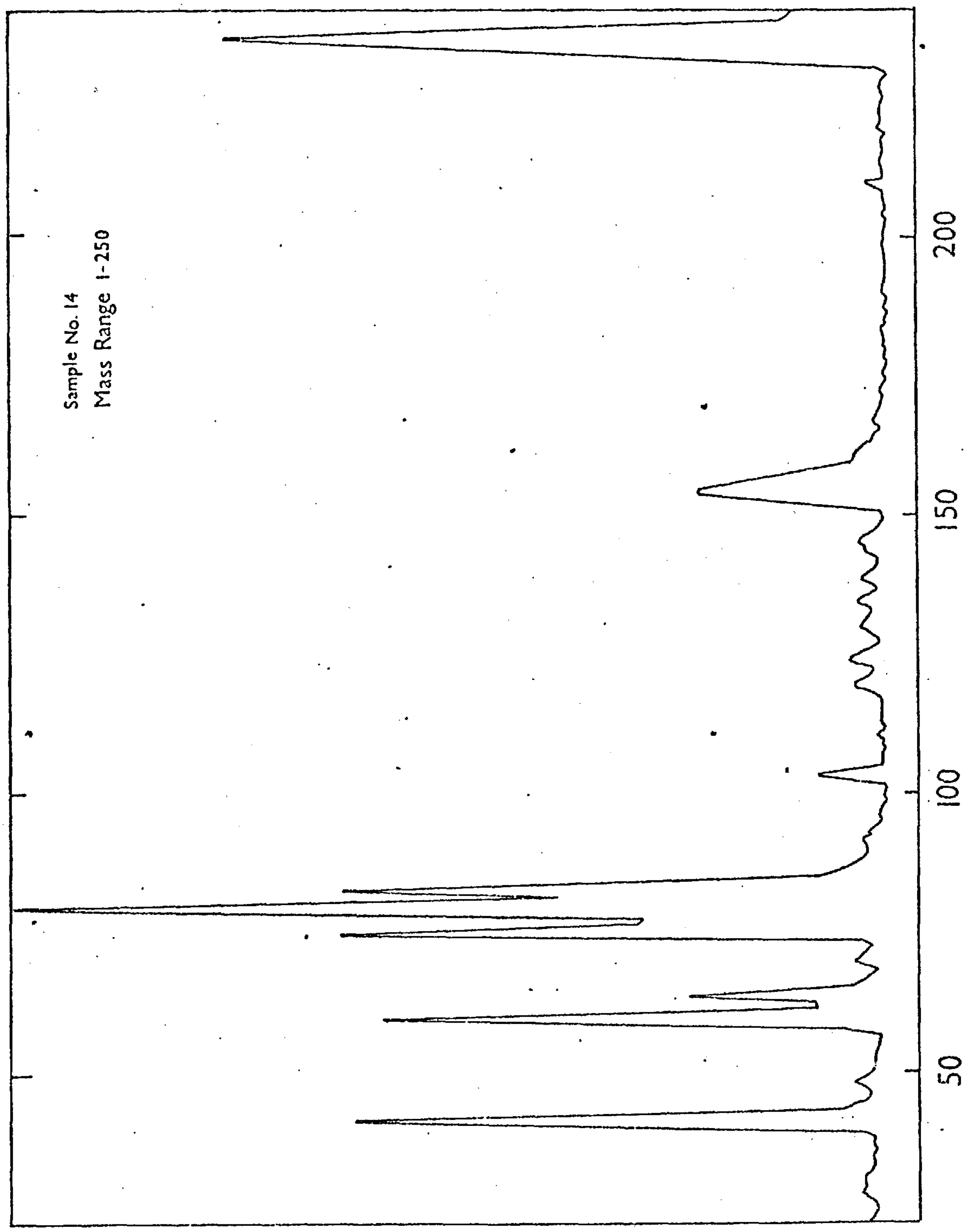


FIGURE 19 Reconstructed Chromatogram of Standard Solution of Terpenes

Figures 20-22 are chromatograms obtained using flame ionisation detection of typical samples taken using the syringe and solvent techniques. The samples involved were: Figure 20, Lebanese Gold resin; Figure 21, Pakistani Black resin; Figure 22, herbal sample. A key to peak identification for these chromatograms is given in Table 4.4.

Table 4.4. Peak Assignments for Compounds in Cannabis Headspace Vapours

Peak Number	Compound
1	α-Thujene
2	α-Pinene
3	Camphene
4	
5	β-Pinene
6	Myrcene
7	Δ-3-Carene
8	Limonene
9	Phellandrene/ocimene
10	
11	Terpinolene
12	Linalool
13	d-Fenchyl alcohol
14	
15	Trans-α-bergatomene
16	Caryophyllene
17	Humulene
18	Selinene

