# THE DEVELOPMENT AND USE OF THERMAL DESORPTION METHODS FOR THE ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS AND VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

**A thesis submitted for the degree of Doctor of Philosophy**

**by**

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## Abstract

In occupational and public health there is a need for measurement and speciation of chemicals in ambient air to achieve control of air pollution and minimize health risks. In this work two methods of analysis are developed for the analysis of polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs) under ambient air conditions. Both methods involve the use of thermal desorption techniques with gas chromatography-mass spectrometry (GC-MS).

For the measurement of polycyclic aromatic hydrocarbons (PAHs) airborne particulate samples are obtained by collection on small glass fibre filters. The volatile materials from these are thermally desorbed in two stages and transferred to a Gas Chromatograph-Mass Spectrometer analytical system. Results from studies of particulate samples obtained from sites in the region of Uxbridge, Middlesex are reported for eight selected polycyclic aromatic hydrocarbons (PAHs). Measurements on samples obtained directly from vehicle emission sources with the engine used under different running conditions are also reported.

In the method of analysis of volatile organic compounds in air, samples are absorbed into 4mm Carbotrap 300 tubes and thermally desorbed and passed into a gas chromatography-mass spectrometry (GC/MS) or gas chromatography (GC) using helium as carrier gas. The Carbotrap absorbers used, show complete absorb/desorb reversibility, are thermally stable and do not react chemically with injected hydrocarbon standards.

To demonstrate the value of the method analytical results obtained under ambient air conditions on the Brunel University campus (Uxbridge, Middlesex) are reported. Six selected low molecular weight aromatic hydrocarbons namely benzene, toluene, ethyl benzene and m-, p- and o-xylene are investigated in detail. The concentrations of these compounds were measured and results related to traffic flow rates and meteorological conditions to established the fact that vehicle exhaust emissions are the main sources of the volatile organic compounds (VOCs) pollution at the collection sites.

A study of volatile organic compounds (VOCs) levels in ambient air in Tehran (Iran) in which 55 hydrocarbons are identified is reported. A detailed study is made of the concentrations of the six hydrocarbons benzene, toluene, ethyl benzene and m-, p-and o-xylene because high concentrations of these pollutants can produce potential health problems. It is shown that the nature of the geographical location and the day time temperature play an important part in determining the composition of the mixture of pollutants in Tehran.

Samples obtained directly from internal combustion engines with and without catalytic converters are also analysed using the method developed and the results show that there is a large depletion in aromatic hydrocarbons when toluene is reduced to a greater extent than benzene. The analytical method is also used to compare vehicle emissions from engines under cold start and hot start conditions.

# ABBREVIATIONS

| | |
|---|---|
| Litre | l |
| millilitre | ml |
| microlitre | µl |
| gram | g |
| milligram | mg |
| microgram | µg |
| nanogram | ng |
| parts per million | ppm |
| parts per billion | ppb |
| minute | min |
| hour | h |
| metre | m |
| kilometre | km |
| centimetre | cm |
| millimetre | mm |
| inch | in |
| Gas Chromatography | GC |
| Mass Spectrometry | MS |
| Thermal Desorption Unit | TDU |
| Flame Ionization Detector | FID |
| Electron Capture Detector | ECD |
| Hydrocarbons | HC |

| | |
|---|---|
| Total Hydrocarbons | THC |
| Polycyclic Aromatic Hydrocarbons | PAH |
| Oxides of nitrogen | $NO_X$ |
| Benzene | B |
| Toluene | T |
| Peroxyacetyl nitrates | PAN |
| Chlorofluorocarbons | CFCs |
| Volatile Organic Compounds | VOCs |
| | |
| Environmental Protection Agency | EPA |
| World Health Organization | WHO |
| Economic Commission for Europe | ECE |
| United Kingdom | UK |
| United States | US |
| United Nations Environment Programs | UNEP |
| Export Panel on Air Quality Standards | EPAQS |
| | |
| Total Suspended Particulate | TSP |
| Thoracic Particle | TP |
| | |
| Spark-ignition | SI |

**Conversion factors volume/volume to a mass/volume**

1 ppb benzene =3.25μg/m$^3$

1 ppb toluene =3.83 μg/m$^3$

1 ppb ethylbenzene = 4.42 μg/m$^3$

1 ppb o-xylene = 4.42 μg/m$^3$

1 ppb m-xylene =4.42 μg/m$^3$

1 ppb p-xylene = 4.42 μg/m$^3$

# Contents

# Chapter One

# Introduction

## 1.1 Defining atmospheric pollution

The whole earth's atmosphere is contaminated to some extent which in many instances arises from the activities of man. There are many different views as to what constitutes pollution of the atmosphere. In attempting such a definition the Engineers Joint Council of the United States in issuing a policy statement on air pollution made the following comment (1).

"Air pollution means the presence in the outdoor atmosphere of one or more contaminants, such as dust, fumes, gas, mist, odour, smoke or vapour in quantities of characteristics and of duration such as to be injurious to human plant or animal life or to property, or which unreasonably interfere with the comfortable enjoyment of life and property".

Other definitions of atmospheric pollution are more useful, such as 'the presence of substances in the ambient atmosphere, resulting from the activity of man or from natural processes, causing adverse effects to man and the environment' (2). An expanded version of this definition will be employed in this text namely, that air pollution is defined as ' the presence in the atmosphere of substances or energy in such quantities and of such duration liable to cause harm to human, plant, or animal life, or damage to man-made materials and structures, or change in the weather and climate, or interference with the comfortable enjoyment of life or property or other human activities'.

Until the 1960s, pollutants were generally only regarded as a problem in the vicinity of individual emission sources or within or near urban areas. Subsequently, studies showed that pollutants were being transported over long distances and were having adverse effects on the environment at locations far removed from the sources of the emissions. Long-range transport of sulphur and nitrogen compounds across national boundaries resulted in increased acidity of precipitation (acid rain) at distant locations and created an international pollution problem. Improved monitoring and detection of trends in atmospheric constituents, together with the modelling of atmospheric processes, have highlighted the fact that pollution problems can and have become global in extent. It has been suggested that pollutants of current local or regional concern, such as anthropogenic heat and toxic chemicals, will give rise to global pollution problems in the future.

Stratospheric ozone depletion caused by various gases, especially chlorine atoms released from chlorofluorocarbons (CFCs), has been a matter of concern since the 1970s but became a major problem in 1985 with the dramatic discovery of a massive seasonal Antarctic ozone 'hole'. In the process known as the greenhouse effect, gases such as carbon dioxide, methane, nitrous oxide, chlorofluorocarbons and low level ozone trap some of the infrared radiation emitted by the earth that would be otherwise lost to outer space. The atmospheric concentrations of these greenhouse gases have been found to be increasing rapidly in recent decades, and many researchers attribute the global warming of 0.5°C during the past century to a human enhanced greenhouse effect. The accelerated global warming expected in the coming decades, together with a rise in sea level due to thermal expansion of the oceans, is expected to have profound effects on world agriculture, natural ecosystems, conservation, energy supplies, freshwater resources and coastal defences (3).

## 1.2 Sources of air pollution

### 1.2.1 Natural sources

Natural sources of air pollution are defined as sources not caused by human activities. An erupting volcano emits particulate matter. Pollutant gases such as $SO_2$, $H_2S$, and methane are also emitted. The emission from an eruption may be of such magnitude as to harm the environment for a considerable distance from the volcanic source. Clouds of volcanic particulate matter and gases have been found to remain airborne for very long periods of time.

Accidental fires in forests and on the prairies are usually classified as natural sources even though they may have been originally ignited by human activities. Such a fire emits large quantities of pollutants in the form of smoke, unburned hydrocarbon, carbon monoxide, carbon dioxide, oxides of nitrogen and ash particles.

Dust storms that entrain large amounts of particulate matter are common natural sources of air pollution in many parts of the world. Visibility reduction during a major dust storm is frequently the cause of severe highway accidents and can even affect air travel. The particulate matter transferred by dust storms from the desert to urban areas causes problems to householders, industry and automobiles (4,5).

The oceans of the world are important natural sources of pollutant materials. The ocean is continually emitting aerosols to the atmosphere, in the form of salt particles, which are corrosive to metals and paints.

An extensive source of natural pollutants are the plants and trees of the earth. Even though these green plants play a large part of conversion of carbon dioxide to oxygen through photosynthesis, they are still the major sources of hydrocarbon on the planet. The familiar blue haze over forested areas is nearly all from the atmospheric reactions of the volatile organic compounds given off by the trees. Another air pollution problem, which can be attributed to plant life, arises from pollen which causes respiratory distress and allergic reaction in humans.

Other natural sources, such as alkaline and saltwater lakes, are usually quite local in their effect on the environment. Sulphurous gases from hot springs also fall into this category in that the odour is extremely strong when close to the source but disappears a few kilometres away (4,5 ).

### 1.2.2 Anthropogenic sources

#### 1.2.2.1 Stationary sources

The reliance of a large proportion of the world's population on industry to produce goods which meet their needs has resulted in transfer of pollution sources from the individual to industry. A great deal of industrial pollution comes from manufacturing primary materials from raw materials for example:

(1) Metals from ore
(2) Lumber from trees
(3) Petrol and chemical crude oil
(4) Stone from quarries
(5) Energy production

Each of these manufacturing processes produces a product, along with several waste products which are potential pollutants. Occasionally, part or all of the polluting material can be recovered and converted into a usable product (4).

Industrial pollution is also emitted by industries that convert primary materials to other products for example:

(1) Automobile bodies from steel

(2) Furniture from lumber

(3) Paints from solids and solvents

(4) Asphaltic paving from rock and oil

Some of the materials(pollutants) listed blow are of concern because they are the natural emission associated with specific industries.

The major stationary sources of emission are industrial processes including power generation and refuse incineration.

Domestic contributions vary significantly with the climate of the country concerned, according to the need for either domestic heating or air conditioning.

Table 1.Specific pollutants and their sources

| Pollutant | Sources |
|---|---|
| Ammonia | Ammonia works |
| Sulphur trioxide | Sulphuric acids works |
| Sulphide, Sulphur | Generating stations, metal smelting, rubber vulcanizing, coke ovens |
| Chlorine and hydrogen chloride | Chlorine works, aluminum works, metal recovery plants, refuse incinerators |
| Chlorinated and hydrocarbons | Dry cleaning establishment |
| Bromides | Motor vehicle emissions |
| Fluorine and fluorides | Brickworks, glassworks, aluminum, smelting, iron works |
| Mercaptans | Oil refineries, coke ovens |
| Metals | Specific to appropriate works |

Table 1.2 Emission factors for the various fuels and various sources in: g $kg^{-1}$ fuels for solids and liquids kg $(10^6 \text{ therm})^{-1}$, for gas

| Sources | $NO_x$ | CO | Hydrocarbons (HC) |
|---|---|---|---|
| (a) Transportation | | | |
| Petrol engine | 16.5 | 401.4 | 19.5 |
| Diesel engine | 30.0 | 41.0 | 6.6 |
| (b)Domestic appliances | | | |
| Coal: bituminous | 1.04 | 45 | 10 |
| Coal: anthracite | 1.5 | 45 | 1.25 |
| Oil | 2.9 | 0.79 | 0.15 |
| Gas | 3452 | 863 | 345 |
| (c) Commercial and industrial sources | | | |
| Coal | 7.5 | 1 | 0.5 |
| Oil (distillate) | 5.3 | 0.71 | 0.13 |
| Oil fuel | 6.7 | 0.68 | 0.13 |
| Refinery oil | 7.8 | 0.65 | 0.13 |
| Gas (commercial) | 5178 | 863 | 345 |
| Gas (industrial) | 9978 | 728 | 129 |
| (d) Power generation | | | |
| Coal | 9 | 0.5 | 0.15 |
| Oil | 9.5 | 0.65 | 0.12 |
| Gas | 12945 | 728 | 43 |
| Coke + breeze | 9 | 0.5 | Neg |

Typical emission factors for the various fuels used are summarised in Tab. 1.2 they are based upon the UK and the USA practice.

Emission factors are heavily dependent upon the source of fuel used and the abatement and control protocols in a particular country (6).

### 1.2.2.2 Mobile Sources

A mobile source of air pollution can be defined as one capable of moving from one place to another under its own power. According to this definition, an automobile is a mobile source and a portable asphalt batching plant is not. Generally, mobile sources imply transportation, but sources such as construction equipment, petrol-powered lawn mowers, and petrol-powered tools are included in this category. In any urbanised society, transportation sources make a major contribution to atmospheric pollution levels. Over the last three decades the balance between the alternative modes of transport have been moderated by the necessity of controlling vehicle emissions.

Table 1.3 Emissions from Mobile sources

| Power plant type | Fuel | Major emissions | Vehicle type |
|---|---|---|---|
| Four-stroke Cycle | Petrol | HC, CO, $CO_2$, $NO_X$ | Car, truck, bus aircraft, marine engine, motorcycle, tractor |
| Two-stroke cycle | Petrol | HC, CO, $CO_2$, $NO_X$, Particulates | Motorcycle, outboard motor |
| Diesel | Diesel oil | $CO_2$, $NO_X$, $SO_X$, Particulates | Car, truck, bus railroad, marine engine, tractor |
| Gas turbine (jet) | Turbine | $CO_2$, $NO_X$, Particulates | Aircraft, marine engine, railroad |
| Steam | oil, coal | $CO_2$, $NO_X$, Particulates | Marine margins |

Mobile sources therefore consist of many different types of vehicles, powered by engines using different cycles, fuelled by a variety of products, and emitting varying amounts of both simple and complex pollutants. Table 1.3 lists the common mobile sources (1).

The predominant mobile air pollution source in all industrialised countries of the world is the automobile, powered by a four-stroke engine and using petrol as the fuel. In the United States, over 85 million automobiles were in use in 1990. If the 15 million petrol-powered trucks and buses and the 4 million motorcycles are included, the United States total for 1990, exceeds 100 million vehicles (4).

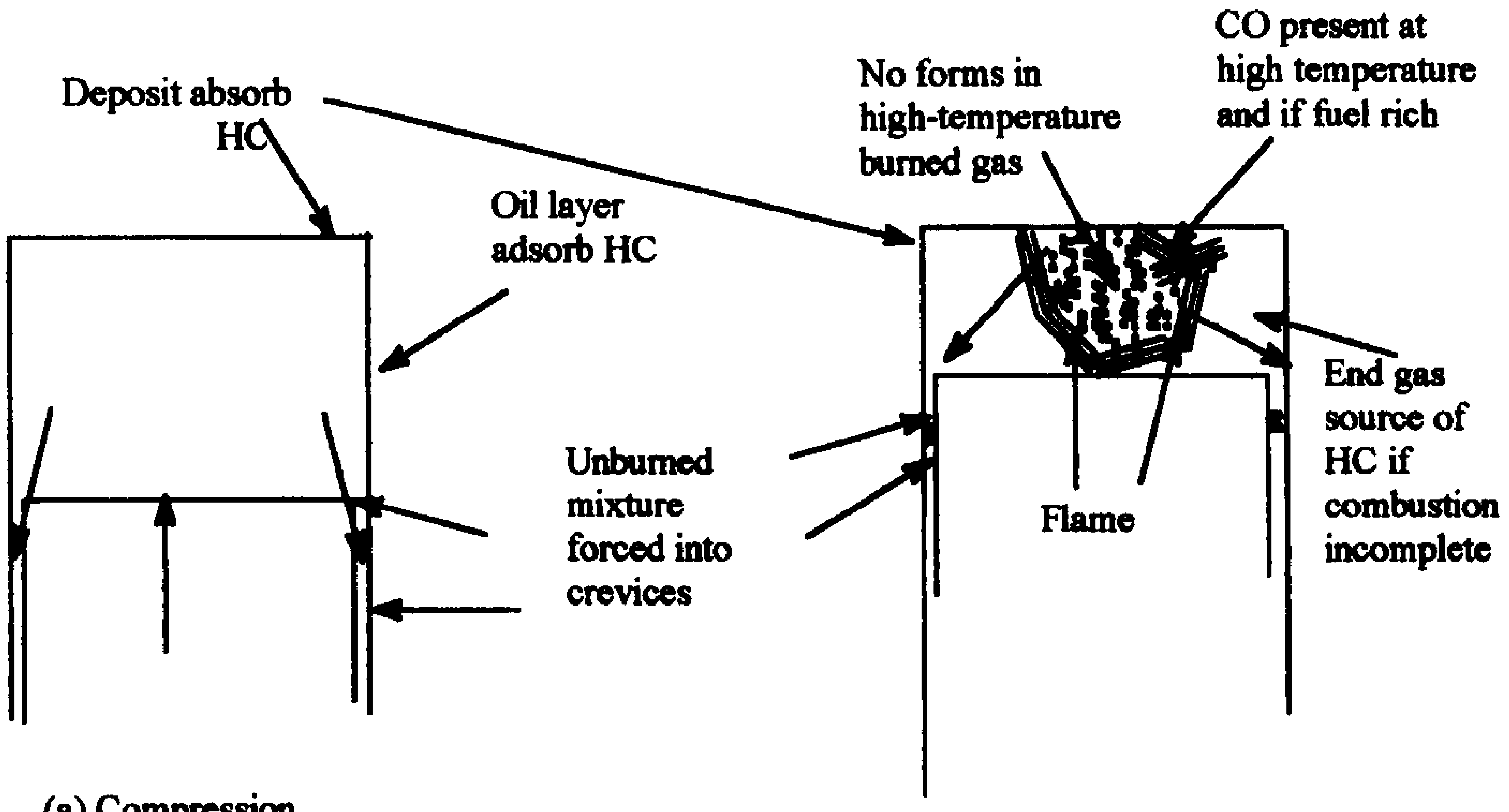
By 1990, there were about 130 million vehicles on European Community roads , with the largest number being in Germany (31 million), Italy ( 24 million), France (23 million), United Kingdom (22 million), and Spain (12 million). The main pollutants emitted from vehicles are carbon monoxide (85 per cent of UK total emissions), volatile organic compounds or hydrocarbons (30 per cent of UK total emissions), oxides of nitrogen (45 percent of UK total emissions) and lead. In addition, road traffic accounts for about 18 per cent of the UK emissions of the green house gas, carbon monoxide (3).

## 1.3 Unburned hydrocarbon emissions

Spark-ignition (SI) and diesel engines are a major source of urban air pollution. The spark ignition engine exhaust gases contain oxides of nitrogen, carbon monoxide and organic compounds which are unburned and partially burned hydrocarbons. The relative amounts depend on engine design and operating conditions.

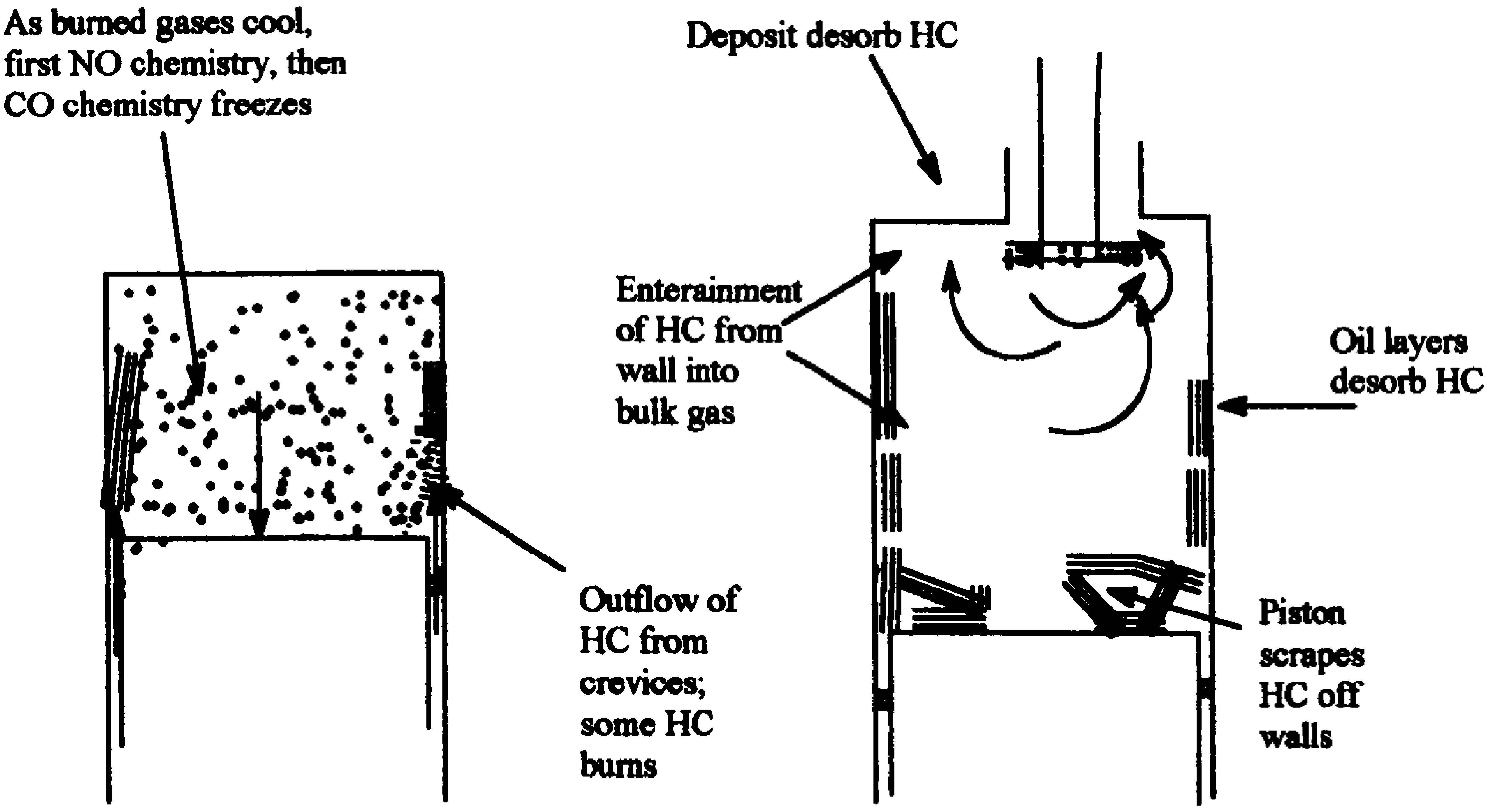
In a diesel engine exhaust, concentrations of $NO_X$ are comparable to those from SI engines. Diesel hydrocarbon emissions are significant though exhaust concentrations are lower, by about a factor of 5, than typical SI engine levels. The hydrocarbons in the exhaust may also condense to form white smoke during engine starting and warm-up. Specific hydrocarbon compounds in the exhaust gases are the source of diesel odour. Diesel engines are an significant source of particulate emissions; between about 0.2 and 0.5 percent of the fuel mass is emitted as small particles which consist primarily of soot with some additional absorbed hydrocarbon material. Diesel engines are not a significant source of carbon monoxide.

The processes by which pollutants form within the cylinder of a conventional spark-ignition engine are illustrated qualitatively in Figure 1.1. The schematic diagram shows



(a) Compression

(b) Combustion



(c) Expansion

(d) Exhaust

**Fig. 1.1 Summary of HC, CO and NO pollutant formation mechanism in a spark ignition engine**

the combustion chamber during four different phases of the engine operating cycle: compression , combustion, expansion and exhaust.Nitric oxide forms throughout the high-temperature burned gases region in the flame through chemical reactions involving the radical formed nitrogen and oxygen atoms. The unburned hydrocarbon emissions have several different sources.

During compression and combustion, the increasing cylinder pressure forces some of the gas in the cylinder into crevices, or narrow volumes, connected to the combustion chamber: the volumes between the piston, rings, and cylinder wall produce the largest contribution. The gas is mostly unburned fuel-air mixture and much of it escapes the primary combustion process. This gas which leaves these crevices later in the expansion and exhaust processes, form one source of unburned hydrocarbon emissions. Another possible source of hydrocarbon emission is the combustion chamber walls. A quench layer containing unburned and partially burned fuel-air mixture is left at the wall when the flame is extinguished as it approaches the wall. It has been shown that the unburned hydrocarbons in these thin ($\leq 0.1$ mm) layers burn up rapidly when the combustion chamber walls are clean, but that the porous deposits on the walls of engines in actual operation do increase engine hydrocarbon emissions. A third source of unburned hydrocarbons is believed to be any engine oil left in a thin film on the cylinder wall, piston and perhaps on the cylinder head. These oil layers can absorb and desorb fuel hydrocarbon components, before and after combustion, thus permitting a fraction of the fuel to escape the primary combustion process. A final source of hydrocarbons in engines arise from incomplete combustion due to bulk quenching of the flame in that fraction of the engine cycle where combustion is especially slow (7).

One of the most important variables in determining spark-ignition engine emissions is the fuel/air equivalent ratio. Figure 1.2 shows qualitatively how NO, CO, and HC exhaust emissions vary with this parameter. The spark-ignition engine has normally been operated close to the stoichiometric air fuel mix, or slightly fuel- rich, to ensure smooth and reliable operation. Figure 1.2 shows that leaner mixtures give lower emission until the combustion quality becomes poor, when hydrocarbon emissions rise sharply and engine operation becomes erratic. The shapes of these curves indicate the complexities of emission control. In a cold engine, when fuel vaporisation is slow, the fuel flow is increased to provide an easily combustible fuel-rich mixture in the cylinder. Thus, until the engine warms up and this enrichment is removed, CO and HC emissions are high.

Under part-load conditions, a lean mixture could be used and this would produce lower hydrocarbon and CO emissions (at least until the combustion quality deteriorated ) along with moderate NO emissions. Use of recycled exhaust to dilute the engine intake mixture lowers the NO levels, but also leads to deterioration in combustion quality.