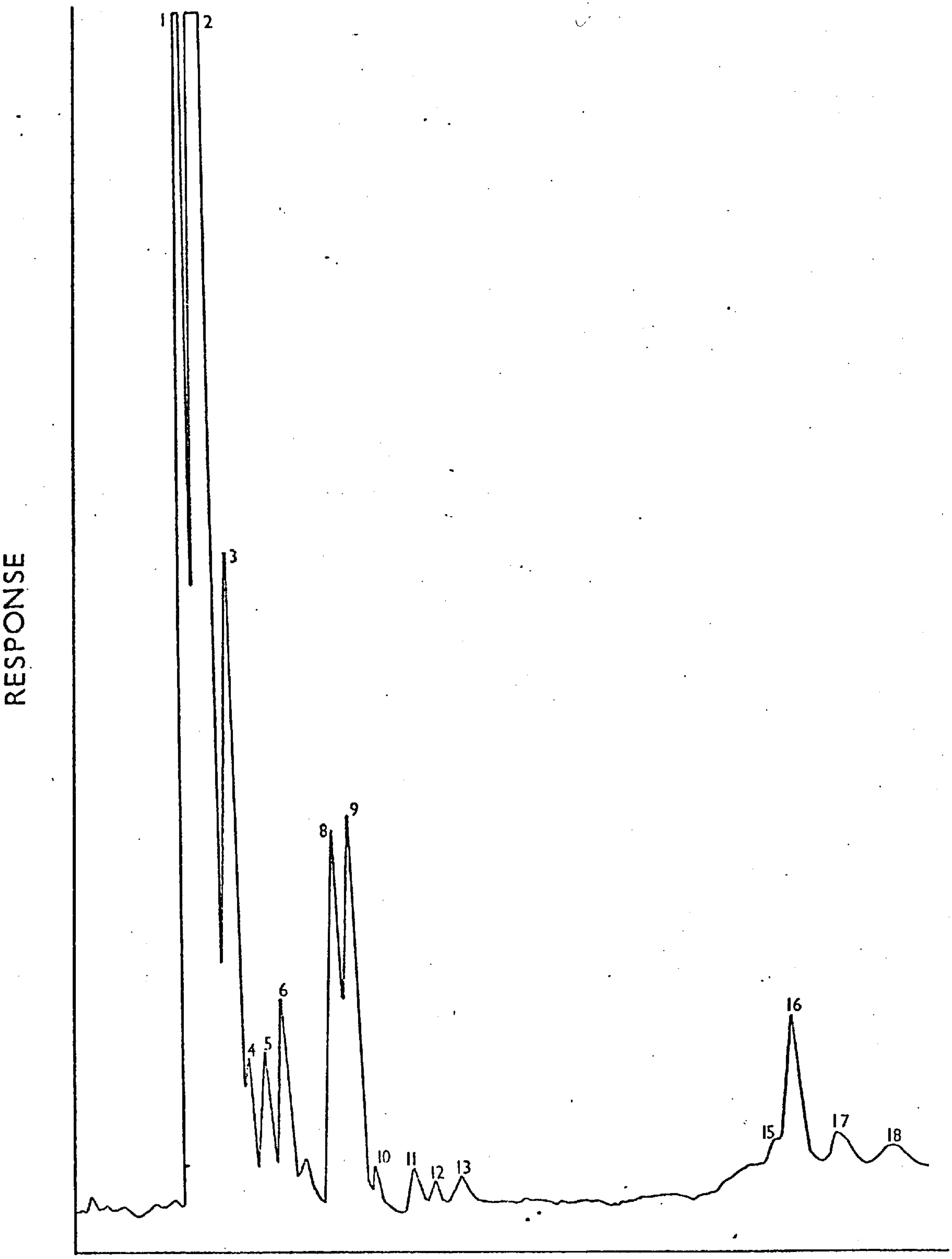


FIGURE 20 Héadspace Above Lebanese Gold Resin

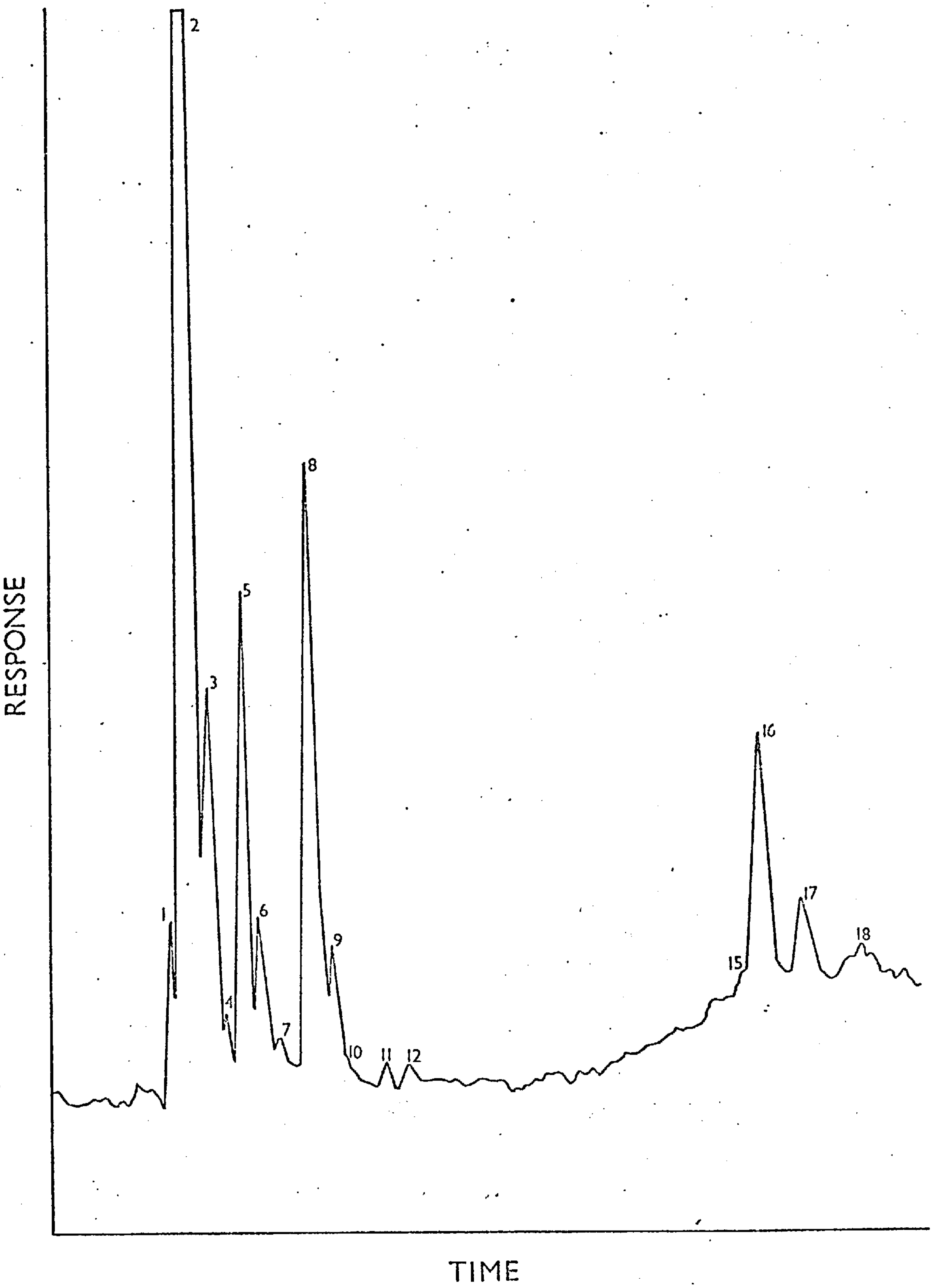


FIGURE 21 Headspace Above Pakistani Black Resin

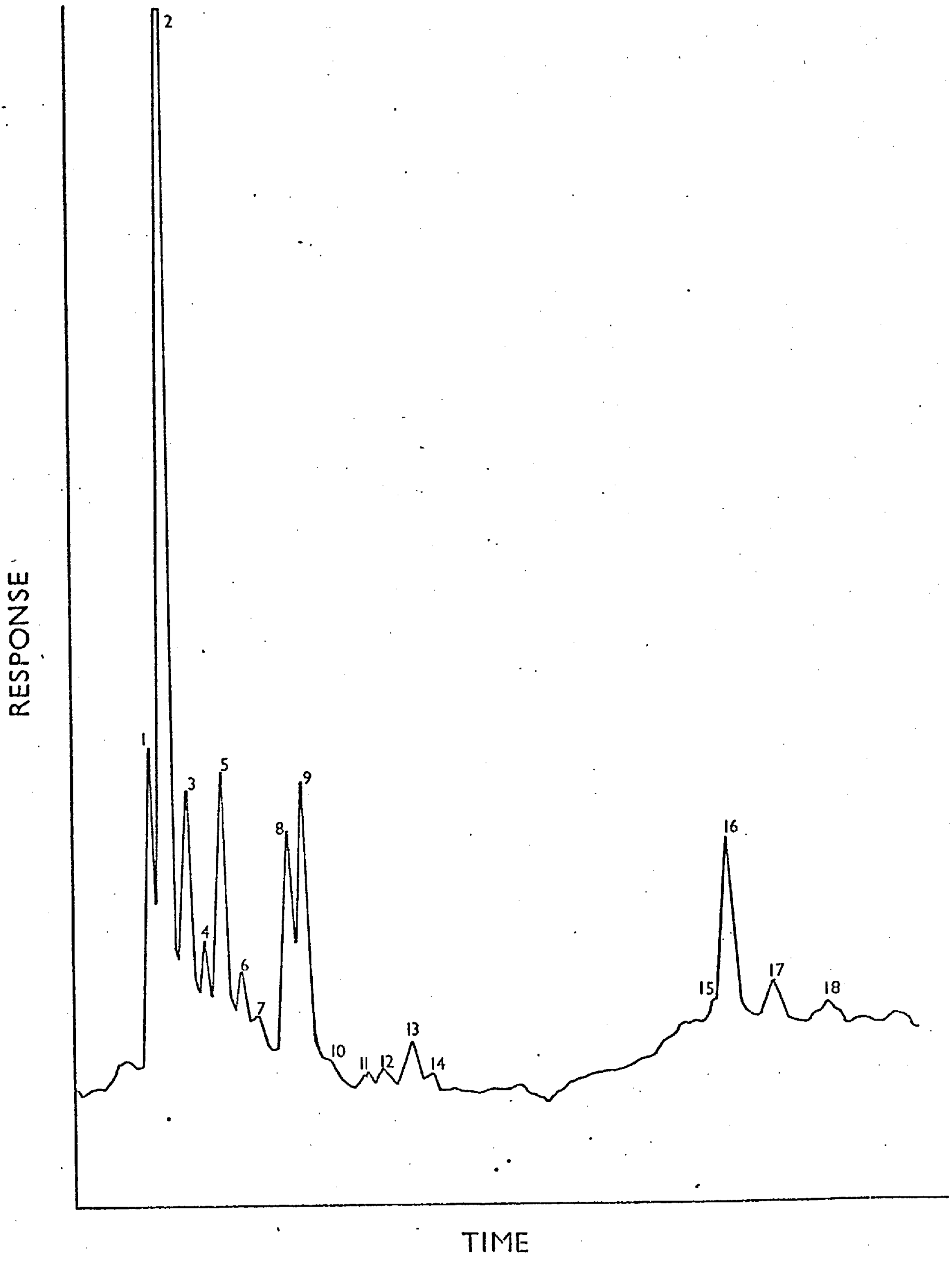


FIGURE 22 Headspace Above Herbal Sample

The assignments in Table 4.5. were made on the basis of retention time data and by match and purity figures obtained from comparison of the mass spectra from samples with those of the standard library tape. A perfect fit in the following table would be indicated by 1.000.

Table 4.5. Typical Match and Purity Figures Obtained from a Gas Chromatograph/Mass Spectral Analysis

Compound	Match	Purity
α-Pinene	0.940	0.954
Camphene	0.745	0.868
β-Pinene	0.755 0.566	0.745 0.977
Myrcene	0.544 0.666	0.977 0.754
Δ-3-Carene	0.571	0.924
2-Methyl-6-heptene-one	0.567	0.723
Limonene	0.737	0.872
Ocimene	0.475 0.788	0.908 1.000
Phellandrene	0.745	1.000
Terpinolene	0.916	0.967
Terpineol	0.757	0.854
Trans-α-bergatomene	0.688	0.705
Caryophyllene	0.787	0.969
Humulene	0.568	0.868

4.7. Conclusions

The compilation of the library tape presented few problems. The variation in purity of reference compounds together with the differences in transfer efficiency of the separator for specific compounds produced difficulties in the determination of both the absolute amounts of individual species required for analysis and also in the relative response factors.

It was evident from both the flame ionisation detector and reconstructed chromatograms that the relative amounts of specific compounds varied greatly from sample to sample, and considerable variation in composition was also apparent for specific samples with time.

The relative amounts of the terpenes in the headspace vapours were determined by injecting 5ml of the headspace obtained above 10g of cannabis contained in a closed vessel, and the results are recorded in Table 4.6.

Table 4.6. Relative Concentrations of Terpenes in the Headspace of Various Cannabis Samples

Compound	Herbal	Resin		Oil
	Kenyan Herbal	Lebanese Gold	Pakistani Black	
Thujene	4	7.8	1.9	0.5
α-Pinene	12.9	159	70.6	32.2
Camphene	0.1	7.9	3	1.2
β-Pinene	1.0	3.3	3.5	3.7
Myrcene	1.1	1.5	0.7	2.7
Limonene	21	8.7	4.4	21.4
Phellandrene/ocimene	0.6		3.5	
Terpinolene		0.6	0.8	
Linalool			0.4	
d-Fenchyl alcohol		0.6	0.6	
Trans-α-bergatomene		0.3	0.2	3.3
Caryophyllene	3.2	1.2	2.9	3.3
Humulene	1.2	0.4	0.8	0.6

CHAPTER 5

ANALYSIS OF VOLATILE ORGANICS IN WATER

5.1. Introduction

Up until the early 1960's organics in water were considered by many as a single parameter. Determinations such as chemical oxygen demand, biological oxygen demand and total organic carbon were parameters used to measure the organic loading of a body of water. Such measurements although useful indicate nothing about the nature of the individual organic compounds present. Little attention was given to the identification of the individual components because at that time there were no techniques available for determining trace organics in complex mixtures. There was also little realisation or a lack of knowledge about the significance of long term and sometimes acute toxic effects caused by many of the compounds. There has been more awareness in recent years and methods for the analysis of organics in water have been developed or are being developed and improved to provide needed information. It has been stated by Grob et al (162), "Present knowledge about organic substances, mostly in water, is biased as analytical research is not directed towards what is in the water or by what we want to find out but by what we are able to find out by using the available methods".

The sources of organic compounds in water are varied. They can arise from domestic and industrial wastes either through inadequate treatment of the waste or no treatment at all. Accidental spills also contribute to the problem as does deliberate dumping, and run-off from road surfaces, agricultural land and waste tips. Decaying animal and vegetable matter give rise to pollutants and organic contaminants also result from algae, micro-organisms such as actinomycetes and bacterial decomposition of organic material.

Although they may present problems in a water treatment plant, natural organics are generally of no great toxicological concern. Man-made organics however are often of great toxicological concern.

Waterborne pollutants can give rise to taste and odour problems and one of the sinks of airborne pollutants is the water system. It is evident that there is a direct link between airborne and waterborne pollutants and certain environmental problems necessitate the measurement of compounds in both media.

Methods have been developed for the measurement of organics in air (Chapters 1 and 2) and in this chapter, techniques are described which enable the determination of volatile organics in water. In this context any organic with a carbon number less than 20 which is amenable to gas chromatographic analysis is considered volatile.

In contrast to air for which adsorption of organics onto a solid adsorbent appears to be the most promising sampling technique many procedures have been envisaged for water; distillation, freeze drying, liquid-solid adsorption, direct aqueous injection, headspace analysis, gas phase stripping and batchwise and continuous liquid-liquid extraction.

If a method is to be acceptable for the qualitative and quantitative determination of organic compounds in a sample it must provide efficient separation and clean up procedures. The technique should also be able to contend with concentrations in the ng l^{-1} range.

The sensitivity of liquid-liquid extraction is limited unless the materials being analysed are of sufficiently low volatility that further concentration via solvent evaporation is possible. In certain cases the extraction solvent may interfere with measurements. Great care must be exercised in the purification of the solvents prior to use because any impurities present will be concentrated when the solvent is evaporated. Similar limitations also apply to procedures involving collection onto solid adsorbents followed by organic solvent desorption and concentration.

In recent years the technique of partitioning trace organics from aqueous samples into a gas phase for subsequent analysis by gas chromatography has gained popularity and several methods have been developed utilising this concept.

One of the earliest reports of this technique was by Swinnerton and Linnenbom (163) who determined $C_1 - C_4$ hydrocarbons by stripping them from water with a stream of helium. This method was later extended to include substances such as benzene and toluene (164).

Novak et al (165) purified helium by passing it through a cold trap, bubbled it through the water sample and dried it over magnesium perchlorate. The stripped organics were retained in a second cold trap.

McAuliffe (166) repeatedly equilibrated the aqueous sample with helium and analysed the gas phase directly. Distribution coefficients obtained by the repeated equilibrations supplemented the retention time data in identifying unknown organics.

Static headspace techniques have been reported (167,168). In one of these (167) a 10ml sample was placed in a 20ml bottle which was heated to 80°C. Using a syringe 1 ml of the headspace was removed and injected into the gas chromatograph. In the other (168) 10 l of water were heated at 60°C for 12 hours after which time the headspace gas was forced through a small amount of activated silica which trapped the organics prior to analysis by gas chromatography. Another technique has been developed (169) in which the headspace over an aqueous sample is continuously swept through a porous polymer trap. A similar method to this has been described (170) where the sample is heated almost to boiling to thermally extract the organics into the headspace. This latter method has been applied to the analysis of drinking water (171,172).

Grob et al (162,173-175) reported a system which they developed and evaluated. A small volume of air is continuously recycled through the water sample and a charcoal filter. The organics are subsequently eluted from the filter using a convenient solvent e.g. carbon disulphide or dichloromethane. This technique has gained widespread acceptance in many laboratories for use in routine analysis.

Bellar and Lichtenberg (176) devised a system for isolating volatile organics from water and demonstrated its validity for the analysis of drinking water (177). It has been used by the EPA in the determination of volatile organics for the National Organic Reconnaissance Survey in the USA (178).

In this technique a 5ml sample is introduced by syringe into the sample compartment of a specially designed purging device. The sample is purged for 11 mins with a purified gas such as helium or nitrogen at a flow rate of 20ml min^{-1}. The purge gas exits through an 1/8 in o.d. stainless steel tube packed with either porous polymer or silica gel to trap the organics. The organics are then thermally desorbed and back flushed into a gas chromatographic column.

A method for the analysis of volatile organics in water

On consideration of the techniques reported in the literature a purging system was devised to enable the routine analysis of volatile organics in water. The sampling and desorption system described in section 1.4.4. was utilised for this application. This meant that the basic trapping technique had already been developed and evaluated and all that had to be determined was whether it was suitable for this application.

Two purging devices were constructed, Figure 23, one capable of holding a 1.5 l sample, the other for much smaller samples had a volume of 60ml. They were constructed to allow finely divided gas bubbles to pass through the sample. Volatile organics are passed from the aqueous phase to the gaseous phase. The organics transferred to the gas were trapped onto a Chromosorb 102 sample tube.

If required, the nitrogen purge gas was purified by passing it through a 'U' tube, packed with an adsorbent, cooled in liquid nitrogen.

5.2. Gas Chromatographic Operating Conditions

Separation of the eluted material was carried out using a 20ft x 1/8in o.d. stainless steel column packed with 3% OV7 on Gas Chrom W AWDMCS. The carrier gas flow rate was 30ml min^{-1} and the column temperature programmed between 30° and 240°C at 8°C min^{-1}.