While nitric oxide and nitrogen dioxide are usually grouped together as NOx emissions, nitric oxide is the predominant oxide of nitrogen produced inside the engine cylinder. The principal source of NO is the oxidation of atmospheric nitrogen. If the fuel contains significant nitrogen, however, the oxidation of fuel nitrogen-containing compounds is an additional source of NO. Petrol contains negligible amounts of nitrogen and although diesel fuels contain more nitrogen, current levels are not significant.

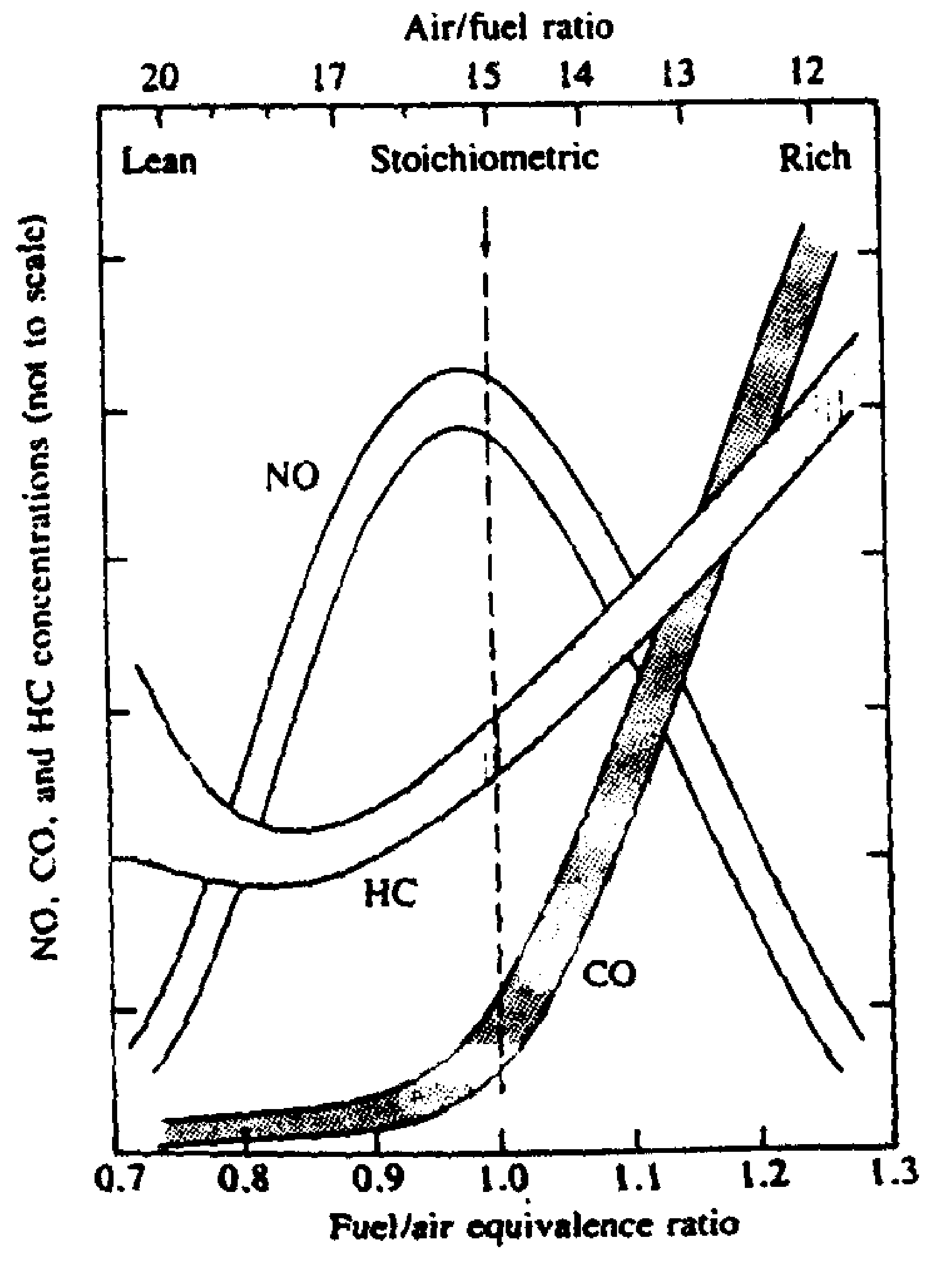


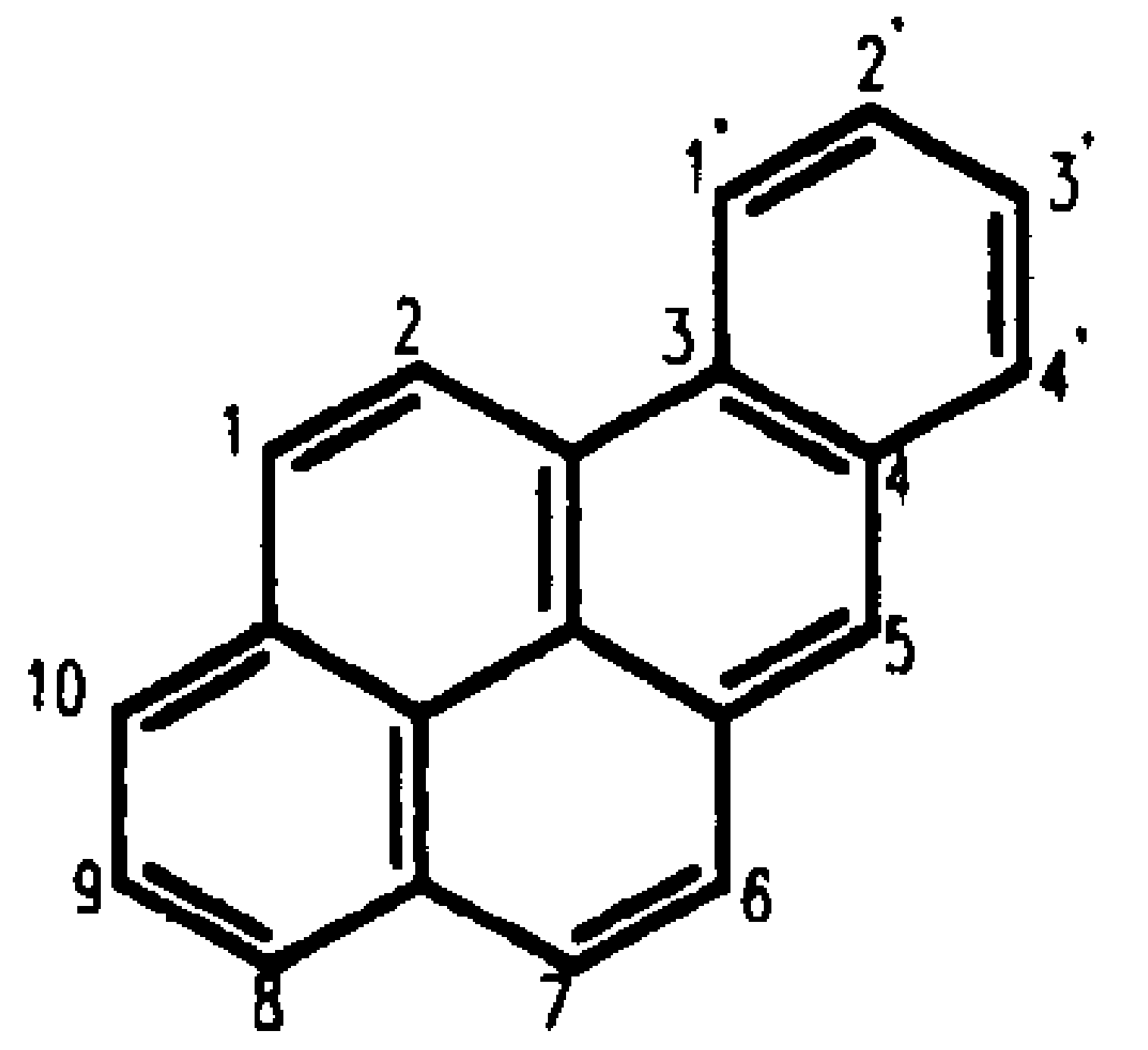
Fig. 1.2 Variation of HC, CO, and NO concentration in the exhaust of a conventional spark-ignition engine with fuel/air equivalence ratio.

Carbon monoxide emissions from internal combustion engines are controlled primarily by the fuel/air equivalence ratio.

Diesel fuel contains hydrocarbon compounds with higher boiling points, and hence higher molecular weights, than petrol. Substantial pyrolysis of fuel compounds also occurs within the fuel sprays during the diesel combustion process. Thus, the combustion of the unburned and partially oxidised hydrocarbons in the diesel exhaust is much more complex than in the spark-ignition engine and extends over a larger molecular size range.

## 1.4 Particulate emission

There are three classes of spark-ignition engine particulate emissions: lead, organic particulates (including soot), and sulphates. The organic particles of greatest concern are polycyclic aromatic hydrocarbons (PAH), which consist of condensed ring aromatic molecules. The most commonly cited example of a PAH compound is benzo(a)pyrene, a compound that can be metabolize in the body to a carcinogenic form:



**Benzo(a)pyrene**

PAHs may be synthesized from saturated hydrocarbons under oxygen-deficient conditions. Hydrocarbons with very low molecular masses, even methane, may act as precursors for the polycyclic aromatic compounds. Low molar mass hydrocarbons form PAHs by pyrosynthesis, at temperatures exceeding approximately 500°C where carbon-hydrogen and carbon-carbon bonds are broken to form free radicals. These radicals undergo a dehydrogenation and combine chemically to form aromatic ring structures, which are resistant to thermal degradation.

Significant sulphate emissions can occur with oxidation-catalyst equipped engines. Unleaded petrol contains 150 to 600 ppm by weight sulphur, which is oxidized within the engine cylinder to sulphur dioxide. This $SO_2$ can be oxidized by the exhaust catalyst to $SO_3$ which combines with water at ambient temperature to form a sulphuric acid aerosol. Levels of sulphate emissions depend on the fuel sulphur content, the operating conditions of the engine and the details of the catalyst system used. Typical average automobile sulphate emission rates are 20mg/km or less (8).

For automobile engines operated with regular and premium leaded petrol (which contains about 0.15 g Pb/litre or $dm^3$) the particulate emission rates are typically 100 to 150 mg/km. This particulate matter is dominated by lead compounds: 25 to 60 percent of the emitted mass is lead. The particulate emission rates are considerably higher when the engine is cold, following start up and the exhaust temperature has a significant effect on emission levels. The particle size distribution with leaded fuel is about 80 percent by mass below 2μm diameter and about 40 percent below 0.2 mm diameter(9). Most of these particles are presumed to form and grow in the exhaust system due to vapour phase condensation enhanced by coagulation. Some of the particles are emitted directly, without settling. Some of the particles either form or are deposited on the walls where agglomeration may occur.

Diesel particulates consist principally of combustion-generated carbonaceous material (soot) on which some organic compounds have become absorbed. Most particulate material results from incomplete combustion of fuel hydrocarbons; some are contributed by the lubricating oil. The emission rates are typically 0.2 to 0.6 g/km for light-duty diesels in an automobile. In larger direct-injection engines, particulate emission rates are 0.5 to 1.5 g/brake kW.h. The composition of the particulate material depends on the conditions in the engine exhaust and particulate collection system. At temperatures above 500°C, the individual particles are principally clusters of many spheres or spherules of carbon (with a small amount of hydrogen) with an individual spherule diameter of about 15 to 30 nm. As temperatures decrease below 500°C, the particles become coated with adsorbed and condensed high molecular weight organic compounds which include:

unburned hydrocarbons, oxygenated hydrocarbons (ketones, esters, ethers, organic acids), and polynuclear aromatic hydrocarbons (7).

## 1.5 Photochemical Oxidants

Photochemical oxidants are secondary pollutants produced by the action of sunlight on an atmosphere containing reactive hydrocarbons (volatile organic compounds) and oxides of nitrogen (10). The complex series of photochemical reactions produce various oxidants with the most important being ozone and peroxyacetyl nitrate (PAN) as indicated below. See also Fig 1.3.

$$NO_2 + h\nu \longrightarrow NO^{\bullet} + O^{\bullet}$$

$$O^{\bullet} + HC \longrightarrow RC\dot{O} + RC\dot{H}_2$$

$$RC\dot{O} + O_2 \longrightarrow RC\dot{O}_3$$

$$RC\dot{O}_3 + NO^{\bullet} \longrightarrow RC\dot{O}_2 + N\dot{O}_2$$

$$RC\dot{O}_2 + O_2 \longrightarrow RC\dot{O} + O_3$$

$$RC\dot{O}_3 + N\dot{O}_2 \longrightarrow RCOONO_2 \quad \text{(PAN)}$$

The key to the atmospheric photochemical process is the photolysis of the nitrogen dioxide molecule by ultraviolet radiation during daylight hours. The ozone ($O_3$) so formed reacts rapidly with the nitric oxide produced in the photolysis reaction such that there is no significant net ozone formation. In this steady state, the ozone concentration is a function of the ratio of nitrogen dioxide ( $NO_2$) to nitric oxide (NO) concentrations (10,11). Equilibrium is disturbed, however, by other reactions which oxidize nitric oxide to nitrogen dioxide, and which result in the accumulation of ozone and other photochemical products.Hydrocarbons, or more appropriately organic emissions, are the consequence of incomplete combustion of the hydrocarbon fuel. The level of unburned hydrocarbon (HC) in the exhaust gases is generally specified in terms of the total hydrocarbon concentration expressed in parts per million carbon atoms.

Based on their potential for oxidant formation in the photochemical atmospheric chemistry, hydrocarbon compounds are divided into nonreactive and reactive categories.

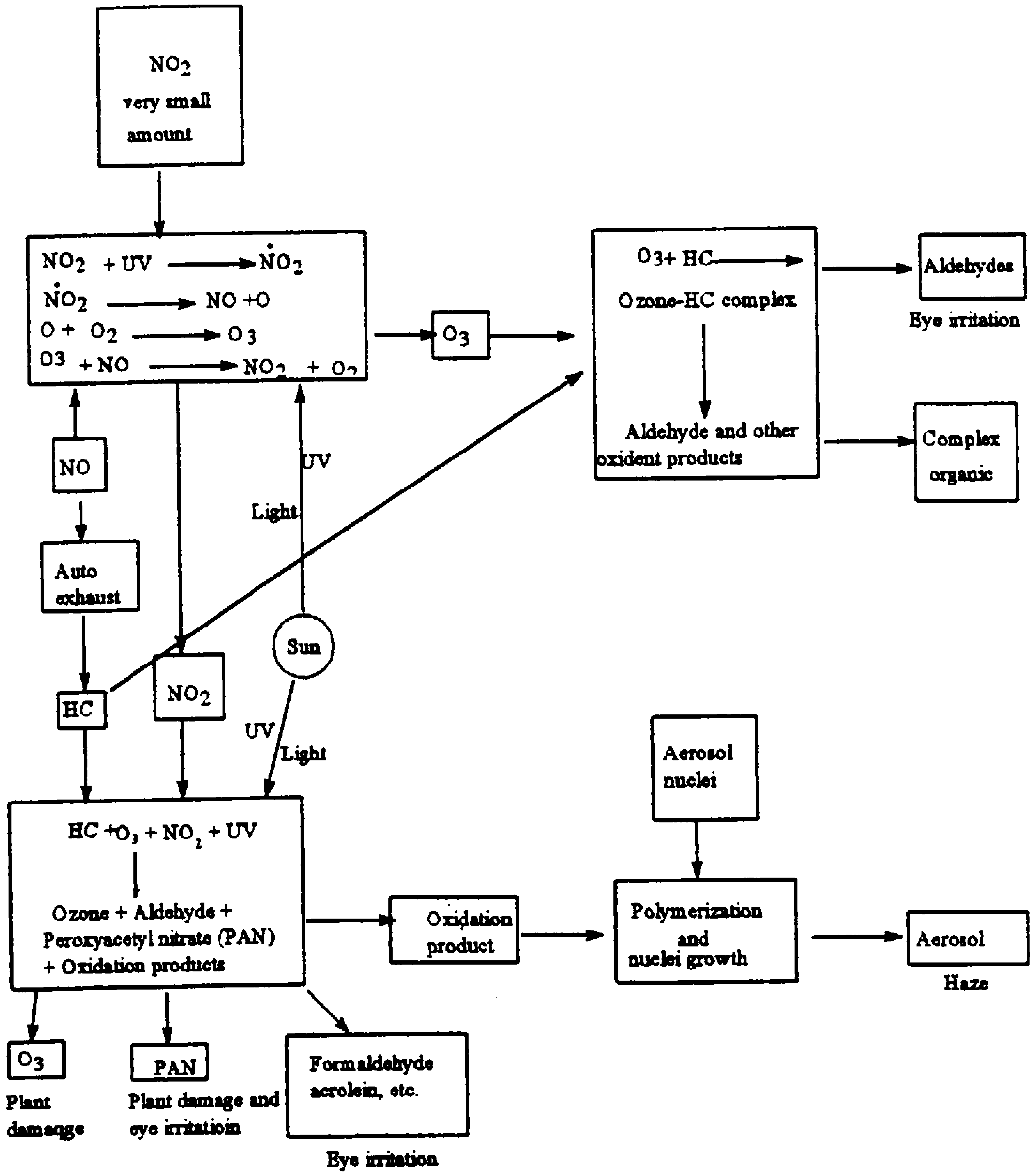


Fig. 1.3 Photochemical smog formation source: modified from Faith and Atkisson, 1972.

Table 1.4 shows one reactivity scale ( A numerical ranking system where each HC is assigned a number giving a measure of how its emissions affect ozone formation) which has been used to estimate the overall reactivity of exhaust gas hydrocarbon mixtures. Other scales are used for the same purpose. The following table refer to the reaction of hydrocarbons listed.

Table 1.4 Reactivity of classes of hydrocarbons

| Hydrocarbons | Relative reactivity☆ |
|---|---|
| $C_1$-$C_4$ paraffins<br>Ethyne<br>Benzene | 0 |
| $C_4$ and higher molecular weight paraffins<br>Monoalkyl benzene<br>Ortho- and para-dialkyl benzene<br>Cyclic paraffins | 2 |
| Ethene<br>Meta-dialkyl benzene<br>Aldehydes | 5 |
| 1-Olefines (except ethene)<br>Diolefins<br>Tri- and tetra alkyl benzene | 10 |
| Internally bonded olefines | 30 |
| Internally bonded olefines with substitution at the double bond Cyclo-olefines | 100 |

☆ General Motors Reactivity Scale (0-100). Based on the $NO_2$ formation rate of hydrocarbon relative to the $N_2O$ formation rate for 2,3-dimethyl-2-benzene.

Scales that assign high values for reactivity to the olefins, which react most rapidly in the photochemical smog reaction, probably best approximate smog-formation potential near the sources of hydrocarbon pollution.

Fuel composition can significantly influence the composition and magnitude of the organic emissions. Fuels containing high proportions of aromatics and olefins produce relatively higher concentrations of reactive hydrocarbons (12,13,14).

## 1.6 Air Pollution Legislation and Regulation in the European Community

The European Community has agreed four Environmental Action Programmes in 1973, 1977, 1983 and 1988. These are noted for their increasing specificity on pollution control standards i.e. moving from emission control to air quality standards, and for their growing interest in transboundary pollution regulation. The main elements of the current Fourth Environmental action plan are following;

a) To identify both indoor and outdoor pollutants.

b) To determine the most appropriate focus for control, measures, i.e. whether to limit the pollutants themselves or the source of the pollution.

c) To set and implement EU wide objectives for substantial emission reduction to combat acid deposition and forest dieback.

d) To reduce in the longer term ambient air concentrations of pollutants to levels acceptable for sensitive ecosystems.

e) To develop appropriate management techniques, such as pollution modelling, monitoring networks and economic approaches to abatement measures.

European air pollution legislation can conveniently be analysed in three parts. One group of directives covers the regulation of products (fuels, motor vehicles), the manufacture and use of which may result in undesirable levels of air pollution. Another part applies to air quality standards, the adherence to ambient air quality levels to which subsequent emission limitations should apply. The third part relates to large combustion industrial plants, mostly power stations, where special attention is being focused on the acid rain effects of coal and oil burning (15).

### 1.6.1 Product standards and air pollution control

#### 1.6.1.1 Vehicle emission

In June 1985, a compromise proposal was put forward under which emission limits were introduced according to engine size, namely, large cars (over 2 litres), medium cars (1.4 to 2.0 litres) and small cars (less than 1.4 litres). Under the rules, the larger the car, the less pollution permitted. The limits were introduced in two stages; the first, to take effect between 1989 and 1992. Although these new limits meant large cars would have to be fitted with catalytic converters, small cars could meet the standards by using lean-burn engines. Medium cars could meet the standards by using either catalytic converters or lean burn engines with an added oxidation catalyst.

The earliest measures, first agreed by the Economic Commission in Europe, but subsequently translated into EC directives, were concerned with the emission of certain pollutants from motor vehicles, notably CO, HCs and $NO_X$.

Table 1.5 lays down the relevant legislation. The points to note here are the general tightening of emission standards over the years and the fact that vehicles meeting these standards should not be barred from entering another country, at least on grounds of environmental protection. Similar regulation of product standards for certain fuels, notably the Pb and benzene content of petrol and the S content of gas oil were introduced to ensure that common environmental standards should enable the freer exchange of trade products across national boundaries. Directive 70/220 applies to CO and HC levels, both of which were reduced in the later Directive 78/665.

The Community revised the previously agreed limits for medium and large cars by introducing revised emission standards for all cars based on an improved test driving cycle which reflected higher out-of-town driving speeds (Table 1.6). Based on

Directive(91-441-EC) all vehicle emission standards must be expressed in grams per kilometre (g/km) rather than gram per test.

Table 1.5 Motor vehicle emission control limits as agreed by the European Council of Environmental Ministers

| g per standard test | | | | | |
|---|---|---|---|---|---|
| Class of vehicle | | Implementation date | CO | $NO_X$ + HC | $NO_X$ |
| >2.0 | | 1988/89 | 25 | 6.5 | 3.5 |
| 1.4-2.0 | | 1991/93 | 30 | 8.0 | * |
| <1.41 | Stage 1 | 1990/91 | 45 | 15 | 6.0 |
| | stage 2 | 1992/93 | 30 | 8.0 | * |

*The European Commission has dispensed with a specific $NO_X$ limit on the grounds that it is seeking a total emission equivalent with the 1983 US emission standards of the order of 1.5-1.6 Mt annually. The Dutch Government would like to see a figure of 4.5-5.5 g per standard test for $NO_X$ given a projected 30-40 per cent increase in small car usage by 2010. Meanwhile the both British industry and the UK Government remain opposed to the introduction of the 3-way catalytic converter, preferring tp rely on foreseeable developments of emission limitation technology, despite forecasts of high $NO_X$ fallout after 1990.

Table 1.6 Standards revised in December 1990 and applicable to all new cars by the end of 1992 (grams per kilometre)

| | CO | $NO_X$ + HC | Particulate |
|---|---|---|---|
| Type approval | 2.72 | 0.97 | 0.14 |
| conformity of production | 3.16 | 1.13 | 0.18 |

### 1.6.1.2 Volatile organic compounds

Volatile organic compounds are released by motor vehicles, industrial processes and from solvents such as those used in paints. Some volatile organic compounds can cause unpleasant effects such as eye irritation, drowsiness and coughing while others such as benzene are carcinogenic. Volatile organic compounds together with oxides of nitrogen, lead to the formation of low level ozone. National emissions of VOCs have risen during the late 1980s and consequently have received increasing attention. 22 Million motor vehicles in the United Kingdom contribute about 30 percent of the UK VOC emissions. The 1989 European community agreement on emission standards for new vehicles, which involves the fitting of catalytic converters from 1993, may help to reduce emissions. More importantly, Britain in November 1991 as a signatory of a United Nations Environment programme (UNEP) protocol to the Conventional Long-Range Transboundary Air Pollution is required to reduce VOC emissions by 30 per cent by 1999, using 1988 as a base level (3,15,17).

### 1.6.1.3 Lead and benzene

The original Pb in petrol directive (78/611/EEC) set the maximum permitted Pb content in petrol at 0.40 g/l. Member states could set a lower limit to 0.15g/l but could not insist on a level below that. The current Directive 85/210 /EEC puts pressure on Member States to reduce Pb content to 0.15 g/l and requires them to ensure that unleaded petrol is fairly freely available. The Directive also limits the benzene content in petrol to 5 per cent by volume. Part of the reason for the acceptance of this Directive was the willingness by the British and German Governments to accept an ambient air quality standard for lead in air of 2 $g/m^3$. A report from Warren Springs Laboratory (1987b) reveals that airborne Pb has been reduced by an average of 53 per cent in the year following reduction of the maximum content of Pb in petrol from 0.4 to 0.15 g/l. This reinforces the view that motor vehicle emissions were by far the most predominant source (88 per cent) of Pb in the atmosphere (17).

## 1.6.2 Air Quality Standard

### 1.6.2.1 Sulphur Dioxide and particulates

During the 1970s, the EC became convinced that there was sufficient medical evidence to justify proposing health protection air quality standards for various pollutants. In July 1980, the EC issued a Directive (80/779/EEC) setting out the maximum concentrations of smoke and sulphur dioxide permitted in urban areas (Table 1.7). In recognition of the synergistic effect of these two pollutants on health , the health protection standard for sulphur dioxide is dependent on the level of smoke present : the more smoke that is present over a particular time-scale, the lower the allowable level of sulphur dioxide.