5.3. Standard Solutions

Standard stock solutions were made by injecting 1 - 10µl of the standard compound into 10ml of either acetone or methanol. Subsamples

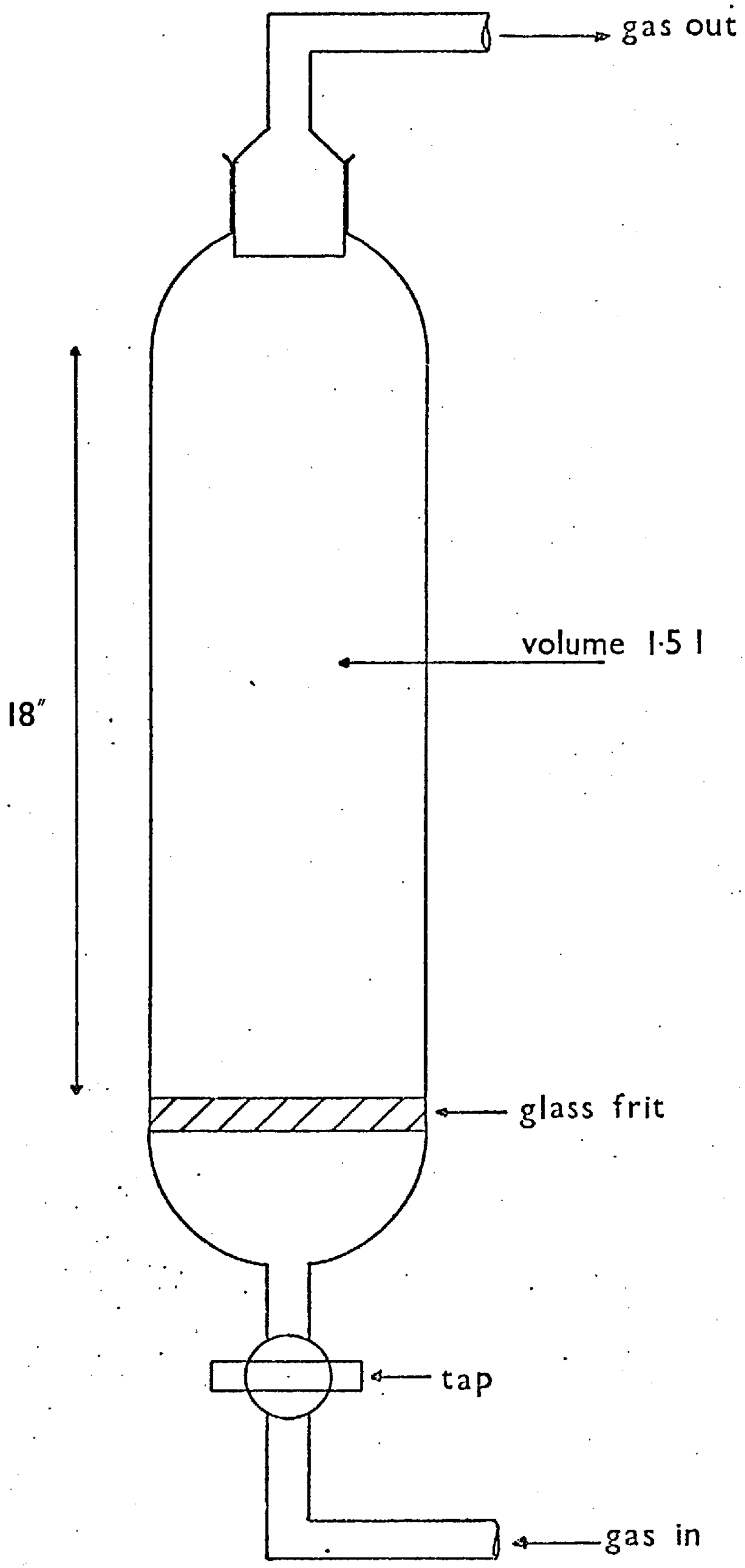


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FIGURE 23 Purging Device

of this were injected into organic free water and these solutions were used in the evaluation of the purging device.

5.4. Mode of Operation

The sample was placed in the purging device and the volume made up to 1.5 l with organic free water which was prepared by the cross distillation of chromic acid and alkali potassium permanganate solutions. Sufficient sample was used to provide adequate material for the subsequent gas chromatographic separation. A sample tube was connected to the exit pipe, the purge gas turned on and the flow adjusted. For normal routine analysis a flow rate of 100ml min^{-1} and a total purge gas volume of 4 l was used.

5.5. Evaluation of the Purging Device

For this normal hydrocarbons in the C_8 - C_{18} range were used.

Effect of purge gas flow rate

Very little variation in the purging efficiency was detected when the flow rate was altered in the range of 20-120ml min^{-1}. At flow rates greater than this the bubble size became too large and the efficiency dropped.

Two sample tubes connected in series

No compounds of interest were ever determined on the second of the two tubes, with total purge gas volumes of up to 15 l and it can therefore be assumed that the breakthrough volume of the sampling tube was not exceeded.

Percentage efficiency of purging normal hydrocarbons from water

In Tables 5.1. - 5.3. mean values obtained from 4 determinations are recorded for the percentage efficiency of purging 0.6 ppb of each compound from water. Typically the spread of results was ± 5% of the mean value.

Table 5.1. Purging at 21°C

Volume of purge gas l	Carbon Number							
	8	10	12	13	14	16	17	18
2	76	67	44	28	20	7	5	5
4	80	78	66	60	45	19	11	8
6	82	78	67	63	49	24	16	12
8	84	80	70	68	53	27	20	13
12	98	84	80	76	61	37	28	14

Table 5.2. Purging at 55°C

Volume of purge gas l	Carbon Number							
	8	10	12	13	14	16	17	18
2	100	100	90	30	11	8	5	5
4	100	100	100	90	63	20	11	10
12	100	100	100	100	100	52	43	35

Table 5.3. Effect of Temperature when 4 l of Purge Gas Used

Temperature °C	Carbon Number							
	8	10	12	13	14	16	17	18
21	80	78	66	60	45	19	11	8
30	88	86	73	66	55	34	20	9
55	100	100	100	90	63	20	11	10

The efficiency of this technique was also tested for aromatic hydrocarbons. These compounds were purged from water with efficiencies similar to those observed for the normal hydrocarbons of similar boiling points.

For hydrocarbons the purging efficiency appears to be a function of boiling point, which is related to vapour pressure.

Effect of ionic strength on purging efficiency

Both sodium chloride and sodium sulphate were individually added to water samples. The effect of the addition of 0-30% w/v NaCl and Na_2SO_4 on the rate at which hydrocarbons were released from solution was investigated.

No effect was observed with the hydrocarbons however, some effect was noticed with polar compounds. Further work should be carried out to determine whether altering the ionic strength of the sample and purging at elevated temperatures would make this technique suitable for the analysis of polar compounds.

5.6. Grob Technique

A Grob stripping system was assembled as described in a recent paper (175).

Experiments carried out using this technique gave very similar results to those quoted in that publication. The stripping efficiency was determined on the C_8-C_{18} range of normal hydrocarbons. In Tables 5.4. and 5.5. the mean value from four determinations is recorded for the percentage efficiency of purging 0.6 ppb of each individual compound from water.

Table 5.4. Effect of Temperature on 2 hour Stripping Period

Temperature °C	Carbon Number							
	8	10	12	13	14	16	17	18
21	65	69	87	57	35	21	12	9
30	82	97	100	60	45	28	22	18
55	98	100	100	75	75	50	38	35

Table 5.5. Stripping at 30°C

Time	Carbon Number							
	8	10	12	13	14	16	17	18
2hr	82	97	100	60	45	28	22	18
20hr	90	92	100	98	92	91	87	86
40hr	80	86	98	100	100	100	98	97

Two Charcoal Filters Placed in Series

A water sample was extracted for 4 hours at 30°C. The water sample was then removed and a second charcoal filter put in its place. The pump was then switched on and allowed to run for 24 hours.

In Table 5.6 the mean results from three determinations are recorded for the percentage extraction efficiencies.

Table 5.6. Two Filters in Series

	Carbon Number							
	8	10	12	13	14	16	17	18
1st Filter	57	69	95	76	74	45	33	30
2nd Filter	42	27	5					

From these results it would appear that irreversible adsorption of the $\geqslant C_{13}$ compounds occurs on the charcoal filter and that it is only by using a solvent that the compounds can be removed. The $\leqslant C_{12}$ compounds however can be stripped of the plug by the circulating gas stream.

5.7. Solvent Extraction

The efficiency of four solvents for extracting hydrocarbons from water was investigated. In each instance 500ml of sample were shaken with 50ml of solvent for 5 minutes. In Table 5.7 the mean value from three determinations is reported for the percentage extraction efficiency of 1 ppb of each individual compound from water.

Table 5.7. Solvent Extraction of Hydrocarbons

Solvent	Carbon Number							
	8	10	12	13	14	16	17	18
Ether	35	35	22	24	27	31	36	40
Cyclohexane	*	25	28	28	30	39	40	48
Hexane	*	24	25	32	32	35	37	40
Dichloromethane	*	42	44	54	56	59	64	66

5.8. Measurements of Organics in Environmental Water Samples

The detection limit of the purging device was 0.01 ppb but it was decided to ignore compounds with concentrations below 0.1 ppb in these initial studies.

5.8.1. River Thames (near Richmond Bridge)

No organic compounds in the C_6-C_{18} range were ever determined at concentrations greater than 0.1 ppb.