Table 1.7 European Community Air Quality standards for suspended particulate

| Reference period | Limit values for $SO_2$ | Associated value for particulate | Absolute limit for particulate |
|---|---|---|---|
| Year* | 80μg/m$^3$<br>120μg/m$^3$ | >40 μg/m$^3$<br>≤40 mg/m$^3$ | 68 mg/m$^3$ |
| Winter* | 130 μg/m$^3$<br>180 μg/m$^3$ | >60 μg/m$^3$<br>≤60 μg/m$^3$ | 111 μg/m$^3$ |
| Year (24h measuring periods) | 250 μg/m$^3$ ·<br>350 μg/m$^3$ ° | >150 μg/m$^3$ ·<br>≤150 μg/m$^3$ ° | 213 μg/m$^3$ |

* Median of daily mean values for appropriate period

· 98th percentile of all daily mean values throughout the year

° Not to be exceeded for more than 3 consecutive days

### 1.6.2.2 Pb and $NO_X$

Air quality standards also apply to Pb in the environment as a result of the implementation of Directive 82/884. This specifies that ambient Pb concentrations should not exceed 2 μg/m$^3$ in urban residential areas and localities exposed to atmospheric Pb other than motor vehicle traffic.

The Directive originally required a regular biological screening of blood Pb levels, but this clause was dropped on the basis of scientific evidence suggesting that such a sampling programme would not give meaningful results, given the intention of the Directive.

The trend towards setting stricter air quality standards was evident in the setting of the nitrogen dioxide standard in 1985. The air quality limit value, expressed as the 98th percentile of recorded hourly mean value over the year, is 200 μg/m$^3$ (approximately equivalent to a median value of 75 μg/m$^3$ ). This value appears particularly strict given that at the time of setting the standard the lowest level at which nitrogen dioxide had been demonstrated to have had an effect was 940 μg/m$^3$ . The air quality standard thus included a four- to five fold safety factor. Some argue that this is unnecessarily strict and that a standard of 300 μg/m$^3$ would have been adequate (which is nearer the top of the range suggested by the World Health Organisation). An air quality guide value of 135 μg/m$^3$ for the 98th percentile and 50 μg/m$^3$ for the 50th percentile of hourly mean values was also specified (15,17).

## 1.7 Limitation of particulates

The USA Environmental Protection Agency ambient quality standard for particulate matter is 150 μg/m$^3$ (previously 260 μg/m$^3$ total suspended particulate). This is a 24 hour mean concentration not to be exceeded on more than 0.27% of occasions.

The annual arithmetic mean standard is 50 μg/m$^3$ particulate matter (PM), (previously 75 μg/m$^3$ total suspended particulate annual geometric mean). The WHO air quality standard for combined sulphur dioxide and suspended particulate matter is summarised in Table 1.8.

## 1.8 Limitation of benzene

The benzene limit has been proposed by the Expert Panel on Air Quality Standards (EPAQS), and is the first of a series promised in the UK Government 1990 white paper on the environment. The proposed AQS for benzene is 5ppb as a running annual average. However, EPAQS has also recommended that "since benzene is a genotoxic carcinogen and since, in principle, exposure to such substances should be kept as low as practicable", the Government should set a deadline for reducing this to 1 ppb. The only other country to have set an AQS for benzene is the Netherlands, which last year adopted a level equivalent to 3 ppb (16).

Table 1.8. WHO Guidelines for combined Exposure to Sulphur Dioxide and Particulate Matter[a]

| Period | Averaging time | Sulphur dioxide ($\mu g/m^3$) | Reflectance assessment black smoke[b] ( $\mu g/m^3$ ) | Total suspended particulate (TSP) [c] $\mu g/m_3$ (gravimetric assessment) | Thoracic particle (TP) [d] $\mu g/m^3$ (gravimetric assessment) |
|---|---|---|---|---|---|
| Short term | 24-hour | 125 | 125 | 120[e] | 70[e] |
| Long term | 1 year | 50 | 50 | - | - |

[a] No direct comparisons can be made between values for particulate matter in the right and left-hand section of this table, since both the health indicators and the measurement methods differ. While numerically TSP/TP values are generally greater than those black smoke, there is no consistent relationship between them , the ratio of one to the other varying widely from time to time and place to place, depending on the nature of the sources.

[b] Nominal ($mg/m^3$) units assessed by reflectance. Application of the black smoke value is recommended only in areas where coal smoke from domestic fires is the dominant component of the particulate. It does not necessarily apply where diesel smoke is an important contributor.

[C] TSP: measurement by high volume sampler, without any size selection.

[d] TP: equivalent values as for a sampler with ISO-TP characteristics ( having 50% cut-off point at 10 mm): estimated from TSP values using site-specific TSP/ISO-TP ratios

[e] Values to be regarded as tentative at this stage being based on a single study (involving sulphur dioxide exposure also)

EPAQS recommendations are intended to reduce benzene levels in air so that it is no longer the main source of individual exposure. Vehicle exhausts are by far the major source of benzene in the UK (see Table 1.9). Levels are highest in urban air, particularly during the winter.

Table 1.9 Sources of benzene emissions in the UK in 1991

| Sources | tonnes/year | % |
|---|---|---|
| Petrol engine exhaust | 39250 | 78 |
| Diesel engine exhaust | 4550 | 9 |
| Evaporation from vehicles | 3350 | 7 |
| Petrol refining and distribution | 1350 | 3 |
| Combustion of oil, wood, etc. | 950 | 2 |
| Gas leakage | 400 | <1 |
| Other industrial processes | -334 | <1 |

## 1.9 Exhaust Gas Treatment

### 1.9.1 Catalytic Converters

The catalytic converters used in spark ignition engines consist of an active catalytic material in a specially designed metal casing which directs the exhaust gas flow through the catalyst bed. The active material employed for CO and HC oxidation or NO reduction (normally noble metal, although base metals oxides can be used) must be distributed over a large surface area so that the mass transfer characteristics between the gas phase and the active catalyst surface are sufficient to allow close to 100 percent conversion with high catalyst activity.

The two catalytic converters configurations commonly used are shown in Fig. 1.4. One system employs a ceramic honeycomb structure or monolith held in a metal can in the exhaust stream.

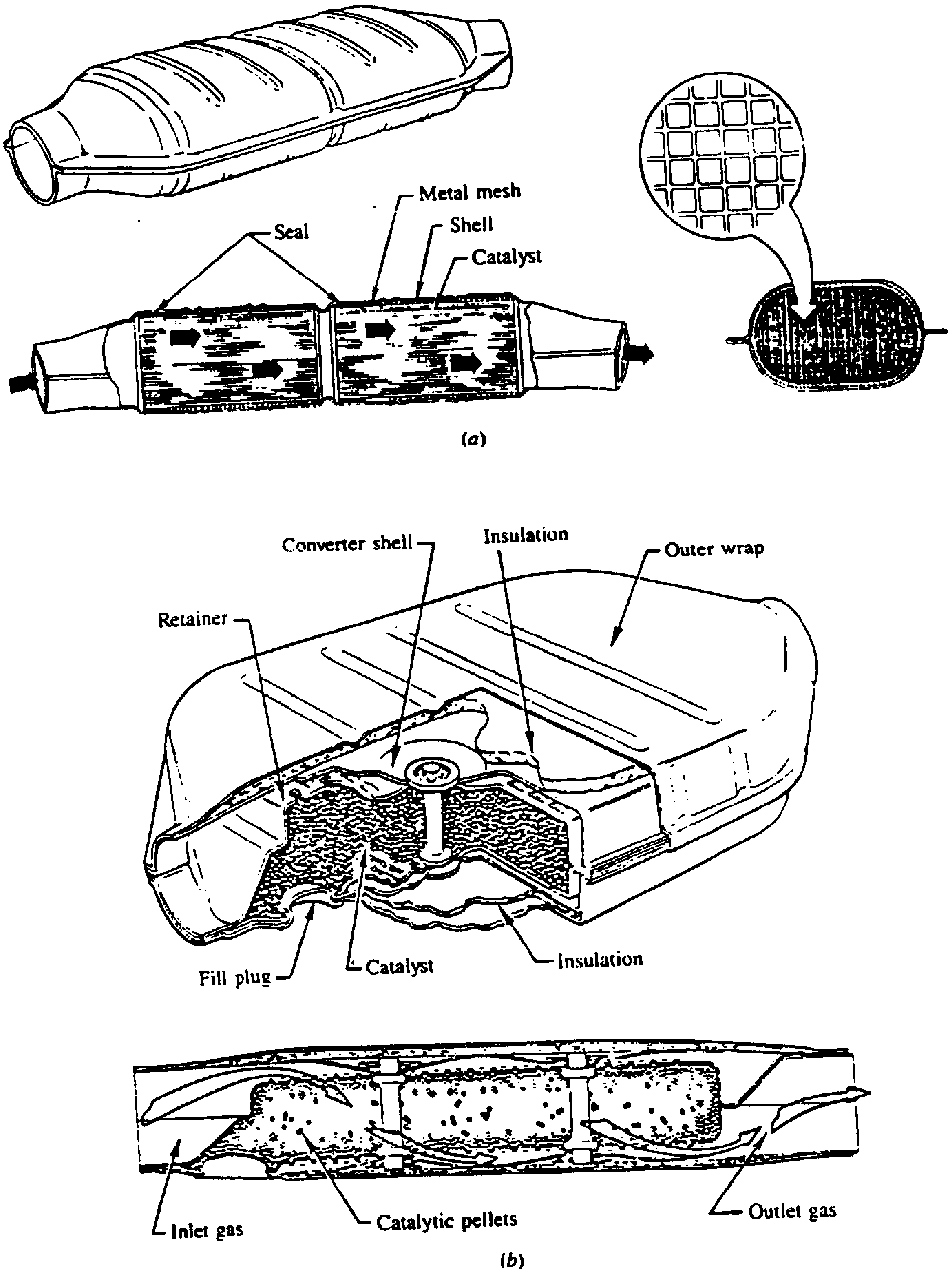


Fig. 1.4 Catalytic converters for spark-ignition engine emission control: (a) monolith design (b) pelletized design.

The active (noble metal) catalyst material is impregnated into a highly porous aluminium washcoat about 20μm thick that is applied to the passageway walls. The typical monolith has square-cross-section passageways with inside dimensions of ~1mm separated by thin (0.15 to 0.3mm) porous walls.

The number of passageways per square centimetre varies between about 30 and 60. The washcoat, 5 to 15 percent of the weight of the monolith, has a surface area of 100 to 200 $m^2/g$. The other common converter design uses a bed of spherical ceramic pellets to provide a large surface area in contact with the flow. With pellet catalysts, the noble metal catalyst is impregnated into the highly porous surface of the spherical alumina pellets (typically 3 mm diameter) to a depth of about 250 μm. The pellet material is chosen to have good crush and abrasion resistance after exposure to temperatures of the order of 1000°C. The gas flow is directed down through the bed to provide a large flow area and low pressure drop. The gas flow is turbulent which results in high mass-transfer rates; in the monolith catalyst passageways, it is laminar.

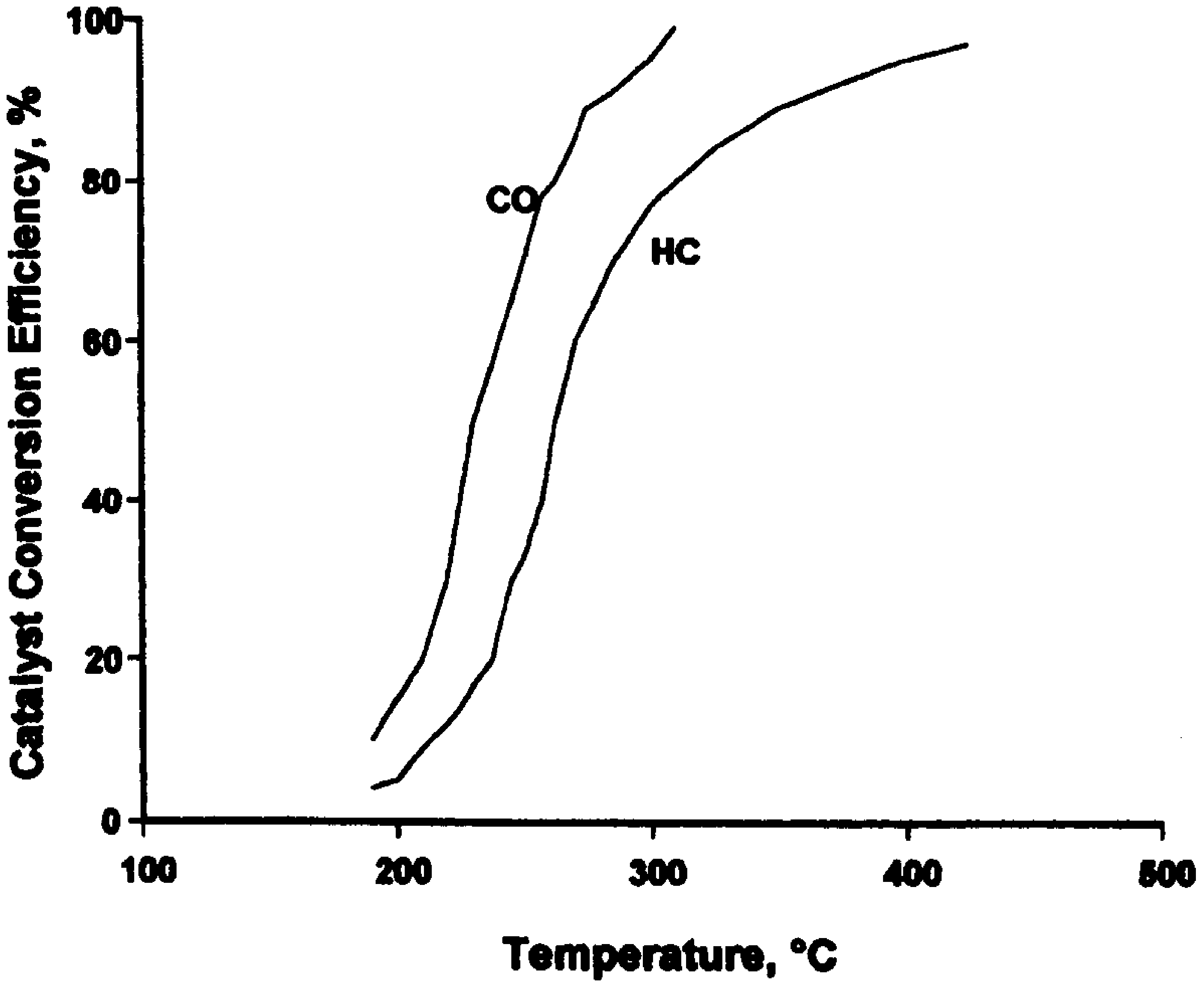


**Fig. 1.5 Conventional efficiency for CO and HC as a function of temperature for typical oxidation catalytic converters**

The function of an oxidation catalyst is to oxidise CO and hydrocarbons to $CO_2$ and water in an exhaust gas stream which typically contains ~12 percent $CO_2$ and $H_2O$, 100 to 2000 ppm NO, ~20 ppm $SO_2$, 1 to 5 percent $O_2$, 0.2 to 5 percent CO, and 1000 to 6000 ppm HC, often with small amounts of lead and phosphorus. About half the hydrocarbons emitted by the SI engine are unburned fuel compounds. The saturated hydrocarbons (which comprise some 20 to 60 percent) are the most difficult to oxidize. The ease of oxidation increase with increasing molecular weight. Sufficient oxygen must be present to oxidise the CO and HC. This may be supplied by the engine itself running lean or stoichiometric or with a pump that introduces air into the exhaust ports just downstream of the valve. Venturi air addition into the exhaust port using the pressure pulsation generated by the exhaust process can also be used to add the required air (7).

### 1.9.2 Particulate Traps

An exhaust treatment technology that substantially reduces diesel engine particulate emission is the trap oxidiser. A temperature- tolerant filter or trap removes the particulate material from the exhaust gas; the filter is then "cleaned off " by oxidising the accumulated particulate. This technology is difficult to implement because:

(1) the filter, even when clean, increases the pressure in the exhaust system.

(2)this pressure increase steadily rises as the filter collects particulate matter.

(3)under normal diesel engine operating conditions the collected particulate matter will not ignite and oxidise.

(4) once ignition of the particulate occurs, the burn-up process must be carefully controlled to prevent excessively high temperatures being reached and trap damage or destruction occuring.

Trap oxidisers have not been put into production for light-duty automobile diesel engines. Their use with heavy-duty diesel engine poses a more difficult problem due to higher particulate loading and lower exhaust temperatures (7).

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# Chapter Two: Effects of Toxicity of Aromatic Hydrocarbons on Humans

## Glossary of medical terms used in this chapter

Adenoma; a benign tumour of epithelial origin that is derived from glandular tissue or exhibit clearly defined glandular structure.

Anorexia; loss of appetite

Aplasia; total or partial failure of development of an organ or tissue.

Case control study; the definition of a disease in a group of individuals contrasted with a similar group of nonaffected individuals (concase or control).

Carcinoma; cancer that arises in epithelium, the tissue that lines the skin and internal organs of the body.

Clotting; coagulation; the process by which a colloidal liquid changes to a jelly like mass.
Cohort study; The study mode that defines the independent variable and follows a group of individuals to examine the incidence (attack rate) of a condition.

DNA (deoxyribonucleic acid); the genetic material of nearly all living organisms, which controls heredity and is located in the cell nucleus.

Dyspnoea; laboured or difficult breathing.

Erythrocyte; red blood cell; a blood cell containing the pigment haemoglobin, the principal function of which is a transport of oxygen. There are normally about $5\times 10^{12}$ erythrocytes per litre of blood.

Haematopoiesis; haemopoiesis; the process of production of blood cells and platelets which continues throughout life, replacing aged cells.

Hyperplastic; the increased production and growth of normal cells in a tissue or organ. The affected part becomes larger but retains its normal forms.

Hypoplastic; underdevelopment of an organ or tissue.

LD$_{50}$; the dose of toxic compound that causes death in 50% of a group of experimental animals to which it is administered: used as a measure of toxicity of drugs.

Lymphatic system; A network of vessels that conveys electrolytes, water proteins, etc. - in the form of lymph - from the tissue fluids to blood system.

Lymphocytosis; an increase in the number of lymphocytes in the blood

Lymphoblastic; an abnormal cell presents in the blood and blood-forming organs in a type of leukaemia

Leukaemia; any of a group of malignant diseases in which the bone marrow and other blood-forming organs produce increased numbers of certain types of white blood cells (leukocytes). Overproduction of these white cells, which are immature or abnormal forms, suppresses the production of normal white cells, red cells and platelets. This leads to increased susceptibility to infection, anaemia and bleeding. Other symptoms include enlargement of the spleen, liver, and lymph nodes. Leukaemia can be classified into acute or chronic varieties depending on the rate of progression of the disease. Classification can also be made according to the type of white cell that is proliferating abnormally; for example acute lymphoblastic leukaemia (see lymphoblastic in this page) and acute myeloblastic leukaemia (see myeloblast in this page).

Leukocyte; white blood cell; any blood cell that contains a nucleus. In health there are three major subdivisions: granulocytes, lymphocytes and monocytes, which are involved in protecting the body against foreign substances and in antibody production.

Monocyte; a variety of white blood cell, 16-20 µm in diameter, with a kidney-shaped nucleus.

Monocytosis; an increase in the number of monocytes in the blood

Myeloblast; the earliest identifiable cell that gives rise to a granulocyte, having a large nucleus and scanty cytoplasm. It is normally found in the blood-forming tissue of the bone marrow, but may appear in the blood in a variety of diseases, most notably in acute myeloblastic leukaemia.

Pallor; abnormal paleness of the skin, due to reduced blood flow or lack of normal pigments.

Papiloma; a benign growth on the surface of skin or mucous membrane (for example in the womb)

Platelet (thrombocyte); a disc shaped structure, 1-2µm in diameter, present in the blood.

Ppm years; average concentration of a compound in units of parts per million(ppm) × number of years

Pulmonary; relating to, associated with or affecting the lungs.

Sarcoma; any cancer of connective tissue. These tumours may occur in any part of the body, as they arise in the tissues that make up an organ rather than being restricted to a particular organ. They can arise in fibrous tissue, muscle, fat, bone, and etc.

Squamo-; prefix denoting , squamous cell; numbers of cell that be determined

Standard Mortality Ratio (SMR); The ratio of the total observed number of deaths in a group under research to the number of expected death in a standard population and multiplied by 100.

Subcutaneous; beneath the skin. A subcutaneous injection is given beneath the skin.

Vertigo; a disable sensation in which the affected individual feels that either he himself or his surrounding are in a state constant movement.

Time-weight-average; Average exposure with concentration a compounds over a day

Vital status; Determination of health or death in a special group.

# 2.1.MONOCYCLIC AROMATIC COMPOUNDS

## 2.1.1.Benzene

### 2.1.1.1.Chemical and Physical Data

Benzene is a clear, colourless liquid with a characteristic pleasant odour at low concentrations but disagreeable odour at high levels. Benzene forms a highly flammable and explosive mixture with air at 1.4 to 8.0 percent benzene in air. It is an excellent solvent. Chemically it is fairly stable, but readily undergoes substitution reactions to form halides, nitro-components, sulphonates and alkyl derivatives. Commercial benzene usually contains varying concentrations of methyl benzene, xylene, phenol and traces of carbon disulphide, thiophene, olefins, naphthalene. Some data for benzene and alkyl derivatives are summarised in Table 2.1.

The photochemical formation of nitrobenzene and nitro-phenols from benzene has been observed in the presence of nitrogen oxides.

Benzene also combines photochemically with halogens to produce eye and mucous membrane irritation. Ozone reacts 10 to 20 times more slowly with benzene than with its methyl substituted derivatives (27,5).

### 2.1.1.2.Sources and Use

Benzene occurs in coal tar and petroleum naphtha from which it is commercially prepared and is also a constituent of petrol. A report from the US Army in 1972 showed that 37 samples of unleaded and leaded petrol averaged 0.8 percent benzene, with the highest value 2 percent. European petrols still contain up to 5 percent benzene, because they are produced from higher aromatic reformats (27).

Some consumer products, such as paint removers, in the past have contained 50 percent or more of benzene. Products with a benzene content above 0.1 percent now have to be adequately labelled with warnings to the consumer (27).

Benzene has been detected in cigarette smoke at 47 and 64 ppm (20), depending on the type used. About 150 air samplers analysed from the areas around Houston Texas (21), over a period of 15 months, revealed an average benzene concentration of 1.3 to 15 ppb

(19). In the Toronto atmosphere, average benzene concentrations were detected at 2 to 98ppb(8), and near Los Angeles levels 60 to 70 ppb were found in 1962.

**Table 2.1 Physicochemical Properties of Some Aromatic Hydrocarbons**

| Compound | B.P [°C(mmHg)] | Density | MP(°C) | Mol. Wt. | Solubility (w/al/et*) |
|---|---|---|---|---|---|
| Benzene | 80.10 | 0.8787 | 5.5 | 78.11 | d/v/v |
| Methyl benzene | 110.62 | 0.8869 | -95 | 92.14 | I/v/v |
| Ethyl benzene | 136.2 | 0.8670 | -94.97 | 106.17 | I/v/v |
| m-xylene | 139.10 | 0.8642 | -47.87 | 106.17 | I/v/v |
| p-Xylene | 138.35 | 0.8611 | 13.26 | 106.17 | I/v/v |
| O-Xylene | 144.41 | 0.8802 | -25.18 | 106.17 | I/v/v |
| Xylenes, mixed | 138.3 | 0.867 |  | 106.17 | I/v/v |

*solubility in water/alcohol/ether: v= very soluble; s=soluble; d=slightly soluble; I=insoluble

## 2.1.1.3.Physiological Response

The inhalation of benzene at certain concentration will produce chronic effects. The levels of intake required to produce effects vary widely with the individuals. Contributing factors are poor nutrition, certain immunology tendencies and consumption of alcohol or drugs.

Some symptoms of interaction to benzene include headaches, dizziness, fatigue, anorexia, dyspnea, visual disturbances and loss of consciousness.

Benzene affects the haematopoietic system and effects are not uniform. Generally three stages can be diagnosed. Initially, blood clotting defects may occur. These are caused by functional, morphological, and quantitative platelet alteration which occur along with generally reduced production of all blood components. At this stage, if diagnosed and treated, the effects are readily reversible.

At a more advanced stage, the bone marrow becomes hyperplastic, then hypoplastic, the iron metabolism is disturbed and internal haemorrhaging occurs. At this stage, diagnosis and treatment should be prompt and intense, and all future exposure to benzene has to be avoided. Clinical findings are erythrocyte counts below 3.5 million, leukocytes below 4500, decreased platelet numbers and increased iron (27).

Unless the patient is treated, a third phase may occur where bone marrow aplasia may become progressive.

It is generally accepted that exposure of humans to high benzene concentrations entails increased risk of developing acute nonlymphatic leukaemia. This knowledge is based on case reports and on results of epidemiological studies of occupationally exposed populations. What follows is a description of the most relevant studies of the risk of acute nonlymphatic leukaemia (ANL) resulting from exposure to high benzene concentrations (see Table 2.2).

Haematopoietic effects bordering on leukaemia have been observed by Aksoy et al. in a number of cases in Turkey. Exposure to benzene in the Turkish shoe industry must have been very high because of the use of benzene as a solvent for adhesive, in many cases around 640 $mg/m^3$ (200ppm). Aksoy attempted to quantify the risk by estimating the number of expected leukaemia cases among the 28,000 workers in the shoe industry. He estimated the expected number at 6 per 100,000 man-years but actually observing 13 per 100,000 man-years On this basis he concluded that in workers in Turkish shoe industry leukaemia was 2.2 times more prevalent than in the general population (10).

According to Aksoy, however, the number of cases decreased in 1974-1975 and no new cases were reported in 1976 following the gradual substitution of benzene by petrol (9) even though the petrol in south-eastern Europe still contained a relatively high percentage of benzene. Aksoy also concluded that genetic and other extraneous factors may play etiologic roles, as observed in two families with the occurrence of leukaemia in pairs of identical twins. This is substantiated by a case of familiar chronic lymphocytic leukaemia that occurred in a family that had worked in the dry-cleaning business for 20 to 30 years (11).

Rinsky et al.(1987), examined 748 workers and was able to establish the vital status for 98.6% of the cohort study(70.3 percent were alive, 28.3were dead and 1.4 were percent lost to follow up). The person-years in the cohort were divided into four categories of exposure. These exposure strata were (a) 1 to 40 ppm-years (b) 40 to 199.99 ppm-years (c)200 to 399.99 ppm-years and (d) more than 400 ppm-years. These boundaries correspond to the cumulative exposure that would result from average annual exposure to less than 1; 1 to 4.99; 5 to 9.99 and 10 or more ppm of benzene, respectively, accumulated over a 40-year working lifetime. To obtain cause-specific Standardised Mortality Ratio (SMR), the observed numbers of deaths from each cases were divided by the expected numbers in standard population and multiplied by 100. Standardised mortality ratio for leukemia, over the four exposure groups (a, b, c and d) were 109, 322, 1186 and 6637, respectively demonstrating a marked, progressive increase in deathes with increasing cumulative exposure. With the aid of detailed estimates of past exposure levels Rinsky et al., found a clear association between cumulative exposure and the incidence of leukaemia in a group of exposed workers (17).

Ott et al. identified 594 workers at Dow Chemical who had all been exposed to benzene in the past. Three workers instead of the expected 0.8 had died of acute nonlymphatic leukaemia (SMR =375). Time-weighted mean exposure for these workers would probably have been of the order of 128 mg/m$^3$ (14).

In 1980 Paganini-Hill et al. reported the results of a cohort study among 1361 workers in the graphics industry. The vital status of 9% of the workers could not be established. Instead of 2.8 expected cases, the researchers observed 7 cases of leukaemia mortality (SMR= 250). Many of the workers had been exposed for over 20 years (15).

In 1992, Midzenski et al., reported neurotoxic symptoms in fifteen workers who had been exposed to high concentrations of benzene. Workers with more than two days of acute exposure were significantly more likely to report dizziness and nausea than those with 2 or fewer days of acute exposure. One year later, 6 workers (40%) had persistent abnormalities and an additional worker with normal hematologic parameters at the time of the initial evaluation subsequently developed an abnormality consistent with benzene exposure. Numerous large granular lymphocytes were observed on 6 (40%) of the peripheral blood smears(35).

Table 2.2 Survey of the results of epidemiological studies of the incident of leukaemia in exposure of worker to benzene

| Author | Type of exposure | Number of people | Height exposure mg/m$^3$ | Number cases of leukemia | Type | SMR |
|---|---|---|---|---|---|---|
| Aksoy, 1972 | Turkish, Shoemaker | | 640 | 26 | Acute nonlymphatic | 210 |
| Infante et al. | Chemical plant | 748 | 200 | 9 | Acute nonlymphatic | 1000 |
| Ott et al., 1978 | Dow chemical | 598 | 0-300 | 3 | Acute nonlymphatic | 375 |
| Thorpe, 1978 | Petrochemical Industry | 3800 | Low | 18 | | 100 |
| Rinsky et al., 1987 | Chemical plant | 748 | 128 | 8 | Acute nonlymphatic | 478 |
| Paganini et al., 1980 | Graphic industry | 1361 | | 7 | Total leukemia | 250 |
| Monson and Fing | Rubber industry | 13570 | | 40 | Lymphatic | 240 |
| Yin et al., 1987 | Various industries | 28460 | 50-500 | 25 | Total leukemia | 574 |
| Parkes et al., 1982 | Rubber industry | 33815 | Low | 31 | Negative | |
| Rushton and Lderson | Petrochemical | 34781 | Low | 30 | Low | 30 |

In the Peoples' Republic of China, Yin et al. compared the fate of 28,460 workers exposed to benzene in various industries ( concentration; 50-500 mg/m$^3$ ) with that of 28,257 workers without benzene exposure. They found 25 cases of mainly acute nonlymphatic leukaemia in the former group compared to only 4 in the later (29).

So far the results of the epidemiological studies described are roughly compatible although some deviant findings have also been reported. Monson et al., followed using 13,570 workers in the American rubber industry. Part of this cohort had been exposed to benzene in the past and indeed showed an excess leukaemia mortality, but this was said to be due to lymphatic leukemia, rather than the nonlymphatic leukaemia usually found (13).

In an assessment by Hughes et al., in 1994 for the Canadian Environmental Protection Agency estimates of the average daily intake are presented and available data on the potential health effect in humans are evaluated. Based on the sufficient weight of evidence of carcinogenicity in epidemiological studies and supporting data from studies on experimental animals, benzene has been classified as "carcinogenic to humans". Based on comparison of levels of benzene present in the general environment in Canada with the potential of this substance to induce cancer, the priority for environmental options to reduce exposure in the general environment is considered to be high compared to that of other substances assessed in the priority substances program (37).

In contrast a cohort study, by Parkes et al, found that the number of leukemia cases observed was no greater than expected. In the population studied, 30 cases of leukemia were observed and 32 cases in a control group. Exposure level to benzene in studied group were below 0.03ppm (16).

The 1994 study Lagorio et al., reported on the mortality of a cohort of 2665 filling station managers who had exposure to petrol fuel from the Latium region (Italy).
The overall analysis for standardised mortality ratios (SMR) showed a significantly decreased mortality from all causes, mainly due to a deficit of cardiovascular disease and malignant neoplasms. Non-significant increased risks for esophageal cancer (SMR 241, 90% confidence interval), brain cancer (SMR 195) and non-Hodgkins lymphoma (SMR 173) were found for the men and mortality due to lung cancer and leukemia was lower than expected (36).

Inhaled benzene is readily absorbed by blood, from which it is strongly taken up by fatty tissues, for the non-metabolised compounds the process is reversible and benzene is excreted through the lungs. The main metabolism of benzene is action in the liver where benzene is converted to phenol. The benzene epoxide intermediate in this reaction is probably responsible for unique toxicity of benzene, which involves damage to bone marrow (38).

According Rushmore et al. (1984) and Kalf et al (1985) benzene has an effect on DNA in chromosomes, and this has been confirmed by some radioactivity tracer experiments which have shown that benzene is incorporated into DNA. A great number of experiments have shown that benzene is capable of inducing chromosome damage in yeast, fungi, plants, insects, and the human body (40,41).

Epidemiological research has shown that exposure to comparatively high benzene concentrations results in sometimes persistent chromosome aberration in bone marrow cells and peripheral lymphocytes (2).

Benzene as a component of fuel petrol is known to be a carcinogen and link between benzene and leukemia has been known in most epidemiological studies. As mentioned, benzene has been emitted to air from exhaust pipes as unburned hydrocarbons and also coming to the air from leaks or from evaporation in carburettors, therefore it is important to measure benzene in air and also from car exhaust because they are major sources. Because of the known toxic effects of benzene, control is important and new legislation by Air Quality Standards in the UK recommends 5 ppb for permitted levels, consequently evaluation and measurement of benzene in air is one important objective in this research (4).

### 2.1.2.Methyl benzene

#### 2.1.2.1 Properties, Sources, and Use

Methyl benzene is the lowest molecular weight member of the alkyl benzene series which in general, possess properties similar to benzene.

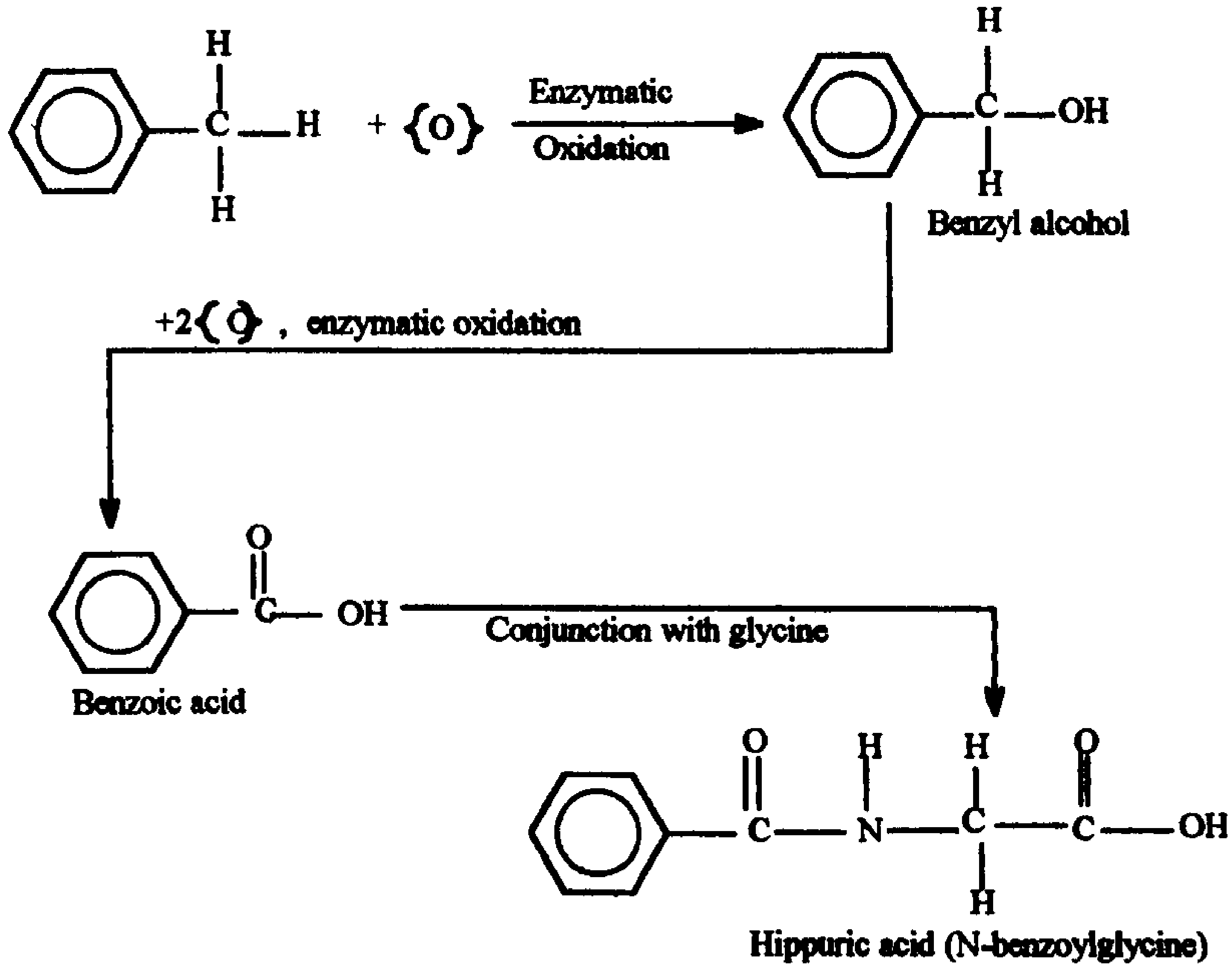
Methyl benzene, $C_6H_5CH_3$, is a clear colourless, non-corrosive, flammable liquid with a sweet pungent, odour. Further physicochemical properties are included in Table 2.1.

Methyl benzene has been measured in the urban air at 0.01 to 0.05ppm and probably stems from production facilities, automobile and coke oven emissions, petrol evaporation and cigarette smoke. It can also occur in human respiratory air of smokers and non-smokers (32,33,34). Methyl benzene is a component of high flash aromatic naphtha which is produced from crude oil during primary distillation. Methyl benzene ,in the past

,has been recovered from byproducts of the coal tar industry. Presently, methyl benzene is produced from petroleum and specifically from methyl cyclohexane containing naphtha by the catalytic reforming process. Re-forming of n-heptane at 977°C yields about 62 percent methyl benzene. Methyl benzene is also a pyrolysis product of thermal cracking and is used extensively as a solvent in the chemical, rubber, paint and drug industries, as a thinner for inks , and suspension solution for navigational instruments.

### 2.1.2.2 Physiological Response

Experience in the varnishing and painting industries has shown methyl benzene to be a moderate toxicant. According to one case it has been shown to be a cardiac sensitizer and fatal carditoxin. In several cases of habitual "glue sniffing" renal, neural and especially cerebellar dystrophy occurred. Workers in a pharmaceutical plant in France exposed to methyl benzene fumes developed Leucopenia, and especially neutropenia (27).



Metabolic oxidation of toluene with conjugation to hippuric acid, which is excreted with urine

In a 1994 study under control of the Canadian Environmental Protection Agency, methyl benzene has been classified as "unlikely to be carcinogenic to humans". The estimated average daily intake of methyl benzene for the general population is 68 to 131 times less than the tolerable daily intake derived on the basis of data from bioassays in animal species and that calculated from clinical studies in human volunteers (26).

Skin and Inhalation Exposure: prolonged contact of methyl benzene with the skin may cause drying which causes fissured dermatitis. It is not, however a dermal sensitizer (27).

Methyl benzene, when inhaled, is 93 percent retained by the human system. Absorption of methyl benzene in the oral cavity is 29 percent. Both sources then contribute to the methyl benzene uptake into the vascular systems followed by distribution to various tissues and further metabolism.

Methyl benzene in the human system is subsequently oxidised to benzoic acid and in turn, conjugated with glycine to form hippuric acid which is excreted in the urine.

### 2.1.3.Xylene

Xylene (dimethylbenzenes), occurs in three isomeric forms, as o-,m-, or p-Xylene, or the 1,2-, the 1,3-, and the 1,4-dimethylbenzene, respectively.

Xylene occurs in many petroleum products, in coal naphtha, and as an impurity in petrochemical products, such as benzene and methyl benzene. o-,m-, and p-Xylene have been identified among the volatile products in tobacco smoke. m- and p-Xylene have also been detected also in particulate matter samples of Houston community air.

The three isomers possess similar properties and readily dissolve fats, oils and waxes. They also are commercially available separated or mixed as colourless, flammable liquids. Further physicochemical properties are given in Table 2.1 (27,5).

Xylene is produced by catalytic reforming and depending on the feedstock, yields of above 85 percent can be achieved. Commercially, xylene is also recovered from coal tar, yielding a typical mixture of about 10 to 20 percent of the ortho , 40 to 70 percent of the meta, and 10 to 25 percent of the para isomer, but may also contain 6 to 10 percent of important including ethyl benzene, benzene, methyl benzene, trimethylbenzene, phenol, thiophene, pyridine and nonaromatic hydrocarbons. Purification can be achieved by fractional distillation.

Xylenes are used widely as thinners and solvents for inks, rubbers, gums, resins, adhesives, and lacquers, and as paint removers. They are also used in the paper coating industry as solvents, as emulsifiers in agricultural products, as fuel components, and commonly in the chemical industry as intermediates (7).

### 2.1.3.1 Physiological Response

Prolonged exposure to Xylene fumes may produce conjunctivitis of the eye and dryness of the nose, throat, and skin.

In a 1994 study under the Canadian Environmental Protection Agency, xylenes were classified as "unlikely to be carcinogenic to humans". Total average daily intake of xylenes for the general population in Canada based on data on concentrations in ambient and indoor air, drinking water and at self-serve petrol stations were found to be less (by 16 to 40 times) than the tolerable daily intake derived from laboratory studies (26).

In a 1993, Uchida et al., surveyed 107 men and 68 women who were exposed to Xylene vapours in the boot manufacturing industry. The intensity of exposure was such that the sum of the three isomer concentrations was 14 ppm as a geometric mean and 21 ppm as an arithmetic mean. As controls, 241 nonexposed workers (116 men and 125 women ) were recruited either from the same factories or from factories in the same regions. There was an increased prevalence of subjective symptoms in the exposed workers which were apparently related to the effects on the central nervous system and to local effects on the eyes, nose, and throat, although dose-dependency of the symptoms was evident in only a limited number of cases (possibility because the intensity of exposure was rather low). It was further observed that the findings of haematology and serum biochemistry of liver and kidney functions were generally negative, showing that Xylenes are not toxic to the haematopoietic organs (25).

Xylene is absorbed mainly through the mucous membranes and pulmonary system. Pulmonary retention of vapours in human subjects amounts to about 64 percent for all participants and Xylene isomers tested. Absorbed Xylene is translated through the vascular system, but to a lesser degree than benzene. Generally, Xylenes are metabolised to the corresponding o-,m-,or p-toluic acids ($CH_3C_6H_4COOH$), and excreted in urine, free or conjugated with glycine as methyl hippuric acid ($CH_3C_6H_4COONHCH_2COOH$).

Xylene absorbed through the skin has been found to be 80 to 90 percent eliminated as methyl hippuric acid. Inhaled m- and p-Xylene by human volunteers has been shown excreted as urinary m- and p-methyl hippuric acid. (23,24,25).

### 2.1.4 Ethyl benzene

Ethylbenzene, phenylethane, $CH_3CH_2C_6H_5$, is a colourless, flammable liquid with a pungent odour. Being heavier than air, its vapours may travel a considerable distance and ignite and backflash. It evaporates about 94 times more slowly than ether. Further physicochemical data are presented in Table 2.1. The main use of ethylbenzene is in the production of styrene and synthetic polymers, and as a solvent and component for automotive and aviation fuels.

Ethylbenzene is absorbed through the skin at low rate and is a more powerful irritant than its lower homologues. Ethylbenzene has been detected in subcutaneous adipose tissue samples in workers three days after low to high exposure to styrene and related rubber manufacturing components.

However, methyl benzene, xylenes and ethylbenzene are not very toxic in low concentrations. These pollutants emitted to the air from car exhausts will react with $NO_X$ under UV radiation leading to smog formation. According to a study by Atkinson (1990) photochemical reaction of Xylene with the free radicals of oxygen and $NO_X$ is 10 to 15 times higher than with benzene and also 3 to 5 times higher than with toluene. Therefore it is important to measure each of these materials in the atmosphere (42).

Another reason to control aromatic hydrocarbon is the suggestion from some studies ( Pedersen et al. (1980), Candeli (1983) )that an increase in aromatic hydrocarbon in fuels increases PAH emission from car exhaust (47,48).

## 2.2 Polycyclic Aromatic Hydrocarbons

### 2.2.1 Polycyclic Aromatic Hydrocarbons in general

Fused ring systems occur in linear, staggered, or three-dimensional configurations. The simplest linear three-ring system is anthracene; when staggered, it is phenanthrene. (see Figure 2.1). The biological activities of PAHs change with alkyl substitution, at which point the materials may inhibit or promote their own progressive oxidative metabolism.

For physicochemical data see Table 2.3 and for physiological characteristics see Table 2.4.

Polycyclic aromatic hydrocarbons (PAH), are not carcinogens. Some of these compounds or their derivatives have carcinogenic or cocarcinogenic potential which depends on structure, cellular transport, storage potential, enzyme inducibility, oxidative metabolism, rate of excretion, and other factors. Carcinogenic potential also depends upon the type of biological system, tissue , immunologic, and nutritional state involved.

**Anthracene**; Anthracene, $C_{14}H_{10}$, is the simplest tricyclic aromatic compound. It crystallises as monoclinic plates but sublimes. The crystals are clear white with violet fluorescence when pure, and are yellow and fluorescent green with tetracaine and naphthalene as impurities (27).

**Phenanthrene**; Phenanthrene, $C_{14}H_{10}$ (Figure 2.1), an isomer of anthracene, is a crystalline solid (27).

**Benzanthracene;** benza(a)anthracene, 1,2-benzanthracene, 2,3-benzo phenanthrene, benzo(b)phenanthrene, $C_{18}H_{12}$, is a crystalline solid at room temperature. It is generated in the petrol engines and emitted in exhaust gas at 17.3 μg/min from petrol and up to 56.3 μg/min from other petroleum products (27).

**1,2-Benzo phenanthrene** ; benzo(a)phenanthrene, chrysene, $C_{18}H_{12}$, is a solid material. Chrysene can be isolated from crude petroleum and coal tar. It occurs in cigarette smoke and has been detected at 1.5 to 13.3 ng /$m^3$ in community air (27).

**Pyrene**; pyrene, benzo(d,e,f)phenanthrene, $C_{16}H_{10}$ is a colourless solid, soluble in organic solvents. It occurs in pyrolysis processes at lower temperatures and has been detected in the US community atmosphere in 12 cities from traces to 35 ng/$m^3$(27).

**Benzo(a)pyrene** ;3,4-benzo pyrene, formally named 1,2-benzopyrene, with an empirical formula, $C_{20}H_{12}$, crystallises as yellow needles.

Most experimental work on benzo pyrenes has been carried out with benzo(a)pyrene, because of evidence that it is an animal carcinogen and that is suspected to be active in humans (27).

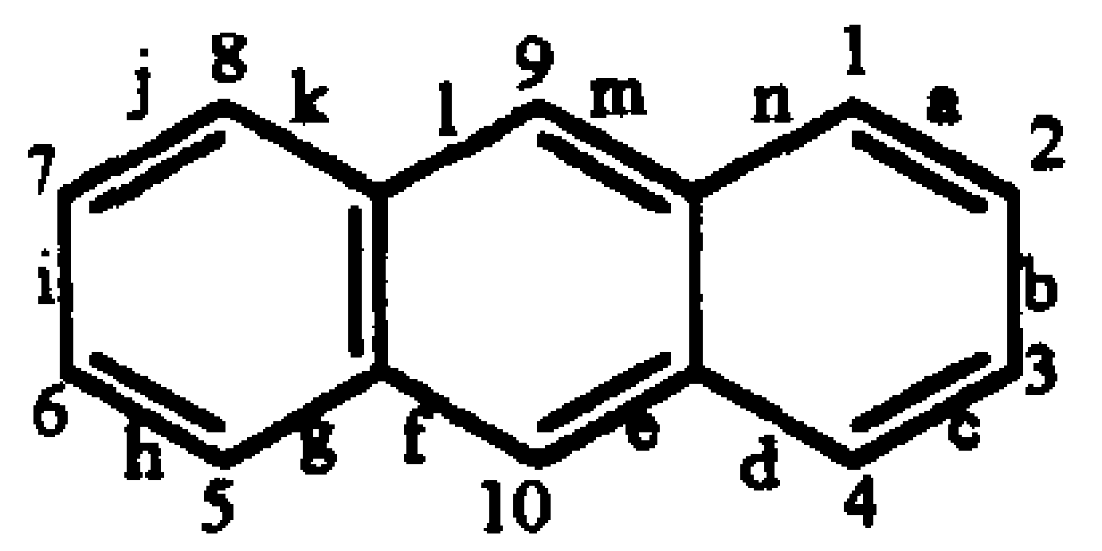
**Benzo(e)pyrene** ;1,2-benzo pyrene, Bep, $C_{20}H_{12}$, is a position isomer of benzo(a)pyrene.