5.8.2. Motorway Site

Run off samples were analysed after the oil film had been removed. No organics were determined in these samples above 0.1 ppb. This was also the case for water running from the motorway service area drain.

5.8.3. River Stour (Suffolk)

The purging device, solvent extraction and the Grob technique were all used to determine levels of organics in the River Stour.

At the Haverhill sewage works, along reaches of the River Stour and in drinking water abstracted from the river there has been an intermittent odour problem. Odorous compounds arise from trade effluents that discharge into a foul sewer serving the Haverhill works.

A preliminary investigation has been carried out in an attempt to trace the source of these compounds and to ascertain the usefulness of the analytical techniques for the determination of organics in environmental samples. The technique used to ascertain the source of the odorous compounds was the production of characteristic 'fingerprints' or 'profiles' of the volatile organics present in the various water samples analysed. These 'fingerprints' were then compared to determine if there was any correlation between them. Figures 24-27 are typical chromatograms obtained during the period of this work.

Sampling

All samples were collected as grab samples in winchester bottles which had been thoroughly washed with chromic acid prior to use.

Extraction of organics

Two extractions were carried out with each technique on every sample. One with internal standards - which in this instance were straight chain hydrocarbons - the other without internal standards. When dealing with unknown environmental samples it is not sufficient to assume predetermined extraction efficiencies because these can change with slight variations in purging conditions. For quantitative work the extraction efficiency of each compound must be calculated relative to that of the internal standards.

Results

Analyses were carried out on samples of trade effluent, the sewage works' influent and effluent and river water from the Wixoe reservoir intake which is two miles downstream from the treatment works.

Because the techniques were not calibrated for each compound individually the relative response factor was taken to be the same for each compound.

In Table 5.8 the concentrations of the numbered peaks are recorded. These numbers refer to peaks on the chromatograms Figures 24-27. Concentrations were calculated on consideration of the results obtained from the three extraction techniques. The compounds in the trade effluent were mainly essential oils and other compounds used in the perfume and flavour industry.

Table 5.8. Concentration of Compounds in Water Samples

Peak Number	Concentration in ppm			
	Trade Effluent	Sewage Works Influent	Sewage Works Effluent	Wixoe Intake
1	1.92	0.66		
2	2.53	0.03		
3	0.29	0.17		
4	0.27	1.21		
5	0.25	0.08		
6	0.83	0.02		
7	1.36	0.07		
8	2.76	0.11		
9	1.41	0.22		
10	3.99	0.89	0.02	0.0004
11	24.00	2.91	0.15	0.004
12	0.58	0.06		
13	1.88	0.19		
14	0.29	0.03	0.03	0.003

In Table 5.9 the variation in the concentration of Peak 10 is recorded for the three sampling trips. The relative amount of this compound to the other compounds was similar in every instance.

Table 5.9. Variations in Levels over the Survey Period

Date	Concentration in Trade Effluent ppm
31.5.77	24
26.6.77	0.0058
19.7.77	0.28

Levels on the 26th June were low because most of the factory was closed down and only one section was in operation. Almost all the organics in the river water can be traced back to the trade effluent. It is

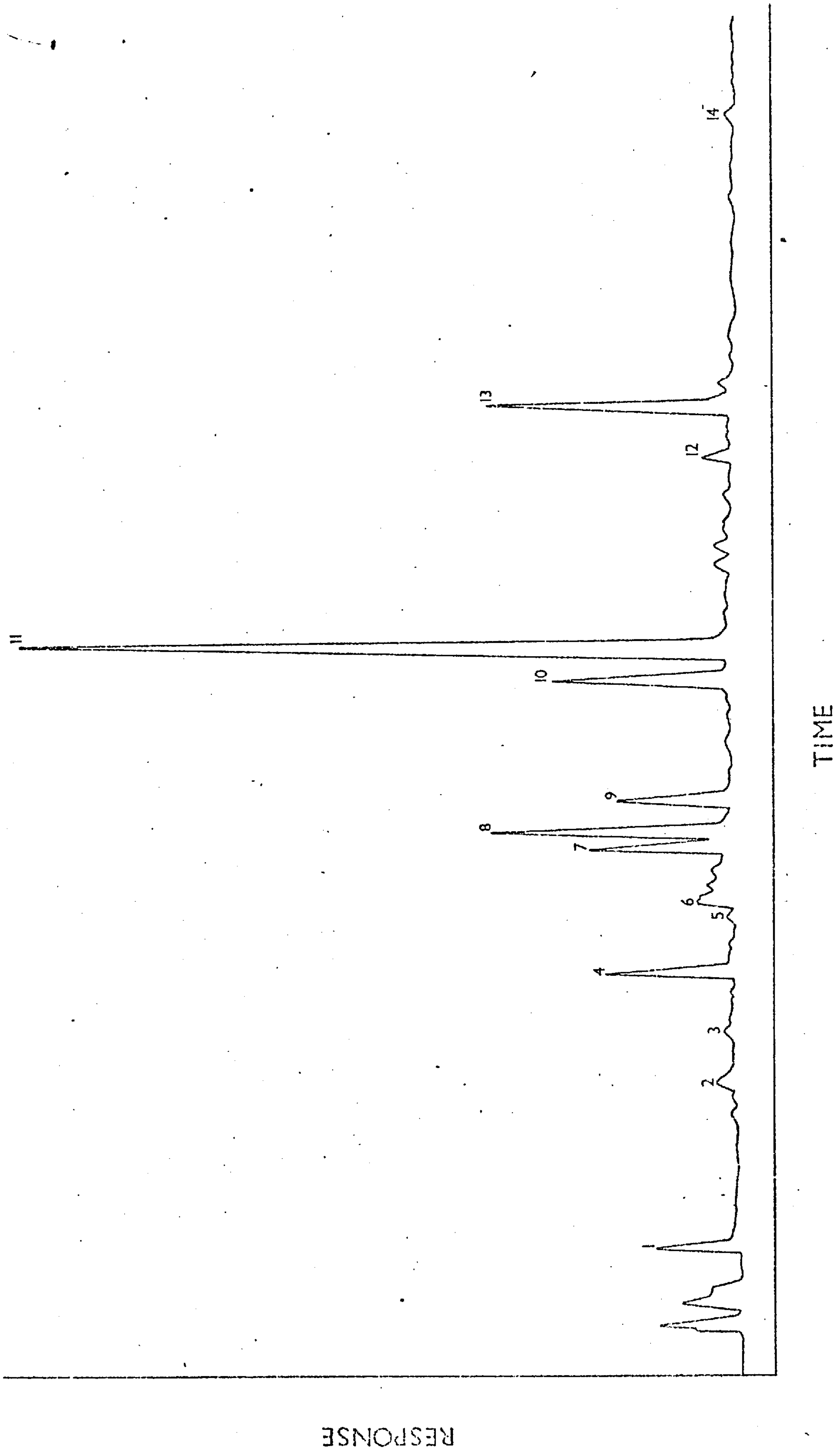

FIGURE 24 Trade Effluent

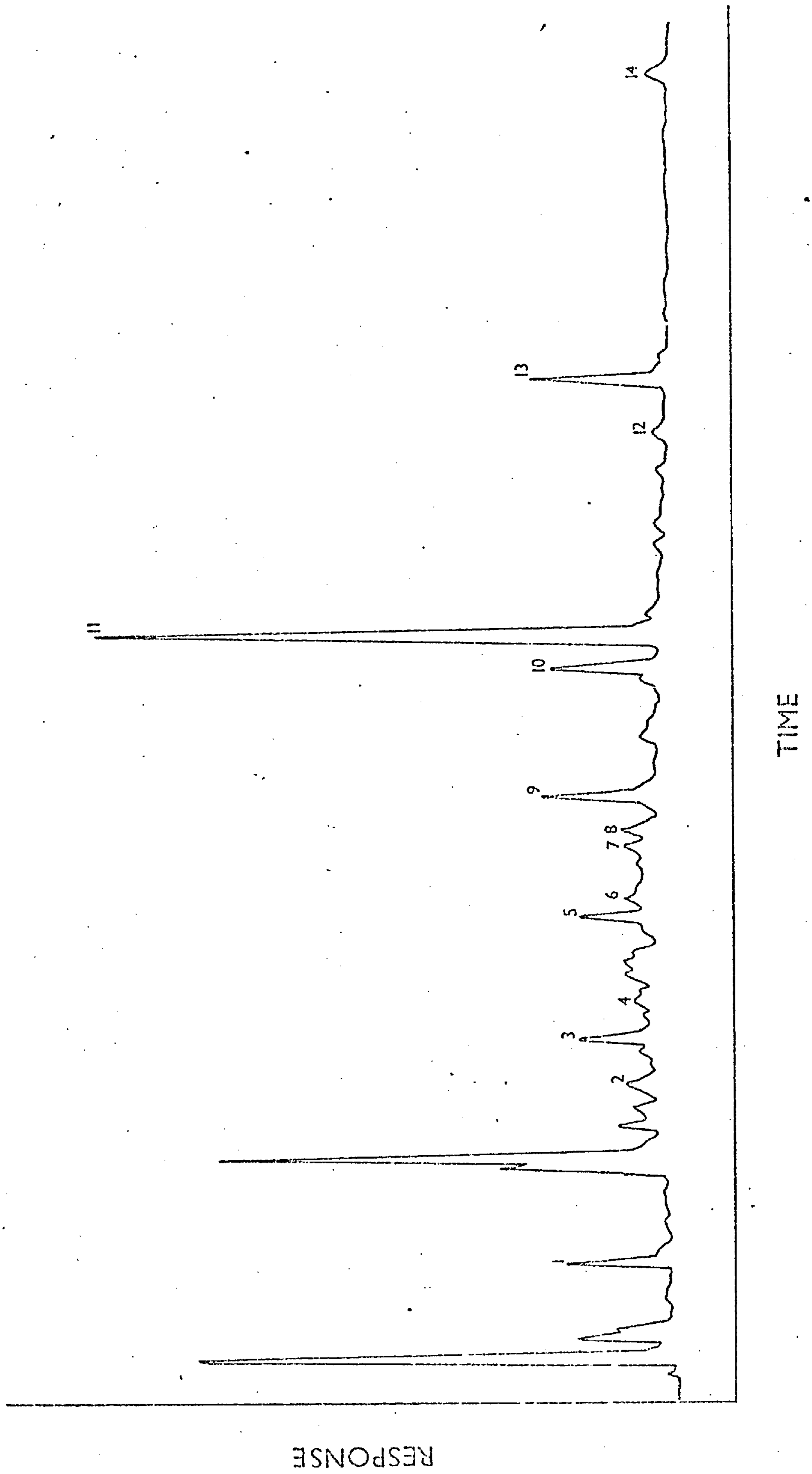

FIGURE 25 Sewage Works Influent

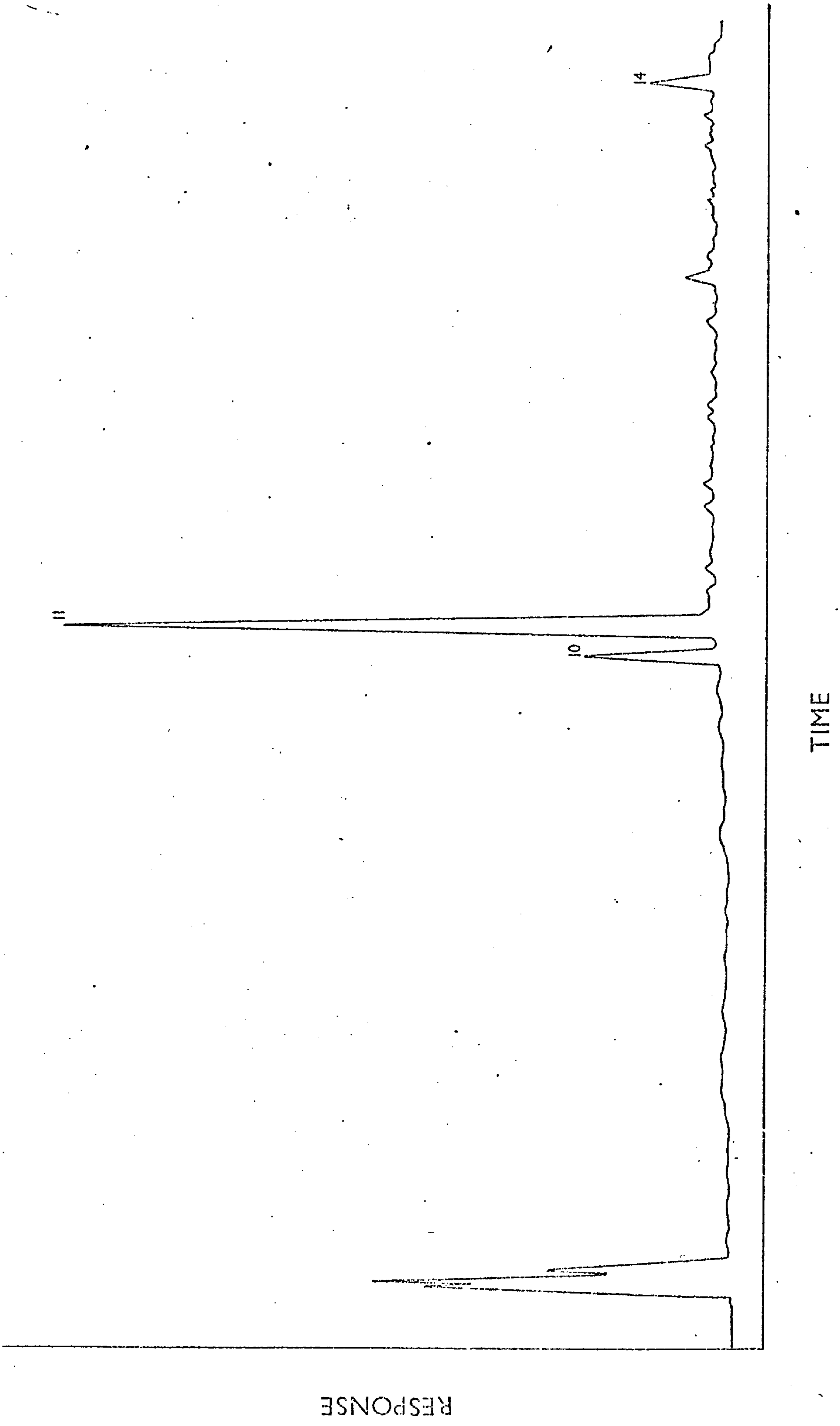

FIGURE 26 Sewage Works Effluent

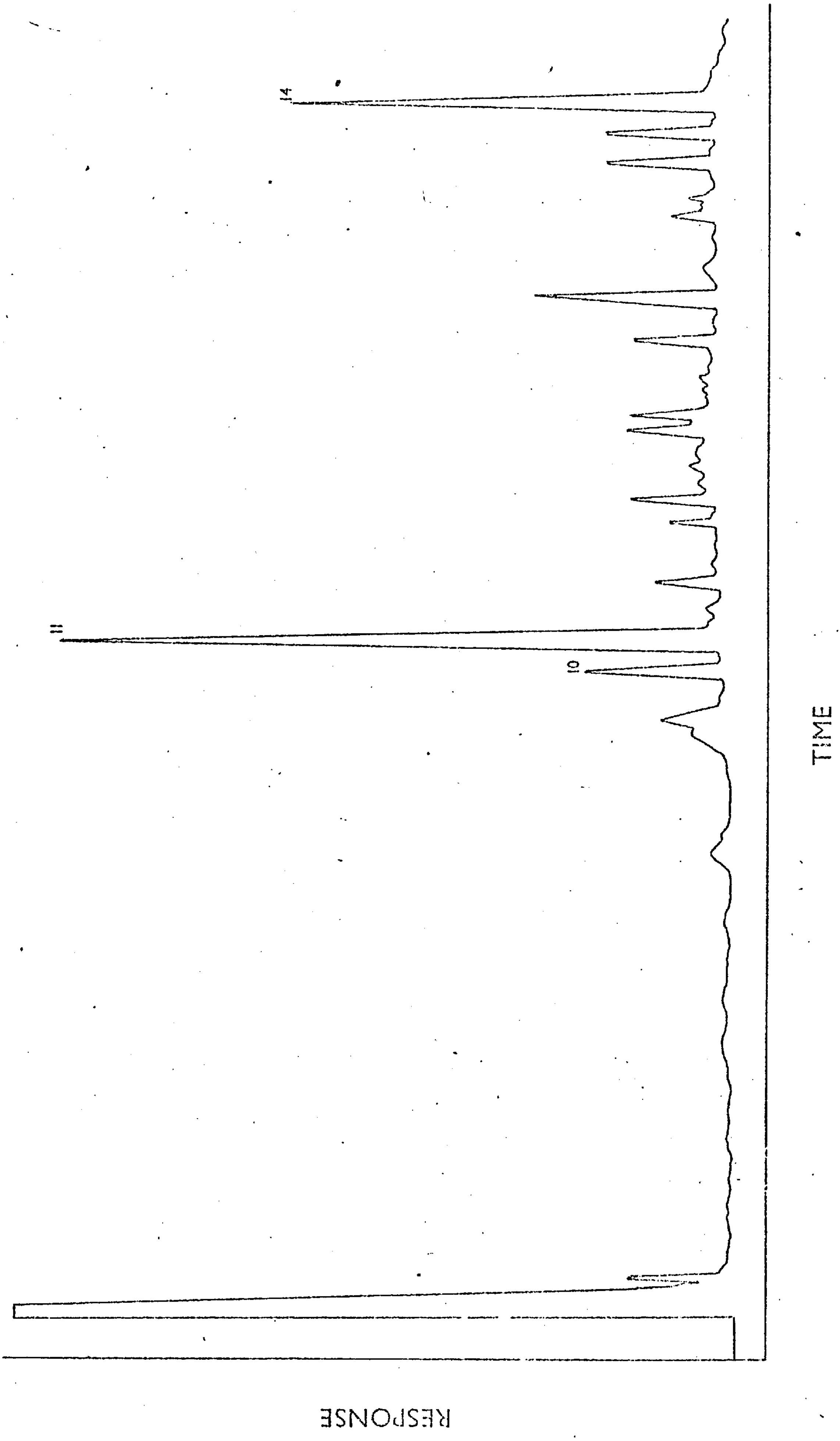

FIGURE 27 River Stour at Wixoe Intake

therefore likely that the odorous compounds giving rise to the problems at the sewage works and in the river originated in the trade effluent. This cannot be stated with absolute certainty because the odour may arise from the presence of very minor components which were not detectable by the techniques used in this study. Further work should be carried out employing tracer compounds to ensure that the same body of water discharged in the trade effluent was sampled at the point of discharge, as it entered and left the sewage works and from the river as it passed the Wixoe intake. The volume of water flowing should also be determined to ascertain the dilution effects on various days.

To ascertain whether any of the compounds in the trade effluent were odorous a splitter was incorporated at the outlet of the gas chromatographic column so that a fraction of the flow could be vented to the atmosphere. In this way the odour of the eluted compounds was ascertained and in the trade effluent over 20 odorous compounds were determined.

The concentrations of the more volatile compounds were determined in the air above the final effluent channel and in every case these were approximately four orders of magnitude lower than those found in the water samples.

5.9. An Appraisal of the Advantages and Disadvantages of the Three Analytical Techniques Employed

On comparison of the chromatograms Figure 28 it is evident that when using the solvent extraction technique there are peaks that do not occur when the analysis is carried out using a purging technique. These extra compounds are most probably polar compounds that the purging techniques fail to strip from the water. Therefore if polar compounds are to be determined in a sample it would appear that solvent extraction must be used. One difficulty that arises with the use of solvents is the clean

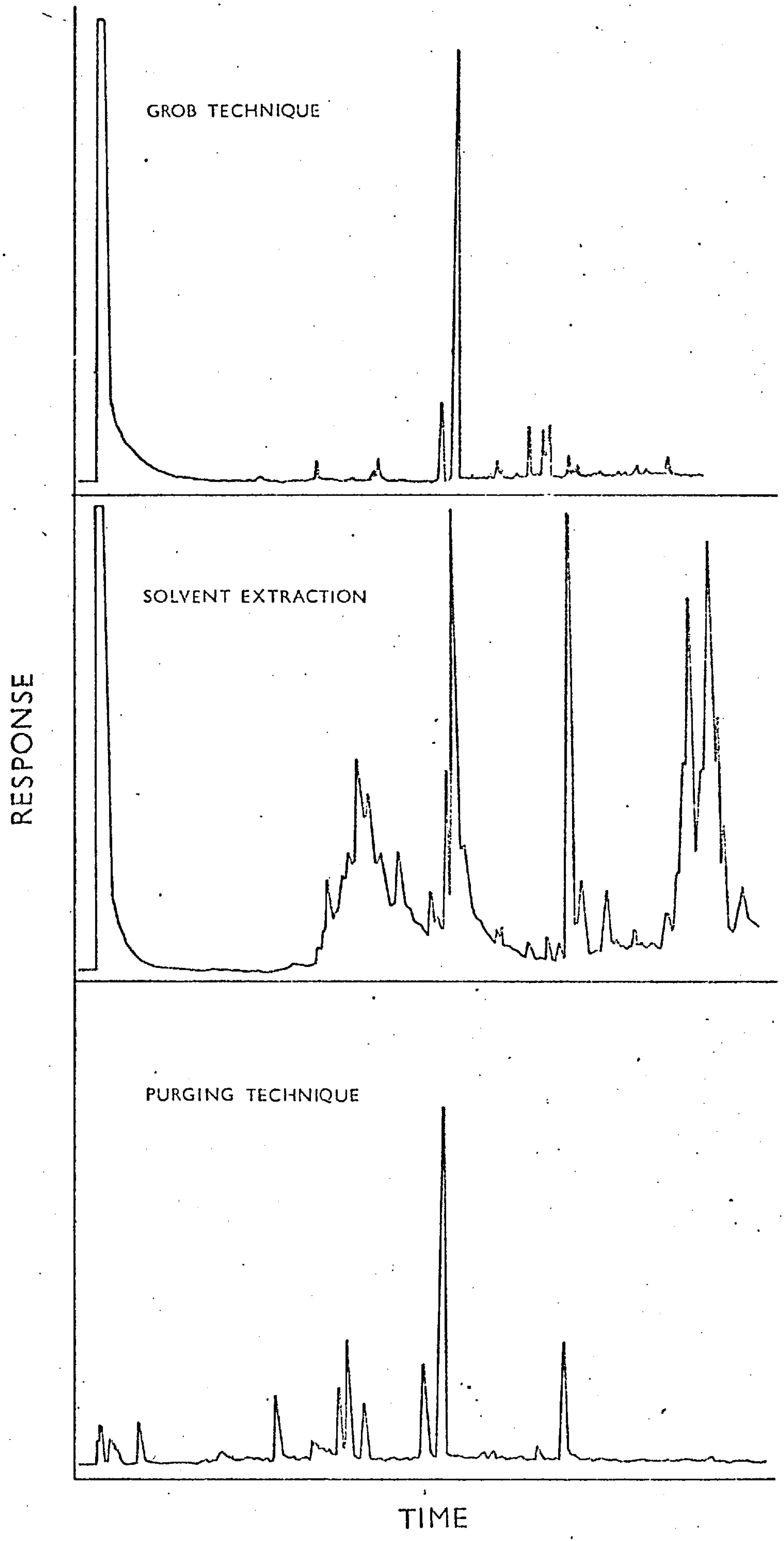

FIGURE 28 Chromatograms of Trade Effluent Obtained Using Three Techniques

up procedure required if turbid samples are to be analysed. However, with the purging technique dirty samples can be analysed directly.