Table 2.3 Physicochemical Properties of Some Polynuclear Aromatics

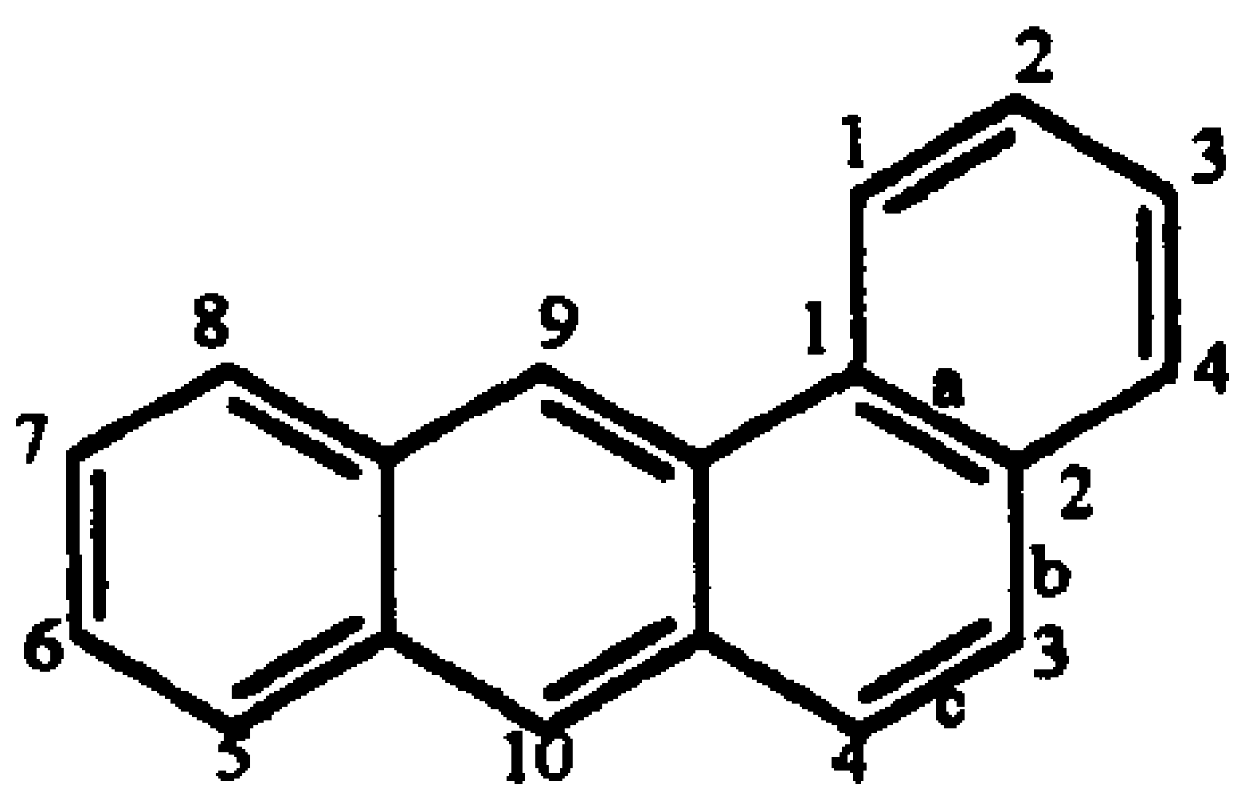
| Compound | B.P [°C(mmHg)] | Density | MP(°C) | Mol. Wt. | Solubility (w/al/et$^a$) |
|---|---|---|---|---|---|
| Anthracene | 340 | 1.283 | 216.2-216.4 | 178.23 | I/d/d |
| Phenanthrene | 340 | 1.179 | 101 | 178.23 | I/s/s |
| 1,2-Benzanthracene | 435 | | 162 | 228.29 | I/d/s |
| 1,2-Benzophenanthrene (chrysene) | 448 | 1.274 | 254 | 228.29 | I/d/d |
| Pyrene | 393 | 1.271 | 156 | 202.26 | I/s/s |
| Benzo(a)pyrene | 312 | | 176.5-177.5 | 252.32 | I/d/s |
| Benzo(e)pyrene | | | 178-179 | 252.32 | I/v/s |

### 2.2.2.Physicochemical relationships

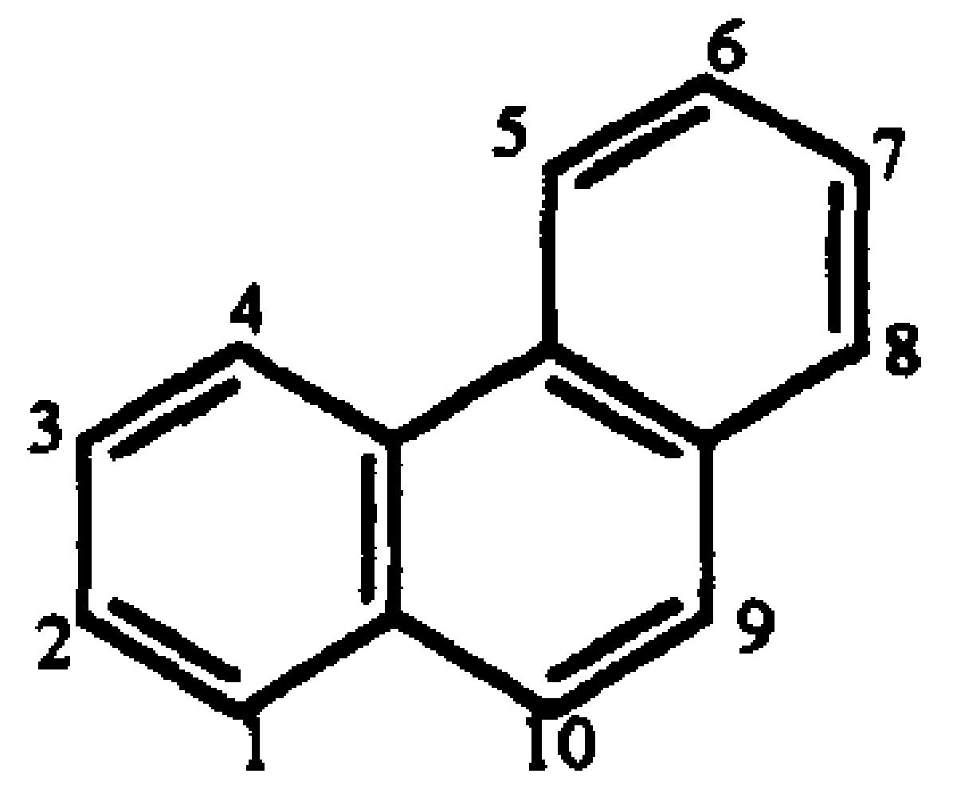
The majority of studies reported have been concerned with benzo(a)pyrene, possibly since it is more widely distributed in the environment and appears to have relatively high biological activity.



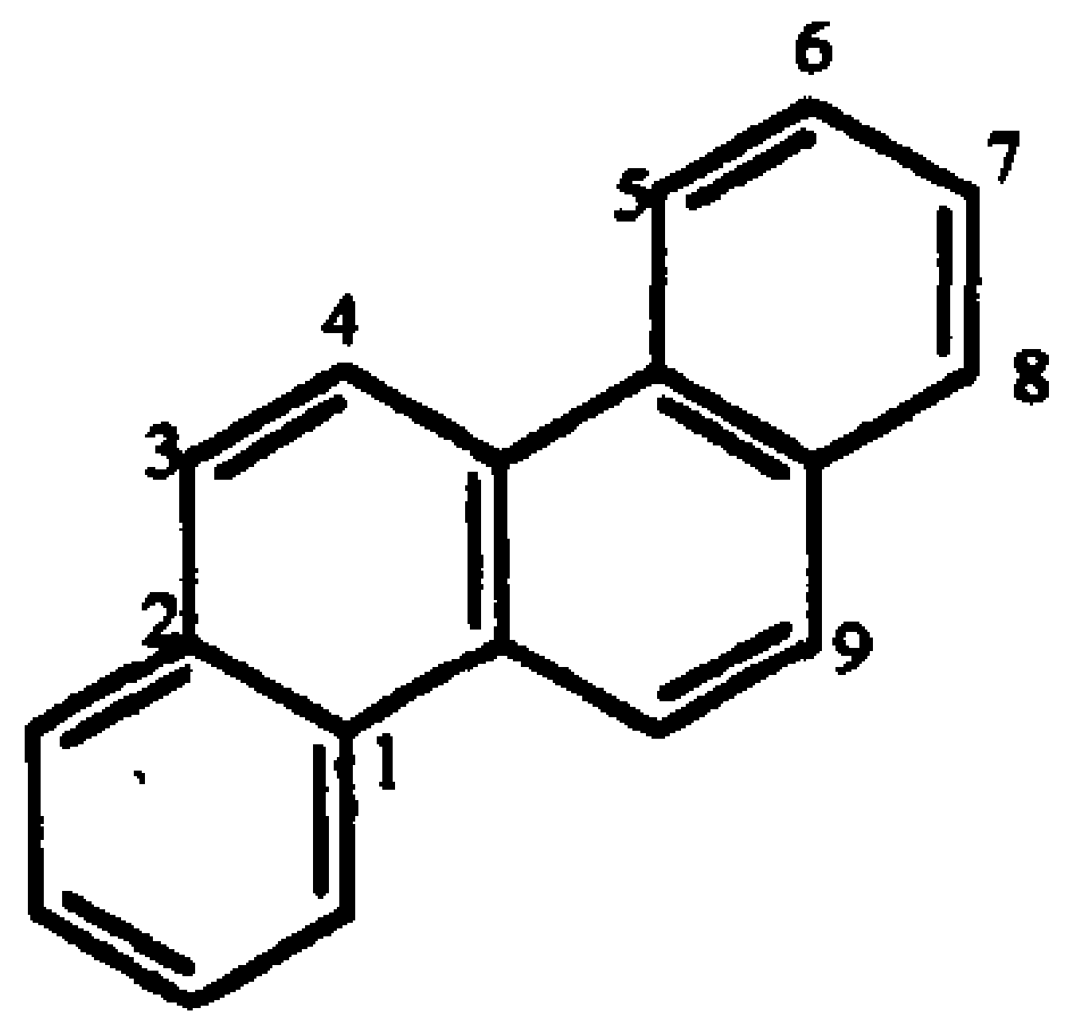
Anthracene



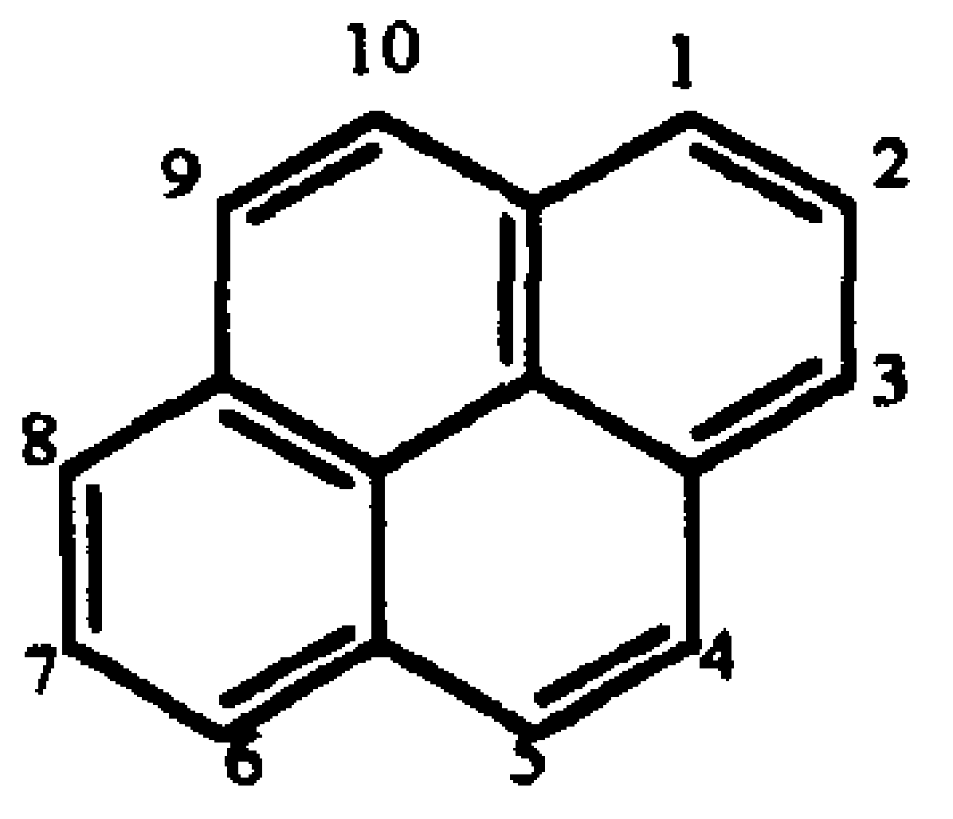
1,2-Benzanthracene



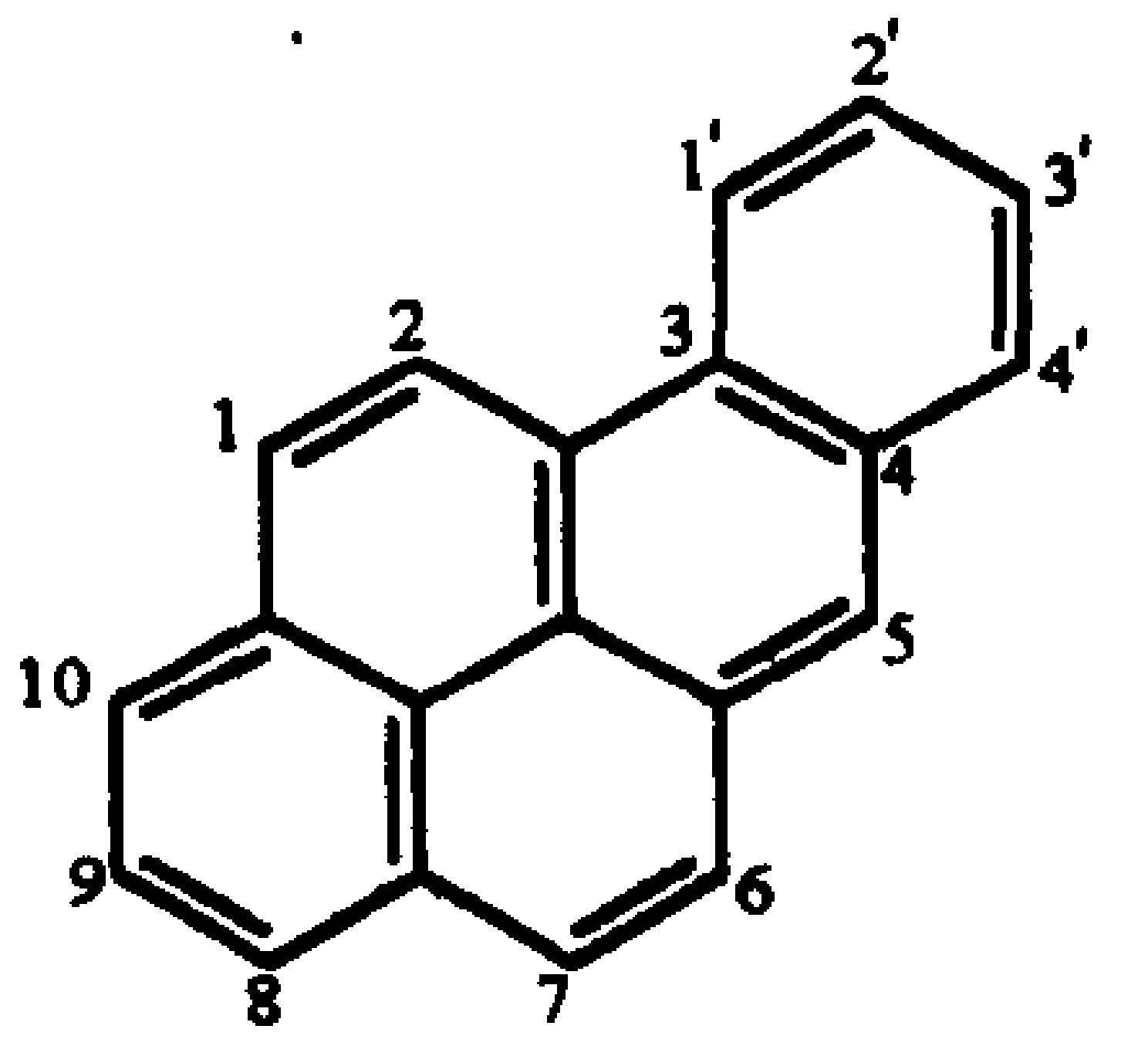
Phenanthrene



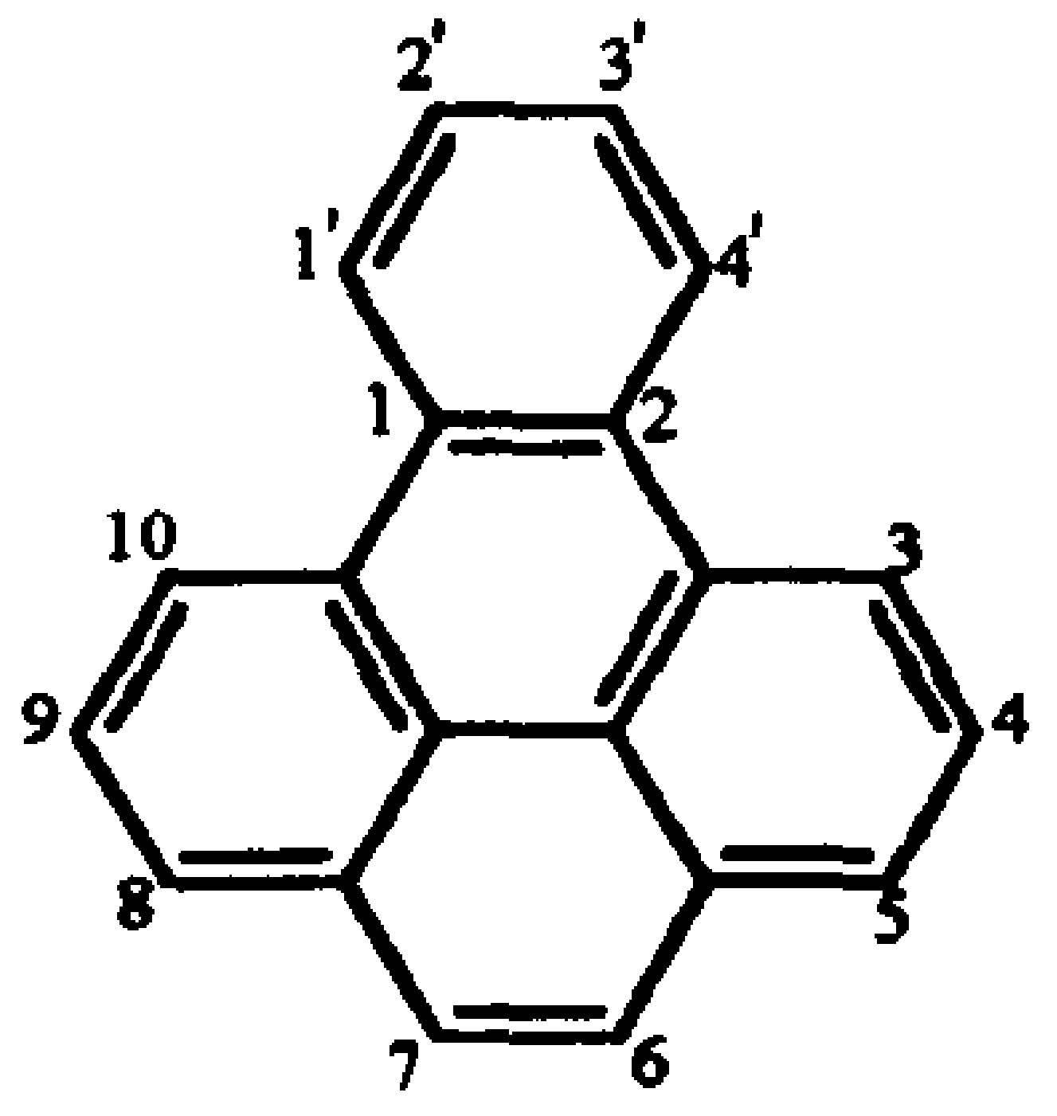
Benzo(a)phenanthrene
(1,2-benzophenanthrene, Chrysene)



Pyrene



3,4-Benzopyrene or Benzo (a) pyrene



1,2-Benzopyrene or Benzo(e)pyrene

**Figure 2.1 Structure of some polynuclear aromatic hydrocarbons (according to rule of IUPAC)**

Table 2.4. Physiological Response to Polynuclear Aromatic

| Material | Route of entry | Species | Dose / concentration | Effect |
|---|---|---|---|---|
| Phenanthrene | Oral | Mouse | 700 mg/kg | $LD_{50}$ |
| Benzo(a)Pyrene | Subcutaneous | Rat | 50 mg/kg | $LD_{50}$ |
| Anthracene | Oral | Rat | 4.5 g over >1000 days | No tumours |
| 1,2-Benzophenanthrene (chrysene) | Dermal | Mouse | 0.3-7.5% in benzene or mouse fat | 2 of 5 samples tested weakly tumorigenic when dissolved in benzene |
| 1,2-Benzanthracene | Oral<br>SC | Rat<br>Mouse | 200 mg/s.d./310 days obs.<br>0.05mg/isc × 22-28 mo obs.<br>0.02 mg/isi × 22-28 mo obs<br>1.0 mg/isi × 22-28 mo ob<br>5.0 mg/isi × 22-28 mo obs | No mammary tumours<br>11% with tumours after 315 days<br>24% with tumours after 346 days<br>34% with tumours after 298 days<br>55% with tumours after 299 days, dose-action related |
| Phenanthrene | Oral<br>Dermal<br>Subcutaneous | Rat<br>Mouse<br>Mouse | 1 ml/s.d./310 days obs.<br>0.5%×m 6 wk/tot. 20 appln.<br>5mg/appln. × 372 days | No mammary tumours<br>Slight increase over control in benign tumours<br>No tumorigenic effects |
| Benzo(a)Pyrene | Oral | Rat<br>Mouse | 1 mg/g food during pregnancy<br>100 mg/s.d. × > 50 days obs.<br>0.15 mg/g food × 80-140 days | Teratogenic effects of stillbirths<br>Mammary tumours in 8 of 9 rats<br>Gastric papillomas, squamous cell carcinomas, pulmonary adenomas treated |

| | | | | |
|---|---|---|---|---|
| Benzo(a)Pyrene | SC | Primate | 10 mg in 0.2 ml olive oil s.d. × 7 mo obs. | offspring<br>One of 2 animals died within 24 hr, the second developed a palpable nodule in 6 mo, at 7 mo measured 30 mo, at 7 mo measured 30 ×40 × 21 mm at injection site<br>sarcoma on heart muscle |
| | Dermal | Mouse | 1% soln.2 × /wk × 200 days | First tumour after 70 days; after 200 days all animals affected |
| | | Rabbit | 0.3% benzene solution 2 × /wk × > 400 days | At 400 days, 1 carcinoma, 10 of 12 animals exhibit skin tumours |
| | SC | Mouse | 0.09 mg/s.d. ×183 days obs. | Tumour yield within statistical range at 78% |
| | | | 4 mg + 0.2 ml carbowax days 11, 13, 15 | Pulmonary adenoma in progeny, general 2.36 adenomas/mouse |
| | | | 4 mg as above + 2 drops | Skin papilloma in 23.6% of |

s.d = single dose isc = intrascapular SC=skin contact

### 2.2.3 Physiological Response

The International Agency for Research on Cancer (IARC) has classified polycyclic aromatic compounds that have been found in vehicle exhausts into three groups 2A, 2B and 3. Group 2A shows evidence of carcinogenity in humans , Group 2B shows evidence of carcinogenicity in animals and Group 3 is unclassified. A significant number of the compounds are in group 2. Diesel exhausts have been classified in Groups 2A and petrol exhaust in Group 2B (46).

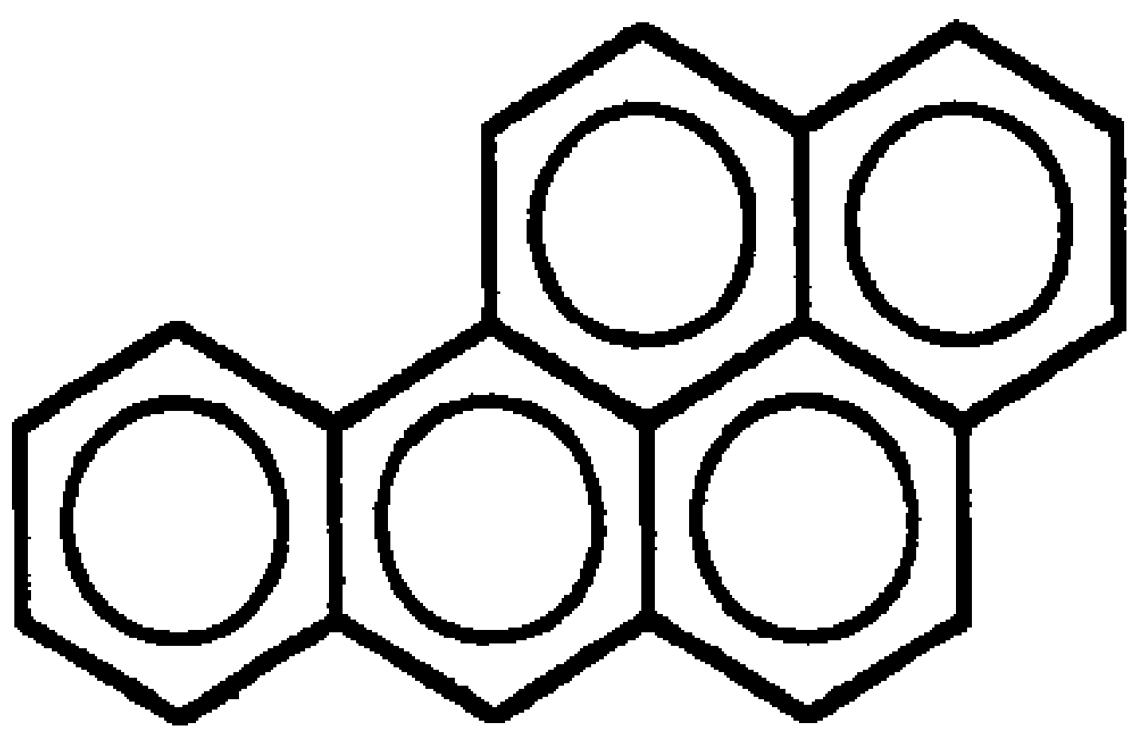
There is still uncertainty about the significance of the carcinogenity of these compounds in people exposed to normal levels of vehicle pollution. A Department of Health study (43) in London in 1987 concluded that animal studies lent support to the possibility of a carcinogenic effect but for humans exposure at a far lower dose there was no positive result.

The possibility that carbon particles without adsorbed organic compounds might be carcinogenic was suggested by Nicula et al (1993). They showed that in rats prolonged exposure to high concentrations of diesel exhaust particles and of organic mutagen poor carbon black particles led to similar increases in prevalence of lung tumours(44). A 1992 report by MAPE (Medical Aspects of Air Pollution Episodes) concluded that carbon particles did not pose a significant threat to health. However, a precautionary approach should be adopted in the light of recently published epidemiological studies and a reduction of particulate emissions is recommended (45).

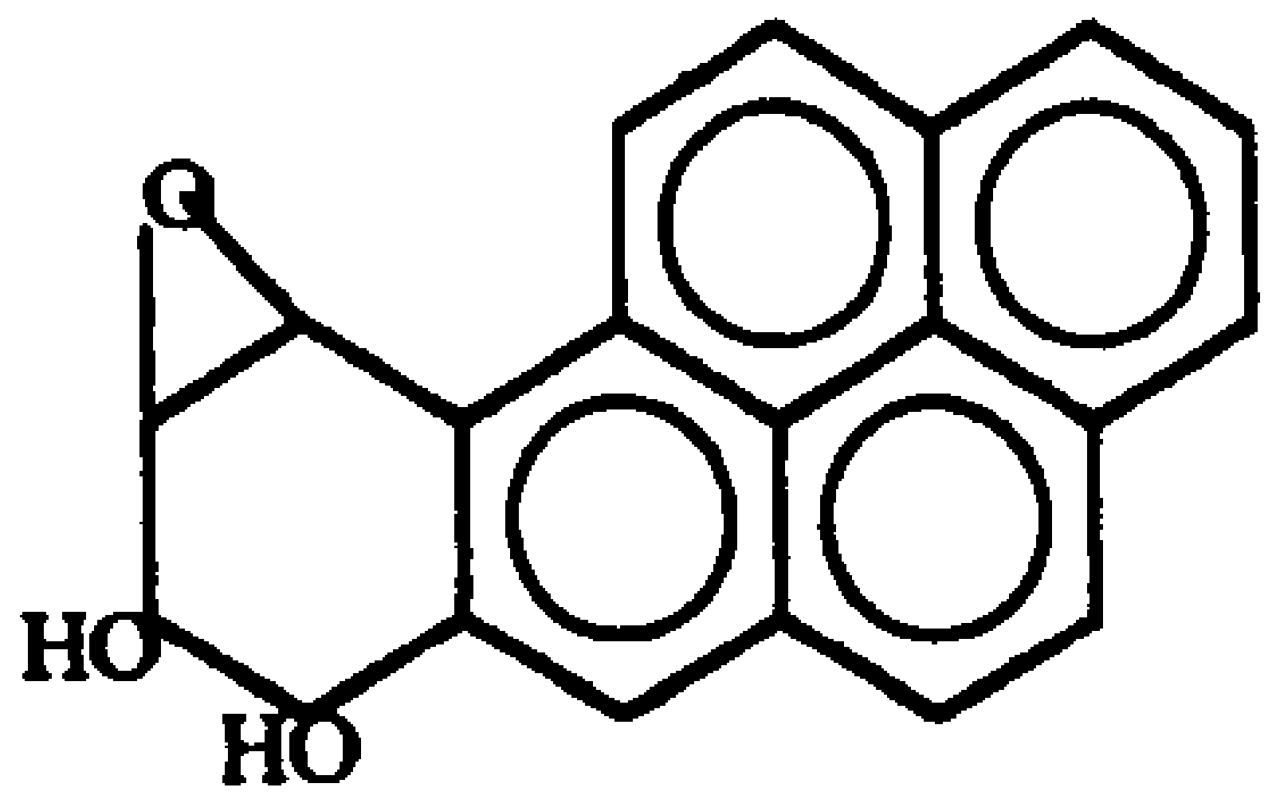
Table 2.3 Classifications of Carcinogenicity of Some particulate Associated Exhaust Pollutants

| Compound | IARC Group |
|---|---|
| Anthracene | 3 |
| Phenanthrene | 3 |
| Fluoranthrene | 3 |
| Pyrene | 3 |
| Benzo(a)anthracene | 2A |
| Chrysene | 3 |
| Benzo(a)pyrene | 2A |
| Benzo(e)pyrene | 3 |
| Benzo(ghi)perylene | 3 |
| Benzo(j+k)fluoranthrene | 2B |
| 2-Nitrofluorene | 2B |

Polycyclic aromatic hydrocarbons are metabolised through epoxides, hydroxides, and their conjugates are solubilized and excreted. Benzo(a)pyrene is the most studied of the polycyclic aromatic hydrocarbons. Some metabolites of PAH compounds, particularly the 7,8-diol-9-epoxide of benzo(a)pyrene are known to cause cancer.



Benzo(a)pyrene



7,8-Diol-9,10-epoxide
of benzo(a)pyrene

## 2.3 Objective of the Research Programme

The purpose of the research described in this thesis is to determine the significance of motor vehicle emission on air pollution. The work was carried out under the following headings:

1. Development of a method for analysis of polycyclic aromatic hydrocarbons by Thermal Desorption and GC-Mass spectrometry.

2. Characterisation of polycyclic aromatic hydrocarbons in ambient air conditions at a site in Uxbridge including quantitative measurement of eight PAHs at local sites using the analytical method developed.

3. Measurement and determination of polycyclic aromatic hydrocarbons (PAH) from vehicle emissions under different engine conditions using the analytical method developed.

4. Development of a method for analysis of volatile organic compounds (VOC) using the Carbotrap system.

5. Determination and measurement of some volatile organic compounds under ambient air conditions at Brunel University campus using the Carbotrap analytical method developed.

6. Evaluation of qualitative and quantitative analysis of volatile organic compounds using samples from vehicle emissions under different starting catalytic conditions, using the Carbotrap analytical method developed.

7. Determination and measurement of some volatile organic compounds under ambient air conditions in Tehran and relating the results to pollution sources, time of day, geographical location and the potential health hazards arising from the pollution.

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# Chapter Three: Sampling and Analytical Methods for Volatile Organic Compounds and Polycyclic Aromatic Hydrocarbons

## 3.1 Introduction

All industrial processes contribute to the pollution of our environment. The greatest man-made contributions to atmospheric pollution are processes of combustion in power generation, in industrial plants, in automobile and aircraft engines, and in domestic heating. Such processes are responsible for the generation of a wide range of pollutants; amongst those pollutants which have received considerable attention in recent years are unburned hydrocarbons and polycyclic aromatic hydrocarbons (PAHs). More recently, interest in this general field has been concentrated on investigations into the identification and measurement of levels for aromatic hydrocarbons. Benzene, a component in unburned hydrocarbons from exhaust, is known to be a carcinogen from epidemiological researches.

In this chapter, the methods of analysis of gases and PAHs are considered and finally some problems in sampling and analysis are illustrated.

## 3.2 Sampling hydrocarbons

When airborne, gases and vapours are in the form of individual molecules and thus tend to diffuse easily into the air and spread rapidly throughout an area. For air sampling purposes the properties of solubility, vapour pressure and reactivity can be exploited in selecting the proper collection procedures. There are two basic methods for collecting integrated samples of gases and vapours: (i) passive sampling; in which the medium is simply exposed to contaminated air , allowing the compounds of interest to passively diffuse through or permeate it and (ii) active sampling that involves a battery-powered pump actively pulling air through an appropriate medium (7). In active sampling, three types of sampler can be used; solid sorbent sampling, impinger sampling and sampling into bags.

### 3.2.1 Solid Sorbent Sampling

Sampling with sorbent tubes is done for analysis in both occupational and environmental exposure. In both cases a pump is used to pull air through the sorbent. The sampling medium can involve different solid sorbents including charcoal, silica gel, tenax, chromosorb, propak and molecular sieve. Solid sorbents are specific for distinct groups of compounds and one sorbent will not work with all compounds Most solid sorbents do not differentiate between compounds during collection so unwanted compounds as well as the target compounds may be collected. On the other hand, because of the wide range of vapour pressure and breakthrough volumes for organic gases of interest there is no one solid sorbent that can collect all gases and vapours simultaneously (7,6). When more than one compound present can be collected on a sorbent tube, the amount of any individual component collected will be reduced. A reduction in sampling time or volume may be required because of the higher overall concentration being presented to the tube.

The biggest concern in collecting material in a sorbent tube is whether breakthrough can occur. Breakthrough occurs when the front section of a tube is saturated with the compounds and enough of it accumulates in the backup section so that it begins to exit the tube with the air stream. Breakthrough is defined as the presence of 25% or more of a contaminant in the rear portion of a sorbent tube . In this situation, it is very likely that sample has been lost through the tubes. Where results indicate breakthrough has occured, the best interpretation is to assume that actual concentrations were higher. When selecting sorbents the potential for water absorption must be considered if high humidity conditions are present at the site to be sampled. Flow rate will also impact on the ability to retain gases and vapours on a sorbent where they are above the optimum flow rate specified for a method. Increasing the flow rate above the optimum level may result in a proportional decrease in the ability of the sorbent to retain contamination. Table 3.1 lists factors affecting the collection behaviour of solid sorbents.(7)

### 3.2.1.1 Charcoal Sorbents

Charcoal is one of the most commonly used sorbents and is useful for sampling a wide variety of organic gases and vapours, including several different compounds at a time. Both the National Institute of Occupational Safety and Health (NIOSH) and Occupational Safety and Health Administration (OSHA) methods specify the use of charcoal tubes for a wide variety of organic compounds.

Charcoal can be derived from a variety of carbon-containing materials, but most of the charcoal used for air sampling is coconut- or petroleum-based. The NIOSH recommends coconut charcoal which has a higher capacity than petroleum charcoal for most compounds, although in some cases such as ethylene oxide collection a different type of charcoal is used. Ordinary charcoal is "activated" by steam at 800-900°C, causing it to form a porous structure. Activated charcoal is not useful for sampling certain types of reactive compounds, such as mercaptan and aldehydes, due to its high surface reactivity with these compounds (7,6).

Inorganic compounds, such as ozone, nitrogen dioxide, chlorine, hydrogen sulphide, and sulphur dioxide, react chemically with activated charcoal.

Charcoal tubes have been used for sampling monocyclic aromatic compounds such as benzene , toluene, xylene etc. The most common charcoal tube in use for occupational sampling was designed according to NIOSH recommended specifications to include fabrication of glass tubing 7cm long with a 6-mm outside diameter and a 4-mm internal diameter. The charcoal used is 20/40 mesh-size. A 100-mg front section is separated from a 50-mg backup section by a piece of urethane foam. A second piece of foam sits at the outlet to prevent granules from being sucked out of the tube during sampling. An unused tube will have both ends flame-sealed (5).

Table 3.1 Factors affecting the collection behaviour of solid sorbents.

| Factor | Effects |
|---|---|
| Temperature | Adsorption is reduced at higher temperatures.<br>Increased temperature is proportional to increased breakthrough. Reaction rate are increased at higher temperatures. |
| Humidity | Water vapour is adsorbed by polar sorbents, increasing the likelihood of breakthrough for chemicals. Increased humidity is proportional to increase breakthrough. |
| Flow rate | High sampling flow rate can lead to breakthrough at lower volumes. Volumes vary with type of sorbent. |
| Concentration | Breakthrough capacity increases with increasing concentration of contaminant. |
| Nature of sorbent | Decreases in sorbent particle size are proportional to an increase in sampling efficiency and drop in pressure |
| Size of tube | A doubling of the sorbent volume doubles the concentration required for breakthrough |

Under the sampling conditions described in this method, the front bed efficiently traps airborne analytes. The backup bed is monitored to ensure that no compounds have passed through the front bed. Such a breakthrough would indicate a possible sample loss and, therefore, would nullify sampling (5).

### 3.2.1.2 Silica gel

Silica gel is an amorphous form of hydrated silica derived from the interaction of sodium silicate and sulphuric acid. It is the adsorbent recommended for collecting alkyl and aryl organic amines, such as aniline and o-toluidine 2-dibutylaminoethanol, 2-diethylaminoethanol, 2,4-xylidine, dimethylacetamide (7,5). Silica gel shows an increase in breakthrough capacity with increasing humidity and for this reason under high humidity conditions sample will be lost due to saturation with water vapour. The ability of silica gel to absorb water vapour and displace collected components is its chief disadvantage. Some methods specify that silica gel should be washed to rid it of any impurities. Washing may be achieved using distilled water or in some cases inorganic acids.

### 3.2.1.3 Tenax

Tenax is a polymer of 2,6-diphenyl-p-phenylene oxide and can be used to collect organic bases, neutral compounds, and high boiling compounds. Tenax GC has a high thermal stability, being able to withstand temperatures of up to 350°C, which permits it to be used for thermal desorption. Tenax reacts with strong oxidizing agents such as chlorine, ozone, nitrogen oxides and sulphur oxides, to form benzaldehyde, acetophenone, and phenol.

Tenax must be conditioned before use and recommended treatments vary from a simple heat treatment, to a Soxhlet extraction with mixed methanol and n.pentane, followed by vacuum drying for 3-5 hours at 110°C and heating the product for1 hour at 170°C under a stream of inert gas.

Sampling volatile organic compounds such as benzene, toluene etc with Tenax is recommended by EPA (6,11).

### 3.2.1.4 Porapak

Porapaks are a group of porous polymers that exhibit a wide range of polarity. Porapaks include modified polystyrenes with various polar co-polymers added to adjust the polarity of the products. The least polar member, Porapak P, is used in gas chromatography columns, and the most polar, Porapak T, can separate water and formaldehyde (7). Sampling from acetone cyanohydrin in air with Porapak is recommended by NIOSH (8).

#### 3.2.1.5 Chromosorbs

The Chromosorbs include copolymers of divinylbenzene with styrene or acrylonitrile, cross linked polystyrenes, polyacrylics and a fluorocarbon (Chromosorb T). Chromosorb 101 is the least polar and chromosorb 104 is the most polar. Chromosorb 106 is a cross linked polystyrene porous polymer that has been used to sample nitromethane and 2-nitropropane according to NIOSH methods.

#### 3.2.1.6 Molecular Sieve

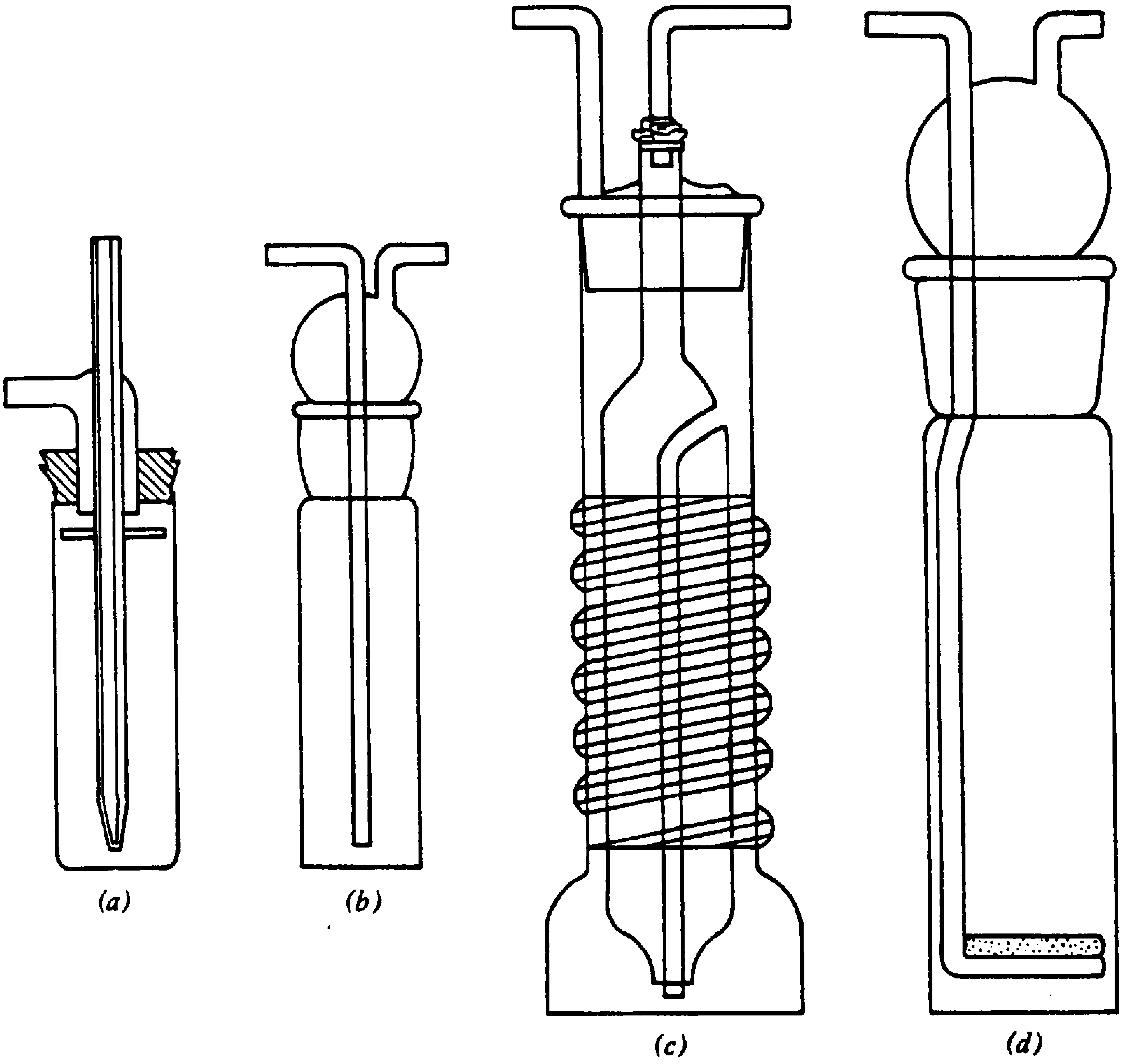
Molecular sieves are inorganic adsorbents and are a group of aluminosilicates of structure consisting of interconnecting networks of silica and alumina tetrahedra. These are made up four oxygen atoms surrounding a silicon or aluminium atom; the electronic charge is balanced by the presence of a suitable cations, such as sodium or potassium. The limiting factor with molecular sieve is humidity. Sampling of benzene, toluene with molecular sieves is recommended in the EPA method TO-2 (11).

### 3.2.2 Impingers

The basic design of the all-glass midget impinger was developed in 1944. Originally the impinger was used primarily for collecting aerosols, especially for particle sizing, but its current application is for gas and vapour sampling. The function of an impinger is to provide sufficient contact between the sampled air and a liquid surface to provide complete absorption of the gas or vapour.

Impingers are usually made of glass with an inlet tube connected to a stopper fitted into a graduated vial such that the inlet tube rests slightly above the vial bottom. A measured volume of absorber liquid is placed in the vial, the stopper inlet is put in place, and the unit is then connected to a pump by flexible tubing. When the pump is turned on, the contaminated air is channeled down through the liquid at a right angle to the bottom of the vial. The air stream then impinges against the vial bottom, mixing the air with the absorber liquid; so that the necessary air-to-liquid contact is achieved by agitation (1,7,12) . EPA recommend the use of impingers for sampling aldehydes and ketones in method TO5. In this method ambient air is drawn through a impinger containing 2,4-

dinitrophenylhydrazine (DNPH reagent) and isooctane over a 2-hour sampling period.Aldehydes and ketones readily form stable 2,4-DNPH. After sampling, the impinger solution is returned to a laboratory for analysis. Reversed phase HPLC-UV (high performance liquid chromatography with an ultraviolet detector)analysis at 370nm is used to analyse for DNPH derivatives (13).



### 3.2.3 Sampling into bags

Bags come in different size, shapes and material. Most bags have a valve to allow for filling using a pump and a septum for injection using springs. The septum can be made of silicone or neoprene rubber and valves commonly are nickel-plated or of stainless steel. Stainless steel valves are less likely to corrode than those that are nickel-plated. Fittings on the bags are often multipurpose. For example, the fitting may contain both a syringe port with Teflon-coated septum and a hose connection. The fitting also acts as a shut off valve for the hose connection (7).

### 3.3 Analysis of monocyclic aromatic Compounds with NIOSH method

In the NIOSH method, an adsorbent tube containing 150mg of coconut charcoal, divided into a 100mg front bed and a 50mg backup bed, is recommended for collecting aromatic hydrocarbons. Under the sampling conditions described in the method, the front bed efficiently traps the airborne analytes. The backup bed is monitored to ensure that no analyte has passed through the front bed. Such breakthrough would indicate possible sample loss and, therefore, would make the sample invalid (8).

To sample airborne vapours, the sealed ends of the adsorbent tube are broken. The sampling device is placed in a holder and then the holder is connected to the inlet pipe of the battery-operated pump. A flow meter is set between the pump and sampler to measure air flow. When sampling is finished, the devices are removed from the holder and caps put on the ends.

After sampling the adsorbent beds are removed, the front bed is sealed and the backup placed in separate vials. The vials typically recommended for desorption have a screw top with a hole in the centre and a Teflon-coated septum to permit sampling with a syringe.

High purity $CS_2$ solvents were used for desorbing the collected gases. Pure $_2CS$ is injected to a GC and peak areas for impurities are obtained. 1ml of pure $CS_2$ is added to the absorbed material through a septum in the vial, 1 µl of this solvent is injected in the GC column. The compound's peak area is measured. To correct for benzene impurity in the solvent, the benzene peak area is subtracted from this experimental area (5,8).

The backup bed of each tube analyses in the same manner and if the total amount of the sampled compound in the backup section is greater than 10% of the total amount in the front section, samples may have been lost due to breakthrough consequently the results are invalid (8).

### 3.4 Analysis of monocyclic aromatic hydrocarbons using the EPA method

In this method ambient air is drawn through a cartridge containing ~1-2 grams of Tenax and volatile organic compounds are trapped on the resin while highly volatile organic compounds and most inorganic atmospheric constituents pass through the Tenax cartridge. The cartridge is then transferred to the laboratory for analysis.

For analysis the cartridge is placed in a heated chamber and purged with an inert gas. The inert gas transfers the volatile organic compounds from the cartridge into a cold trap and subsequently into the front of the GC column which is held at a low temperature. The GC column temperature is then increased (temperature programmed) and the components eluting from the column are identified and quantitated by mass spectrometry. Component identification is normally accomplished, using a library search routine, on the basis of the GC retention time and mass spectral characteristics (11).

### Possible sampling using Carbotrap

Sorbent tubes are the most important samplers for obtaining samples from air.

The Carbotrap is a form of carbon which can be obtained by graphitising, a process that consists of heating carbon at 3000 °C under an inert gas atmosphere and produces polyhedrons of 2000-3000Å size agglomerated by electrostatic forces. This results in a carbon with a very homogeneous surface area of about 100 $m^2/g$ and, unlike active charcoal, has reproducible properties. Graphitised carbon is commercially available as carbopack and Carbotrap. It is stable above 400°C in absence of oxygen, is hydrophobic so that water does not affect its absorptive properties and it exhibits a higher adsorptive capacity than Tenax (6).

It is known that a wide range of compounds can be trapped and desorbed successfully using a Carbotrap.

Although some workers recommend a Carbotrap as a sampler from air as an alternative to other sorbent, there is not an internationally recognized routine method with this sorbent.One of the objectives in the present research is the evaluation of Carbotrap as a sampler and to find out the optimum conditions for sampling from air with this sorbent.

### 3.5 Sampling of PAHs

Most methods for the analyses of organic particulates in ambient air depend on filter collection and some form of chromatographic separation. EPA suggest the use of a glass fibre filter. Glass fibre filters offer comparatively low resistance to air flow, their use is recommended when a large volume of aerosol has to be sampled (13,14,15)

Filters in plastic cassettes are the most common media used to collect occupational aerosols. For a given aerosol and a given filter, the collection efficiency varies with the gas velocity and particle size. With an appropriately chosen filter, the air will pass through, leaving the particulates behind (7). Filters are weighed before and after sampling to determine the weight of entrained particulate material. Prior to collection the filter is conditioned by allowing it to equilibrate over 24 hr in a desiccator filled with Drierite or in a constant humidity-room (45% relative humidity) and weighed to the nearest 0.01 mg before use. If the relative humidity in the weighing area is high (>50%), it is necessary to equilibrate the filter for about 24 hrs in a desiccator containing a saturated solution of calcium nitrate to maintain a rough humidity control at approximately 50%.

It has been suspected that the low volatility of PAHs might prevent their complete retention by particulate filter techniques and may also cause loss after collection (14).

After collection the filters are placed in petri dishes and allowed to equilibrate in the dark under the same condition as those under which the filter was initially weighed. For longer term storage the petri dishes are wrapped with aluminum foil and stored at a temperature below 0°C. The use of sub-ambient temperature for prolonged storage is recommended in order to minimize losses due to evaporation and degradation.

Loss due to evaporation of the more volatile component of the particulates has been observed in an experiment in which the weights of diesel-particulate laden filters stored at room temperature were monitored for a 17-day period beginning within hours of collection. A continual decrease in weight occured throughout the monitoring period, leading to a weight loss of 4.8% of the original sample after 17 days (13).

Butterfield et. al. used solid cyclodextrin to replace glass filter for sampling PAH.

Because solid cyclodextrin complexes with vapour phase PAHs and thereby reduces their volatility. Fluorescence and absorbance spectroscopies can be used to examine the variables that affect the formation of the PAH complexes with cyclodextrin. The use of this system for improved ambient air sampling has been proposed (3).

Optimisation and standardisation of sampling procedures is complicated by the number of experimental parameters which must be considered. These include: the filter type and temperature, filter dimensions, filter weighing conditions (temperature and relative humidity), particle size fractions to be collected, flow rates, collecting time and efficiency. Other factors which can have a pronounced effect on the reproducibility of sampling are the chemical reactivity and the stability of the PAH is during collection and the distribution of PAH between particulate and the solid filter gas phase (7).

### 3.6 Extraction procedures for PAH release from filter

PAHs are soluble in many organic solvents including cyclo-hexane, benzene, chloroform, acetone and alcohols, but the efficiency of any solvent in the extraction of PAH is largely dependent on the nature of the particulate matter under investigation. So strongly are PAHs adsorbed by carbon black, for example that many hours are required to extract airborne particulates into solvents. There is by no means agreement on the length of time for complete extraction, and the various workers in the field have suggested 12 h and 20-30h using cyclohexane. The Intersociety Committee has adopted 24h extraction with cyclohexane and 6-8 h with benzene. A quantitative investigation into the extraction efficiencies of cyclohexane and benzene has been carried out, in which 76% and 95% recoveries of benzo(a)pyrene from enriched air samples were obtained after 6 hour refluxing.