Detergents can also pose problems. With the high purge rate 1.5-2 l used in the Grob technique excessive foaming can occur which blocks the stainless steel tubes. This problem does not arise with the other purging technique developed because of the lower gas flow rates employed.

In both the techniques where solvents are utilised it is possible for compounds of interest to be masked by the solvent. Another problem in the solvent extraction procedure is the loss of volatile components when the solvent is evaporated. It is not possible to accurately determine the quantity of volatile organics lost in this way. Care must be taken in the purification of solvents prior to use, especially when a large volume is evaporated and the impurities are concentrated as well as the compounds of interest.

Neither of the purging techniques appeared to be satisfactory for the rapid determination of compounds whose retention time on the gas chromatographic column were greater than that of the normal C_{18} hydrocarbon. It is however easier to standardise all the parameters affecting the stripping of organics from water than it is to standardise those affecting a solvent extraction procedure.

Care has to be taken that the total quantity of organics stripped from the water does not exceed the capacity of the charcoal filter used in the Grob technique. Another associated factor that may distort results obtained using this technique is the relative adsorption efficiencies of charcoal for various compounds. It is possible to strip the more volatile compounds off the filter whereas the less volatile compounds are irreversibly adsorbed. Progressively more and more sites on the charcoal will be taken up by the less volatile compounds leaving less for the volatile organics. From this it is evident that the longer the stripping of organics from water occurs the smaller will be the contribution of the more volatile compounds in the resultant chromatograms. However, this mechanism should be compensated for if internal standards are used.

It would appear that there are more potential places where leaks could occur causing loss of compounds in the Grob technique than in the other purging system.

A major advantage of both systems in which solvents are used is that high resolution capillary separation of the material in the gas chromatograph can be accomplished. This is impossible using the heat desorption technique where the flows of 30ml min^{-1} needed to desorb the material from the sampling tube are not compatible with those required for capillary column work in which typically flows of 2-5ml min^{-1} are used.