Apart from Soxhlet extraction, ultrasonic vibration is also being increasingly used for release of PAHs as it seems to afford higher recoveries (13).

### 3.7 Analysis of PAHs

Two basic methods have been suggested for analysis of polycyclic aromatic hydrocarbons, gas chromatography or gas chromatography-mass spectrometry and high performance liquid chromatography.

As GC techniques become more refined and generally accepted, due to the superior separation and resolution potential of modern capillary columns, they have gained greater acceptibility, especially in the analysis of PAH is form car exhaust emissions and air particulates. In combination with an FID-detector, or coupled to mass spectrometry, the technique must now be considered the method of first choice for a reliable and reproducible determination of PAH traces in a wide range of matrices.

A simultaneous determination method for polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs (NPAHs) in airborne particulates has been developed by Murahashi-T et al. Airborne particulates were extracted with benzene and ethanol, separated by liquid-liquid partition, then the resultant solution injected into an HPLC system. The mobile phases used were acetonitrile/water (75:25) for PAHs, and acetonitrile/imidazole $HClO_4$ buffer (1 : 1) for NPAHs. By this method, four NPAHs (1,3-, 1,6-, 1,8-dinitropyrenes and 1-nitropyrene) and eight PAHs (fluoranthene, pyrene, benzo(a)pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene and corocene) in sub-milligram quantities of airborne particulate have been determined (2).

A method for the determination of polycyclic aromatic hydrocarbons by high-performance liquid choromatography using a fluorometric detector has been developed. A Hypersil Green PAH column and a program of nine excitation and emission wavelength pairs are used as a detection system. The mobile phase is a linear gradient elution using acetonitrile-water. The relative standard deviations are in the range of 1-10% at concentration levels of 0.02-0.06 ng/µl(n=3). The detection limits are between 0.012 pg/ µl for fluoranthene and 0.45 pg/µl for naphthalene. The method has been applied to the determination of polycyclic aromatic hydrocarbons in particulate air samples from Madrid (4).

### 3.8 Problems with the extraction

The most important problem with the analysis of polycyclic aromatic hydrocarbons is the

Soxhlet extraction of PAHs from the filter because during extraction some of the PAHs evaporate and their recovery decreases with time during the extraction. The length of time (12-24 hr) required for Soxhlet extraction is also a problem in the analysis. Extraction with a solvent is not a sensitive method because only a very small fraction of the final solution can be used for chromatographic analysis. This means that most of the gain in sensitivity achieved by initial concentration is lost in the final dilution. For example, the final volume of the solvent may be 2 ml of which not more than 5 microlitres would be injected into the gas chromatograp resulting in about one thousand fold total dilution.

In the present work it was therfore found necessary to develop a thermal desorption method which is described in chapter 4.

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# Chapter 4: Development of a Thermal Desorption Method for the Analysis of Polycyclic Aromatic Hydrocarbons

## 4.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) occur in particles or in the vapour phase and are often emitted into the atmosphere by way of combustion processes. For example, a partial combustion of fuel in an internal combustion engine results in the formation of trace amounts of PAH compounds. Some of these compounds have been classified as carcinogenic materials by the International Agency for Research on Cancer. Due to their wide range of vapour pressures, some atmospheric PAHs exist exclusively in the gas phase while others are adsorbed on particulate matter. The volatility of these organic compounds controls their transport in the workplace and in the environment in general. PAHs contribute to the pollution inside houses especially in the summer season when windows are open. The measurement of PAHs is important for reasons of health.

Several different sampling and analytical methods for the determination of PAHs in air have been described. The most common sampling method involves pumping the air stream through a sample device (active sampling) with a glass fibre filter often being used to permit high flow rates. Compounds are then extracted from the filter with a solvent and the PAHs are usually analysed by high performance liquid chromatography with a fluorescence detector, or gas chromatography with a flame ionisation detector, or gas chromatography-mass spectrometry (27,28,29).

Due to their volatility, losses of PAHs during extraction are unavoidable and extraction with solvents is not a sensitive method because it dilutes the sample. Other disadvantages of extraction with solvents are the potential toxicity of the solvent and the instability of samples during storage. Recovery of PAHs by any extraction method is about 80 percent (27,28,29) and as a consequence there can be failure to detect some compounds.

The objectives of the work described in this chapter:

1) The development of a procedure for the determination of PAH in air and car exhausts that is more sensitive and gives a higher recovery of analyte than the extraction method. Details of the method developed, which involves a Thermal Desorption apparatus and Carbotrap tubes, are given in section 4.3.

2) The qualitative determination of high molecular weight hydrocarbons in car exhausts.

3) The measurement of the concentrations in particulates of eight polycyclic aromatic hydrocarbons found in car exhausts in diesel and internal combustion engines.

4) The measurement of the concentrations of some PAHs in buildings.

## 4.2 Instrumentation

To develop a method for sampling and analysis of PAHs in air the following pieces of apparatus were used:

1. Sampling pump
2. Flow meter
3. Glass fibre filter
4. Carbotrap 370
5. Thermal Desorption Unit
6. Gas Chromatograph-Mass Spectrometer
7. Weather Monitor

### 4.2.1 Sampling pump

A sampling pump from Charles Austen company, Model Dyma MI 1A, was used to obtain samples of particulates. The pump was connected to the filter holder with a Teflon tube. Calibration and adjustment of the sampling flow rates were achieved by using a flow meter connected between the sampler and the pump. The flow rate of the pump was 2 litre/minute.

### 4.2.2 Flow meter

The sampling pump was calibrated using a flow meter with capacity of 1-5 litre/minute. For high performance, the flow meter was calibrated with a soap bubble flow meter.

**Soap bubble**: Soap bubble flow meter utilizes a volumetric laboratory burette whose interior surfaces are wetted with a detergent solution. The volume displacement per unit time (i.e., flow rate) can be determined by measuring the time required for a bubble to pass between two scale markings which enclose a known volume.

$$Flow\ rate = \frac{Volume\ between\ two\ scale\ markings}{time}$$

### 4.2.3 Glass fibre filter

Whatman Quartz microfibre filters with 3.7cm diameter and 0.2 µm pore size were used to obtain samples of particulates in air. The primary fibre filter used was made of fibre glass, through which air passes leaving particles behind on the filter. Because fibre filters offer comparatively low resistance to airflow, their use is recommended when a large volume of aerosol must be sampled. Filters are most often contained in plastic cassettes that have a pad on which the filter can rest and which is connected to the pump with a Teflon tube.

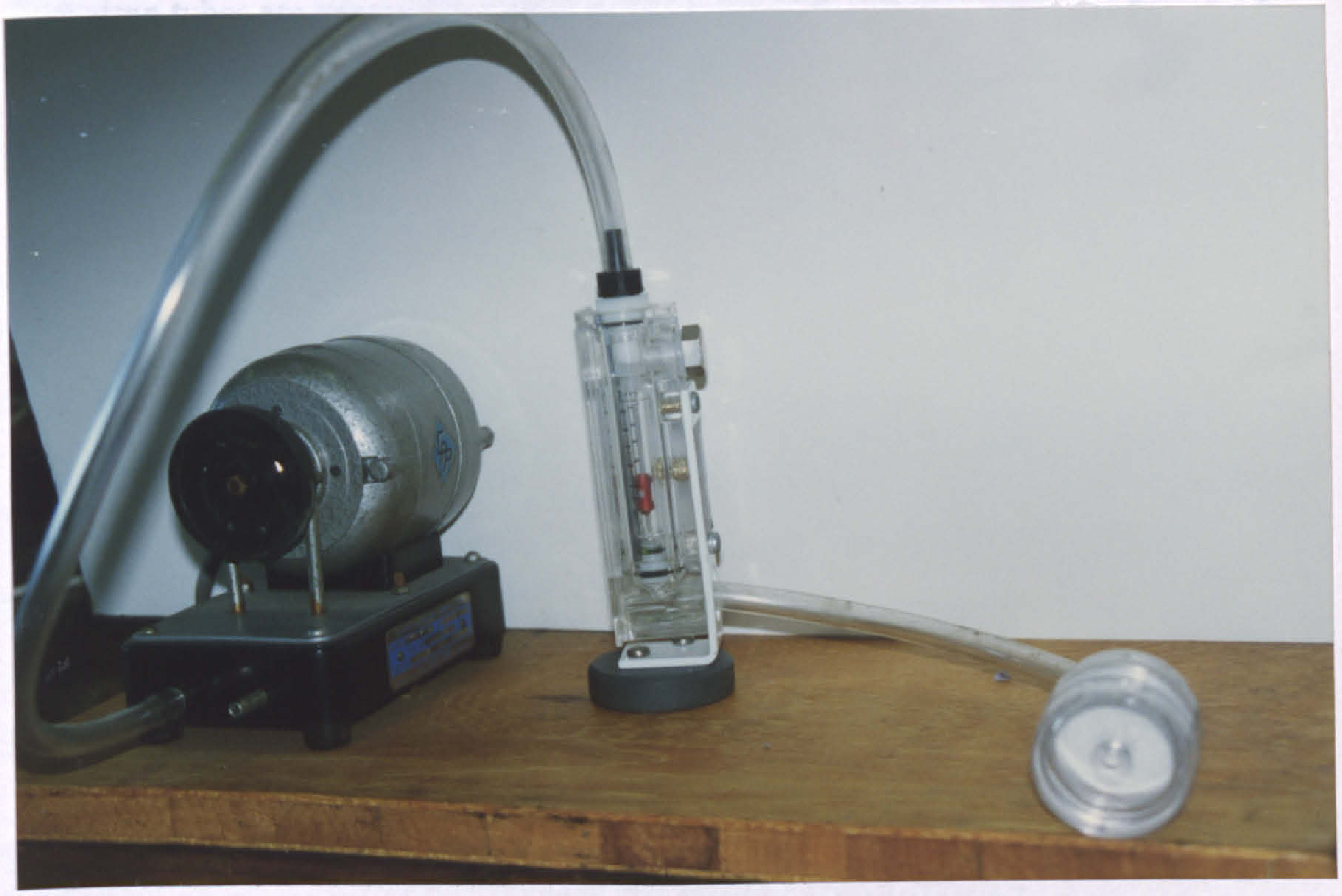


**Fig. 4.1 Sampling pumps and Calibration System**

### 4.2.4 Carbotrap

The Carbotrap is a form of carbon which can be obtained by graphitising, a process that consists of heating carbon at 3000°C under an inert gas atmosphere to produce polyhedrons of 2000-3000Å size agglomerated by electrostatic forces. This results in a carbon with a very homogeneous surface area of about 100 $m^2/g$ and, unlike active charcoal, has reproducible properties. The Carbotrap is stable above 400°C in the absence of oxygen, is hydrophobic so that water does not affect its absorptive properties and it exhibits a higher adsorptive capacity than Tenax (Tenax is explained in chapter 3) (23).

Carbotrap is available in different kinds: Carbotrap 370, 300, 200, 201 etc. The difference between the various Carbotraps is determined by the carbopack contents. These have the designation B,C, F and carbosieve III. Each carbopack has different surface area and traps different molecular sizes of hydrocarbons.

Carbotrap tubes are preconditioned in an oven at 350°C under an inert gas flow for 8 hours before placement in the storage container. Water is related to have a very low breakthrough volume on Carbotrap(23).

#### 4.2.4.1 Carbotrap 370

The Carbotrap 370 used for collecting PAHs desorbed from filters, has three Carbopack B,C and F.

**I) Carbopack B:**

Carbopack B has a surface area of approximately $100 m^2 g^{-1}$ with an excellent trapping ability for a wide variety of organic contaminants with $C_5$ and above (depending on molecular size and shape) both for air sampling and for purge and trap applications.

**II) Carbopack C:**

Carbopack C adsorbents contain a mixture of 20/40 mesh and 60/80 mesh particles. They have an average surface area of approximately $10 m^2 g^{-1}$. This trap has a superior trapping ability for a wide variety of (depending upon molecular size and shape) organic contaminants with 12 or more carbons in sampling and in purge and trap applications (2).

**III) Carbopack F**:

Carbopack F has a surface area of $5 m^2 g^{-1}$ and can trap organic contaminants with 20 or more carbon atoms. The relatively small surface area used permits the adsorbents to effectively adsorb and release high molecular weight airborne contaminants.

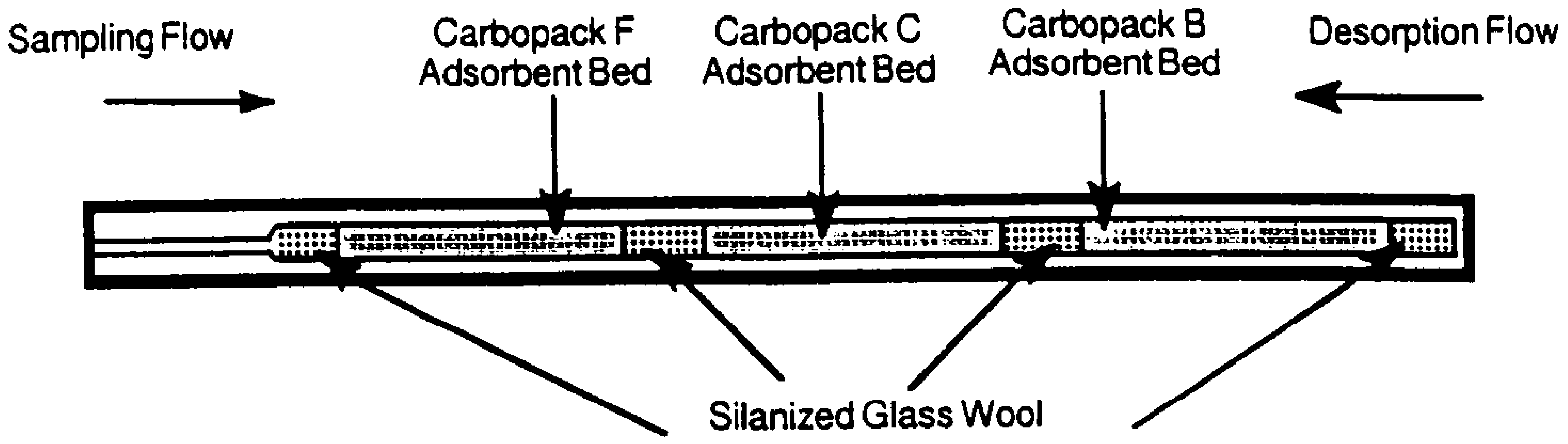


**Fig. 4.2 Carbotrap 370 for focussing of PAHs from filter**

### 4.2.5 Thermal Desorption

As with most new techniques, early attempts using Thermal Desorption were made with laboratory constructed equipment. This usually consisted of a simple heater that surrounded the adsorption tube and a means for passing the carrier gas through the tube, thus sweeping desorbed materials into the chromatograph.

The Supelco Thermal Desorption apparatus is a more advanced design than the earlier single stage units. The desorption oven is designed to heat very quickly (15°C per sec.) to a maximum temperature (400°C) and to produce a sharp injection of desorbed vapour into a gas chromatograph. The desorption oven can be temperature-programmed to enable separation of different volatile fractions. A rapid cooling facility is included to reduce waiting time between analyses.

The gas flow arrangement consists of two separate flow paths A and B, either path may be selected by a manual switching valve (26).

Flow Path A (Figure 4.3)

With the valve handle in the load position, the sample tube desorption chamber is part of flow path A. Through this path, a sample can be transferred from the desorption chamber to the trapping port on the left side of the pneumatic module. The flow should be set with a tube in the trapping port, since changes in system pressure will cause flow changes when the needle valve is used for regulation. Flow path A is primarily used in sample preparation applications such as;

1.**Purification of the sample**. Before samples from air are analysed, the Carbotrap must be placed in the desorption chamber, and kept at a temperature of 350°C for 15 minutes. All compounds released from the Carbotrap are collected.

2.**Sample Focussing**. Samples collected in a 4mm internal diameter (ID) adsorbent tube are thermally desorbed to a 2mm or 1mm ID tube. The decrease in tube internal volume improves desorption efficiency when the sample is subsequently desorbed to the GC column.

3.**Gaseous and Solvent-Based Samples** Gaseous or liquid samples are injected into an empty tube in the tube desorption chamber and are swept onto an adsorbent tube in the trapping port.

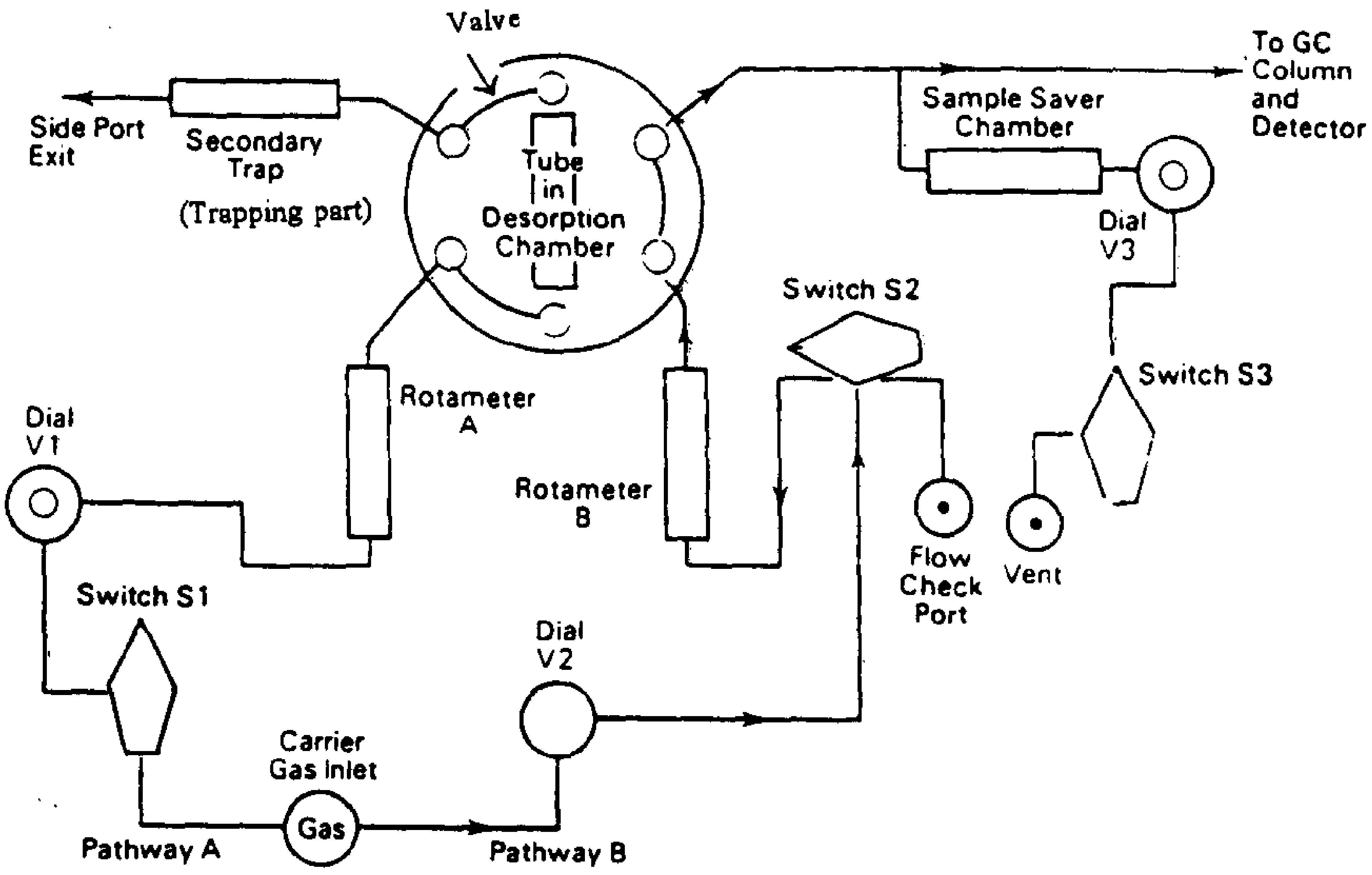
Flow path B (Figure 4.3)

With the valve handle in the heat position, the tube desorption chamber is part of flow path B. Through this path, a sample is transferred from an adsorbent tube to an analytical column. A splitter T-piece between the valve and the column enables the flow to split between a sample saver chamber or vent and the GC column. The amount of a sample diverted from the column is a direct ratio of the split flow to the column flow (26).

In the stand- by position the desorption oven is by-passed and the correct carrier gas flow is maintained through the GC column: when desorption is needed the gas passes through the heated adsorption tube and into the column via a heated transfer line (26).

1. **Dual flow pathway**. The left pathway shown in figure 4.3 followed when to desorb

Valve Handle In Prep (Load) Position



Valve Handle In Desorb (Heat) Position

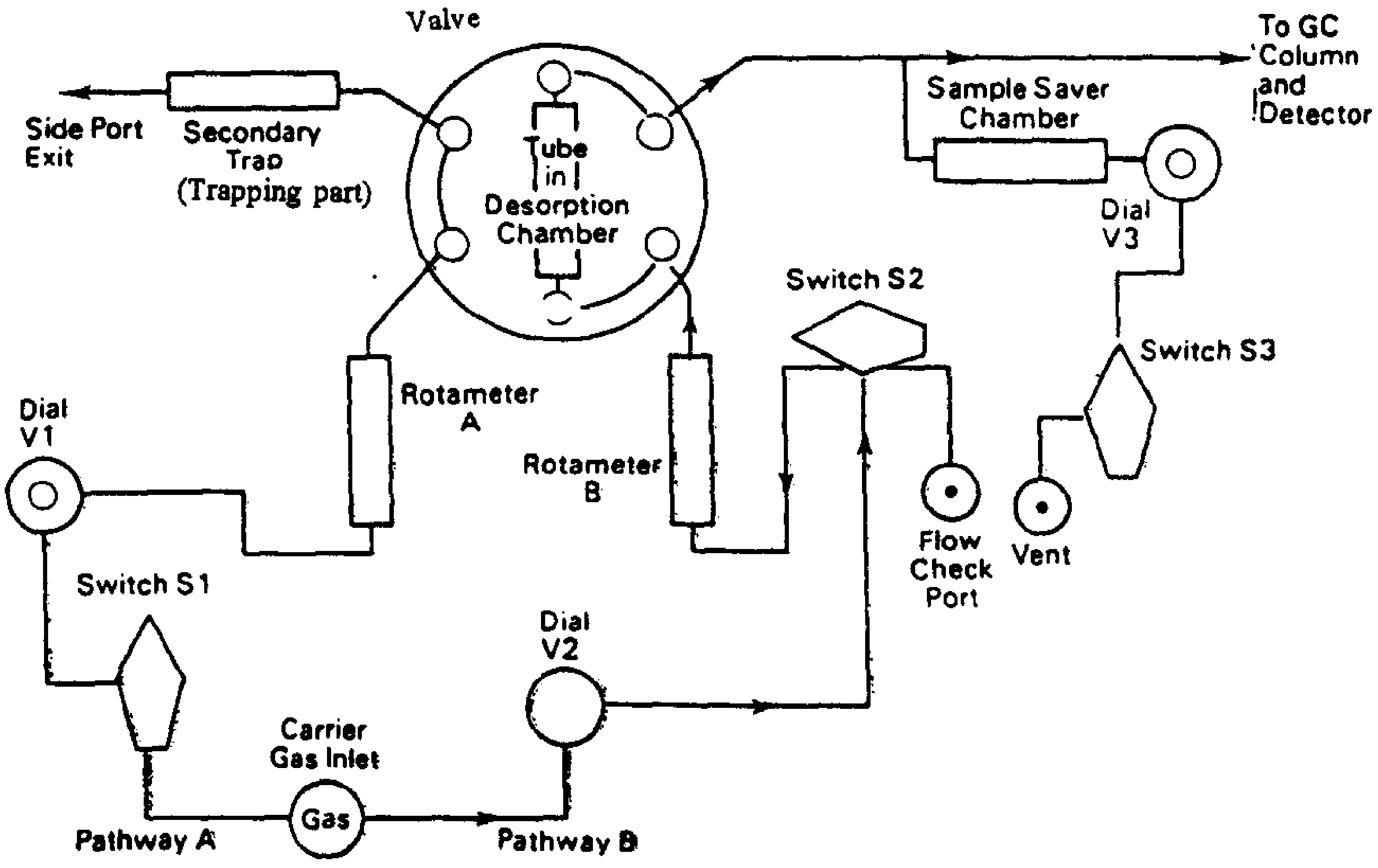


**Figure 4.3 Flow paths through the pneumatic models (a)Valve handle in preparation (load) position (b) Valve handle in desorption (heat) position**

a sample from a large ID adsorbent tube is desorbed on to a narrow ID tube in the trapping port, (for more efficient delivery) and subsequently pass to the GC column. This flow pathway can also be followed to thermally extract components of a solid sample and deliver them to an adsorbent tube in the trapping port. This pathway leads samples to the chromatography column.

2. **Accurate, ballistic heating** : Samples are rapidly heated (e.g. 30°C to 400°C in 26 seconds ) and reproducibly delivered to the analytical column for sharp, symmetrical peaks. Highly accurate temperature control allows reliable thermal fractionation.

3. **Trapping port**. The trapping port is the part of Thermal Desorption Unit that focusses compounds from a wide bore adsorbent to a narrow bore tube for better chromatography.