The detection limits of the individual techniques are as follows: Grob 1 in 10^{13} w/w (162), heat desorption technqiue 1 in 10^{11} w/w and for the solvent extraction technique 1 in 10^{9} w/w. Bellar and Lichtenberg (176) quoted their detection limit as being 1 in 10^{9} w/w.

From the experience gained using these techniques it is apparent that if complex samples are to be analysed a combination of extraction procedures should be used to provide satisfactory qualitative and quantitative results. For polar compounds and those with boiling points above 200°C solvent extraction appears to be adequate if the concentration of the compounds is greater than 1 ppb.

The purging techniques have the advantage of lower detection limits and extraction of the volatile compounds is more reproducible. The heat desorption technique has the advantage over the Grob technique that no low molecular weight compounds are masked by the presence of a solvent.

Typical analysis times for the various techniques not including gas chromatographic separation are: Grob 3 hours; heat desorption 50 minutes; solvent extraction 30 minutes.

CHAPTER 6

SUMMARY AND CONCLUSIONS

The effects on man of individual hydrocarbons at high concentrations have been extensively studied and documented. However, the effects of low levels of hydrocarbons in air containing other contaminants are poorly understood at present. Many consider that most hydrocarbons cause no direct deleterious effects in man at their present or future predicted levels. There is however the possibility of synergistic reactions occurring and the production of secondary pollutants by photochemical reactions in the atmosphere. Products from these reactions can cause eye irritation, plant damage and the haze formed can reduce visibility to 800m. Combustion products are frequently malodorous and can cause a nuisance at very low concentrations. The chemicals responsible for the odours in exhaust emissions have not all been identified but unsaturated aliphatic hydrocarbons and aldehydes are thought to contribute to the problem.

Environmental pollution is dependant to a substantial degree upon, often irregular, human activity and meteorological conditions. The results of air pollution measurements are very dependant upon temperature inversions, wind conditions and upon the rates of emissions. The rates of emissions are in turn dependant upon the time of day. In the morning, heating systems start up and people set off to work in their cars whilst late at night only certain continuous industrial processes are operating. The variability inherent in most environmental measurements means that 'grab' sampling which is often used can only yield limited information.

The determination of the levels of volatile organics and their associated effects on the environment necessitates a multidisciplinary approach to the problem. It is quite feasible that except in certain circumstances e.g. in the vicinity of a chemical plant or a road tunnel no effect that could be considered detrimental to the environment will be found .

Considerable effort has been expended on the measurement of total hydrocarbon levels. The information that can be derived from these measurements is limited because methane is naturally occurring worldwide and often accounts for a large percentage of the total hydrocarbon levels determined. Specific hydrocarbons derived from different sources will have varying degrees of impact on the environment and it is therefore of interest to identify the individual compounds present.

Various techniques are described in the literature for the sampling and analysis of organics at ambient concentrations but at present there is no one procedure which has gained widespread acceptance. There are two main approaches to the problem. The first is the separation of the organics using high resolution capillary columns to facilitate the identification of as many compounds as possible (often over 100) with minimal interest in the quantification of the results. The other approach is to use packed columns to study the variation in concentration of the major compounds present under various conditions.

The second approach was adopted in this work. Levels were normally determined close to roads where the major contribution to hydrocarbons was from motor vehicle emissions. The compounds determined at each site were therefore similar and by studying the variation in the major components present, information about the minor constituents could be deduced.

Concentrations of the minor components of the hydrocarbon mixture are typically in the ppt range. With present instrumentation it is difficult to both rapidly and accurately determine compounds at this level. It is also doubtful whether much time should be spent on detailed analysis of compounds at these concentrations when it is not known whether compounds at concentrations at least three orders of magnitude greater than these have any significant environmental impact. For this reason concentrations of compounds below 0.1 ppb were not recorded in this work.

Methods were developed which allowed the rapid determination of organics in the atmosphere. The method utilising solid adsorbents at ambient temperatures was the preferred technique for routine analysis. It proved easy to use and complete analysis could be achieved within half an hour of sample collection. It was however limited to $\geqslant C_6$ compounds.

Levels of non-methane and individual hydrocarbons were determined at several sites and it is of interest to note that the EPA standard of 0.24 ppm for an eight hour mean was frequently exceeded at the sites in the London area.

This work has demonstrated the difficulty involved in trying to predict levels of hydrocarbons expected at any given site, and the short comings of single point sampling sites. These can yield useful information but it is limited in its application.

Due consideration must be given to the pollutant sources, topography and meteorological conditions of the area under consideration. These factors can explain levels determined in a large area (e.g. Teesside) or the local variations encountered within the confines of a street. The Teesside area is predominantly flat, much of the industrial site being built on reclaimed land. There is a strong prevailing south westerly wind which aids the dispersion of the pollutants. The industrial plants producing organic emissions are some distance apart and the roads in the area are not heavily trafficked. It is therefore not really surprising that levels of hydrocarbons determined away from the roadside were negligible. On Exhibition Road considerable variation was observed in levels determined at different points on the street. Factors affecting levels included: parked ice cream vans, the exit from a GPO sorting office, the exit from an Imperial College car park, traffic lights, parked cars in the street and on the dispersion characteristics of different parts of the street caused by variations in the type of buildings.

It is evident that as many sites as practicable should be used when sampling in a given area where samples are taken simultaneously so that an overall picture of the situation can be derived and local variations accounted for.

The relative concentrations of individual hydrocarbons will vary according to temperature and site. The higher the temperature the greater will be the contribution of evaporative emissions to the hydrocarbon total. Evaporative emissions will also be more significant at sites close to storage containers of fuels e.g. petrol stations.

Once the individual hydrocarbon pattern at a site has been established there seems to be no inherent advantage in monitoring individual compounds as opposed to total non-methane hydrocarbons unless one is interested in studying atmospheric reactions e.g. photochemical smog formation. The constant monitor could be connected so that if a certain predetermined level of total hydrocarbons was exceeded a pump would be switched on to sample air for subsequent individual hydrocarbon analysis to determine whether the hydrocarbon pattern had changed.

It would be advantageous if the constant monitor in the mobile laboratory could be linked to a data aquisition unit. If possible monitors for oxides of nitrogen, sulphur compounds and ozone should be incorporated into the vehicle.

With the limited resources available more effort should be directed towards monitoring programs in which detailed studies of a specific nature should be undertaken e.g. determining the contribution aircraft make to hydrocarbon levels in the vicinity of Heathrow Airport and their significance in relation to other sources.

During the period of this work a report appeared in the Wall Street Journal describing the hazards of ethylene dibromide (EDB) in the atmosphere. It reported that man was being wilfully exposed to a known carcinogen through the addition of this compound to petrol. Levels were determined in the atmosphere with the aid of an electron capture detector and even at a petrol station levels were not thought to pose a health hazard as the maximum level determined was about 1 ppb compared with the threshold limit value of 25 ppm.

Organic compounds in water can give rise to odour problems. A possible sink of airborne pollutants is the water system. It is evident that the relationships governing the distribution of compounds between these two media are important and for this reason a technique was developed which allowed the routine determination of volatile organics in water. This method is only really applicable to the extraction of non-polar compounds with less than 20 carbon atoms. When analysing trade effluents it is advisable to use more than one extraction procedure and compare the results obtained because of the number and type of compounds present.

The techniques developed provided rapid and reliable methods for the determination of volatile organics in representative environmental samples. These methods are simple to operate and a person with no previous experience in this type of work could be instructed in their use within a few hours.

A major disadvantage of the heat desorption technique used is the difficulty of introducing the eluted material onto a capillary chromatographic column. With the complexity in composition of the organic mixture encountered in certain situations this could be a severe limitation because adequate separation may be impossible on a packed column.

The results obtained so far using these techniques are only the groundwork for future studies in the problems of volatile organics in air and water. They do however indicate levels that may be expected in various situations.

Some thought must now be given to their application in environmental situations so that useful information may be gathered about the pathways, fates and effects of volatile organics. Care must be taken not to determine levels just because it is possible to do so.

It would be advantageous to incorporate an internal standard into the sampling system for organics in the atmosphere, this may be possible using a permeation tube system.

Further studies should be carried out on the investigation of odour problems which are at present among the major effects of trace levels of organics. Odours arising from vehicles, sewage works and industrial discharges could all be investigated.

Additional future work could include:-

(i) The determination of the presence and ratio of specific compounds as a method for identifying the pollutant source.

(ii) The development of a technique for the extraction of polar organics from water.

(iii) The measurement of specific industrial emissions and their effect on the environment.

(iv) The determination of individual components in airborne particulate matter and an evaluation of the contribution of bromides from car exhaust in the formation of bromine containing organic compounds in water.

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