3. **Sample saver chamber.** The thermal desorption unit's sample saver/splitter feature enables a sample to be divided and to vent to the atmosphere the portion that does not pass through the GC column or recover a sample for a second analysis.

## 4.2.6 GC-Mass Spectrometry

A Fisons MD800 GC- Mass Spectrometer with a 30 m × 0.25mm, 0.25μm film capillary column was used for the identification of polycyclic aromatic hydrocarbons. This column was coated with poly (5%diphenyl/ 95%dimethyl siloxane) and The upper usable temperature limit for this column is 320°C. The separation of the hydrocarbons was achieved by GC and each component was scanned in the Mass Spectrometer as it eluted from the column. The software of the spectrometer was used to obtained a chromatogram from the total ion current. Each peak in the chromatogram was identified by automatically comparing the MS scan with those in a library data base.

### 4.2.7 Weather Monitor

A weather monitor from Davis company was used for measurement of temperature, humidity, barometric pressure, wind speed and wind direction. This apparatus was connected to a sensor for measurement of temperature and barometric pressure, and connected to an anemometer for measurement of wind speed and wind direction. The apparatus was located on the roof of the chemistry department and the results logged daily.

**Fig. 4.4 GC- Mass-spectrometer linked to Thermal Desorption Unit**

## 4.3 Extraction of PAHs from Filter by Thermal Desorption

### 4.3.1 Calibration of Thermal Desorption with Mass Spectrometry

The GC with Thermal Desorption was calibrated over a period of one month by injection of specified amounts of compounds under different flow conditions of inert gas (helium) and different temperature programmes for the column.

The results have shown that the optimum temperature program for the column is to start at 70°C and increase the temperature to 300°C at the rate to 7°C/minute. The best flow rate of inert gas was found to be between 2-3.5ml/min; increasing the flow rate to more than 5ml/minute causes damage to the GC-Mass Spectrometer.

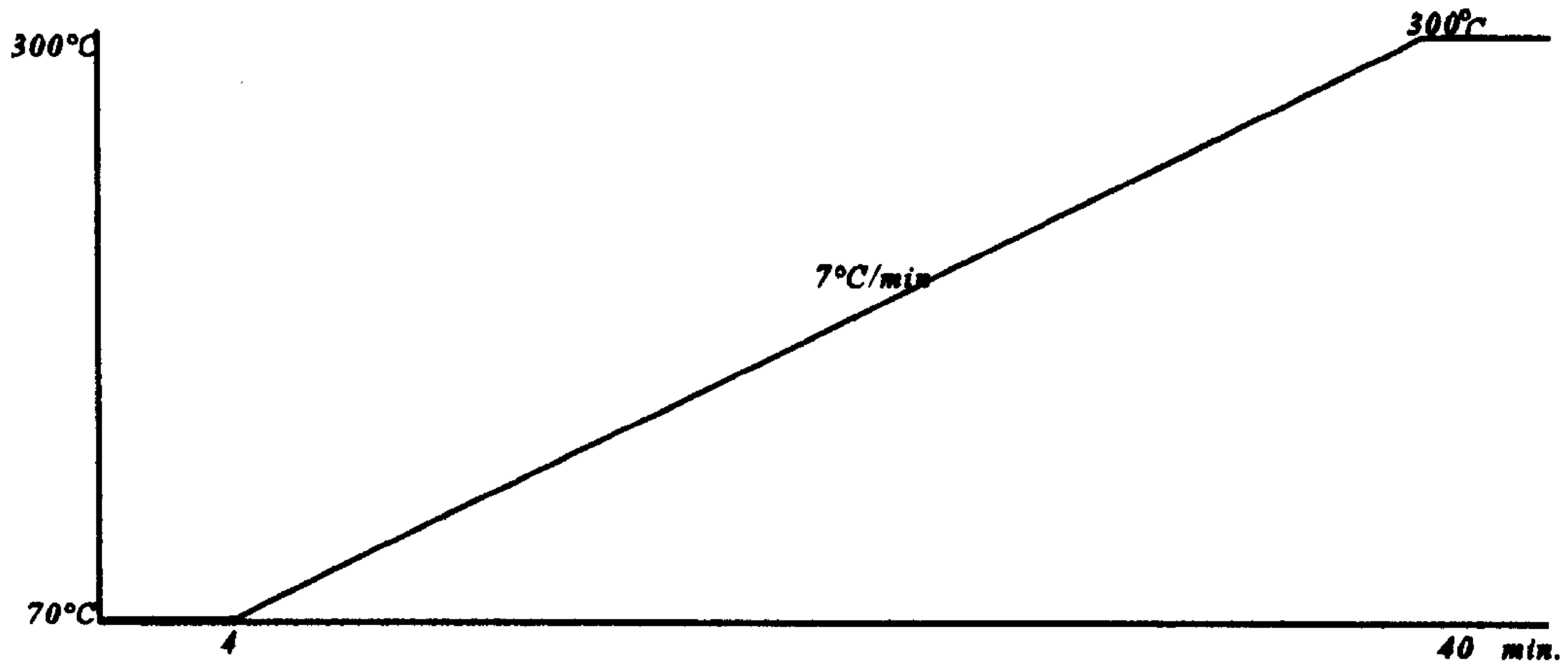


*Fig. 4.5 Temperature program for measurement of polycyclic aromatic hydrocarbons*

### 4.3.2 Evaluation of Carbotrap for focussing

4.3.2.1 Selection of Carbotrap

The best Carbotrap for focussing was determined by the transfer of 1µl of benzo(a)pyrene and chrysene to a 2mm Carbotrap 300, Carbotrap 370 and Carbotrap 200 separately. The results shown in Table 4.1 and indicate that Carbotrap 370 has best recovery for focussing because all of the compounds transfer to GC-MS over a period of 15-20 minutes at a temperature of 310-340°C whereas PAHs stay in Carbotrap 300. Complete removal of PAHs from Carbotrap 300 requires many hours before reconditioning is achieved. One part of the Carbotrap 300 is Carbosieve-III which has a molecular area about 800m$^2$/g for trapping small molecules($C_2$-$C_8$). Use of Carbotrap 300 for focussing PAHs causes large molecules to be strongly absorbed hence they are difficult to desorb. (ie slow reconditioning).

Table 4.1 Amount of benzo(a)pyrene recovery in different Carbotrap

| **Type of Carbotrap** | **Injection volume** | **Recovery (%)** | **Problem** |
|---|---|---|---|
| Carbotrap 300 | 1 μl | 40 | Compounds stay in Carbotrap and interfere with next injection |
| Carbotrap 370 | 1 μl | 95-102 | |
| Carbotrap 200 | 1 μl | 80 | |

#### 4.3.2.2 The importance of Carbotrap focussing

It is necessary to focus compounds from a filter to a Carbotrap because when samples are transferred to the GC-Mass Spectrometer without focussing they can cause the following problems:

1) Injection of soot samples to GC-Mass Spectrometer (without focussing) causes the transfer of some compounds such as CO, $CO_2$, $NO_X$ to GC-Mass Spectrometer during adsorption and this in turn increases the baseline of the chromatogram..

2)The extraction of PAHs from samples with focussing takes 15-20 minutes whereas direct injection of the filters (without Carbotrap) to GC-MS takes a maximum of 9 minutes, which is not long enough to extract all of the components of the samples.

### 4.3.3 Determination of optimum conditions for Thermal Desorption

#### 4.3.3.1 Determination of optimum flow rate for preparation

The optimum flow rate was determined by injection of 1 μl benzo(a)pyrene and chrysene respectively to a Carbotrap at different flow rates. Results Table 4.2 and Figure 4.6 show the % recovery compared with directly injected ie. non-focussed sample. An optimum flow rate is 12-16 ml/minute is indicated.

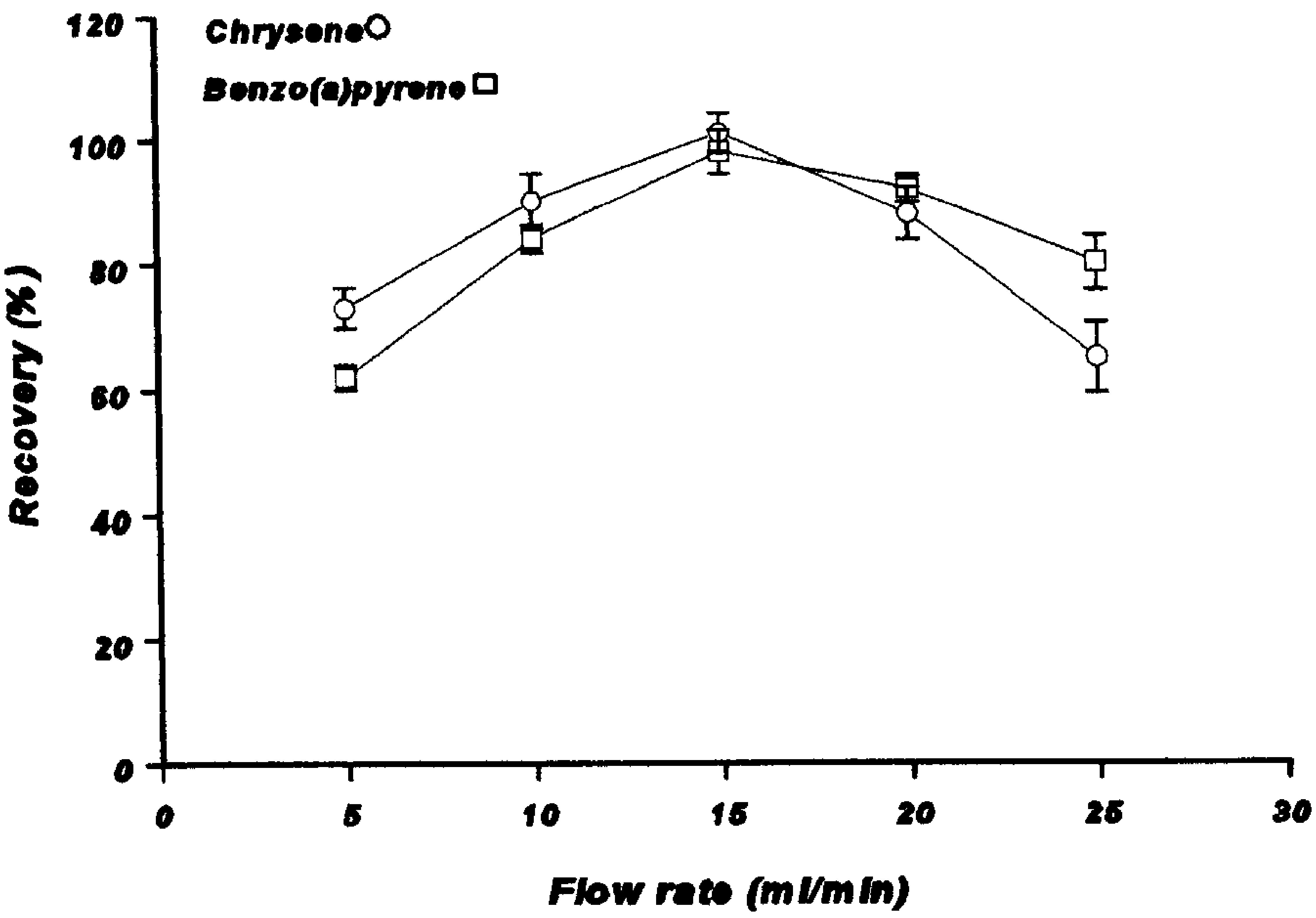


Fig. 4.6 Recovery of chrysene and benzo(a)pyrene with different flow rate for focusing

Table 4.2 Recovery of chrysene and benzo(a)pyrene at different flow rate

| Compounds | Flow rate | Concentration at direct injection (µg/µl) | Mean of Recovery at different flow rate | Recovery (%) |
|---|---|---|---|---|
| Chrysene | 5 | 0.5 | 0.365 | 73 |
| | 10 | | 0.450 | 90 |
| | 15 | | 0.505 | 101 |
| | 20 | | 0.440 | 88 |
| | 25 | | 0.325 | 65 |
| Benzo(a) pyrene | 5 | 0.5 | 0.310 | 62 |
| | 10 | | 0.420 | 84 |
| | 15 | | 0.490 | 98 |
| | 20 | | 0.460 | 92 |
| | 25 | | 0.400 | 80 |

### 4.3.3.2 Length of time for preparation

To determine the optimum time for the preparation of samples 1μl aliquot of benzo(a)pyrene and chrysene were injected into the Carbotrap at different times with a flow rate of 12-16 ml/minute and the results compared with direct injection data in Table 4.3 and Figure 4.7. An optimum preparation time of 13-17 minutes for focussing is indicated.

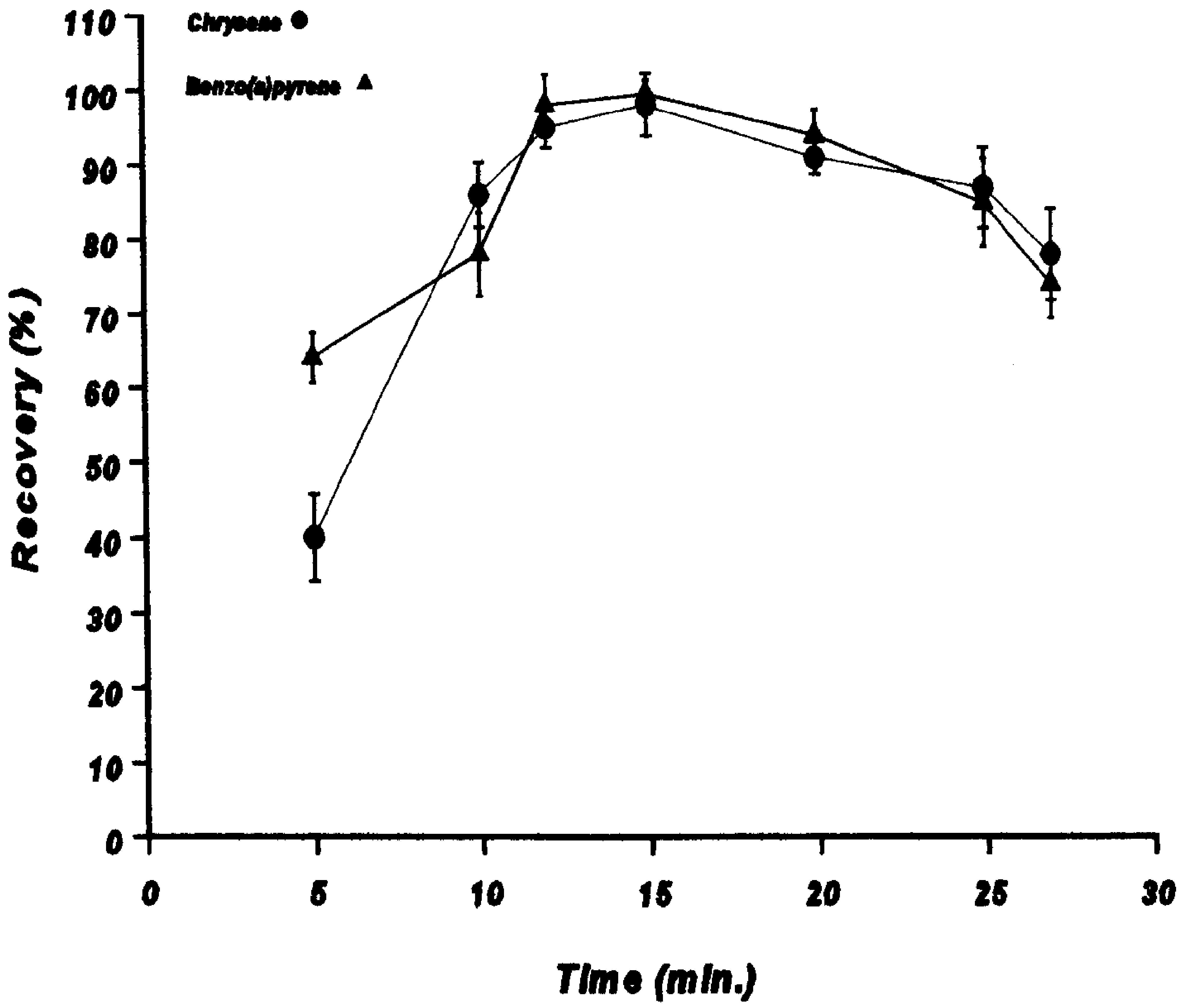


Fig. 4.7 Recovery of chrysene and benzo(a)pyrene with different times for focussing

Table 4.3 Recovery of chrysene and Benzo(a)pyrene at different length of time

| Compounds | Flow rate | Concentration at direct injection (μg/μl) | Mean of Recovery at different time | Recovery (%) |
|---|---|---|---|---|
| Chrysene | 5 | 0.5 | 0.200 | 40 |
| | 10 | | 0.430 | 86 |
| | 12 | | 0.475 | 95 |
| | 15 | | 0.490 | 98 |
| | 20 | | 0.455 | 91 |
| | 25 | | 0.435 | 87 |
| | 27 | | 0.390 | 78 |
| Benzo(a) pyrene | 5 | 0.5 | 0.320 | 64 |
| | 10 | | 0.390 | 78 |
| | 12 | | 0.490 | 98 |
| | 15 | | 0.498 | 99.5 |
| | 20 | | 0.470 | 94 |
| | 25 | | 0.425 | 85 |
| | 27 | | 0.370 | 74 |

#### 4.3.3.3 Determination of optimum temperature for preparation

To determine the optimum temperature for preparation 1 μl of benzo(a)pyrene was injected into the Carbotrap at different temperatures at a flow rate of 10-15ml/minute and a duration of 15 minute. The results are compared with direct injection in Figure 4.8 and Table 4.4, indicate that the best recovery is at a temperature of 340°C.

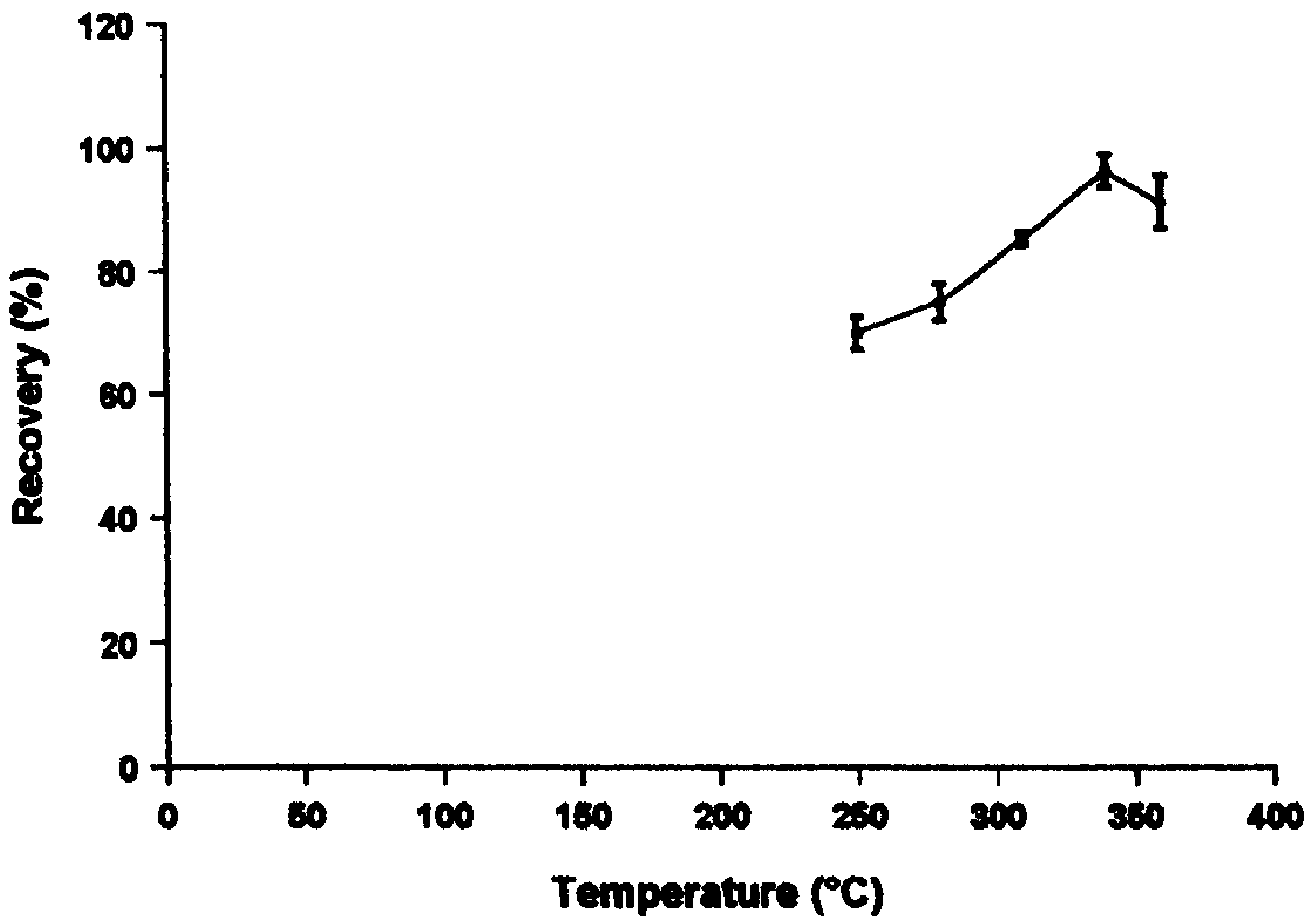


Fig. 4.8 Recovery of benzo(a)pyrene at different temperature

Table 4.4 Recovery of benzo(a)pyrene at different temperature

| Temperature (°C) | Concentration at direct injection (μg/μl) | Mean of Recovery at different temperature | Recovery (%) |
|---|---|---|---|
| 250 | 0.5 | 0.350 | 70 |
| 280 | 0.5 | 0.375 | 75.1 |
| 310 | 0.5 | 0.424 | 84.9 |
| 340 | 0.5 | 0.479 | 95.8 |
| 360 | 0.5 | 0.456 | 91.2 |

### 4.3.3.4 Summary of optimum condition for Thermal Desorption

The optimum conditions for Thermal Desorption are as follows;

Temperature for focussing compounds from filter to Carbotrap: 340°C

Temperature of valve (recommended by company): 220°C

Temperature of transfer line between GC-MS and Thermal Desorption Unit: 230°C

Length of time for focussing compounds from filter to Carbotrap 13-17 minute

Flow rate for focussing compounds: 12-16 ml/minute.

### 4.3.4 Determination of optimum time for sampling

The optimum time for sampling from air, was determined by obtaining different samples for periods of 1, 2, 4 and 6 hours at a flow rate of 2 litre/minute in two days. The wind speed was 0.5-1m/s in one day and in another day was more than 1 m/s. Samples were analysed, and the results shown in Table 4.5. According to these results optimum time for sampling from air is between 1 and 5 hours and depends on wind speed. The time for sampling must be increased when wind speed is more than 2 m/s.

Table 4.5 Concentration of Benzo(a)pyrene in ambient air sampled at different time periods

| Hour of sampling | Wind speed (m/s) | Concentration $\mu g/m^3$ | Wind speed (m/s) | Concentration $\mu g/m^3$ |
|---|---|---|---|---|
| 6 | 0.5-1 | 3.9 | >1 | 0.89 |
| 4 | 0.5-1 | 2.8 | >1 | 0.67 |
| 2 | 0.5-1 | 2.5 | >1 | - |
| 1 | 0.5-1 | 3.1 | >1 | - |

### 4.3.5 Sample collection

Samples were obtained from air with a sampling pump and filters (described in section 4.2.1 and 4.2.3 ). A flow meter was used to measure the flow rate of the pump (described in section 4.2.2). The flow rate of the pump can change during sampling, so the flow rate was checked before and after each sample collection. If the samples were obtained over more than 2 hours the flow was checked at an intermediate point during sampling as well. After sampling, the glass fibre filter was transferred to a dried plastic container which was sealed with tape.

Average flow rate is calculated according to the following equation:

$$Q_A=\frac{Q_1+Q_2+\ldots+Q_N}{N}$$

$Q_A$ = Average flow rate in litre/minute.

$Q_1$, $Q_2$, ... $Q_N$ = Flow rates determined at beginning, end, and intermediate points during sampling

N= Number of points.

Volume of sampling air was calculated as following:

$$V=Q_A \times t$$

V= Volume sampled in litres at measured temperature and pressure

t= Sampling time (minutes)

$Q_A$= Average flow rate (litre/minute)

The volume of air must be changed to volume of air under standard conditions 25°C and 760 mmHg and is calculated from the following equation:

$$V_S=V_m\times\frac{P_A}{760}\times\frac{298}{273+T_A}$$

$V_S$ = Volume at standard conditions (l)

$V_m$ = Volume of air (l)

$P_A$ = Average barometric pressure, mmHg

$T_A$ = Average ambient temperature, °C

The barometric pressure and the temperature were measured using a weather monitor (described in section 4.2.8).

### 4.3.6 Analysis of samples

A Thermal Desorption unit linked to a GC-MS was used to analyse the samples. Thermal Desorption was used for preparation of the samples and the transfer of compounds to the GC-MS.

#### 4.3.6.1 Preparation of sample

To prepare a sample, the filter was cut with a scissors into small pieces which were placed in an empty tube which was then placed in the chamber of a Thermal Desorption

Unit. The Carbotrap 300 was placed in the trapping part of the Thermal Desorption Unit to focus compounds. The Thermal Desorption Unit was set at optimum conditions of temperature, flow rate and length of time which are 340 °C, 12-16ml/minute and 13-17 minutes. PAHs were transferred from the filter to the Carbotrap under these conditions.

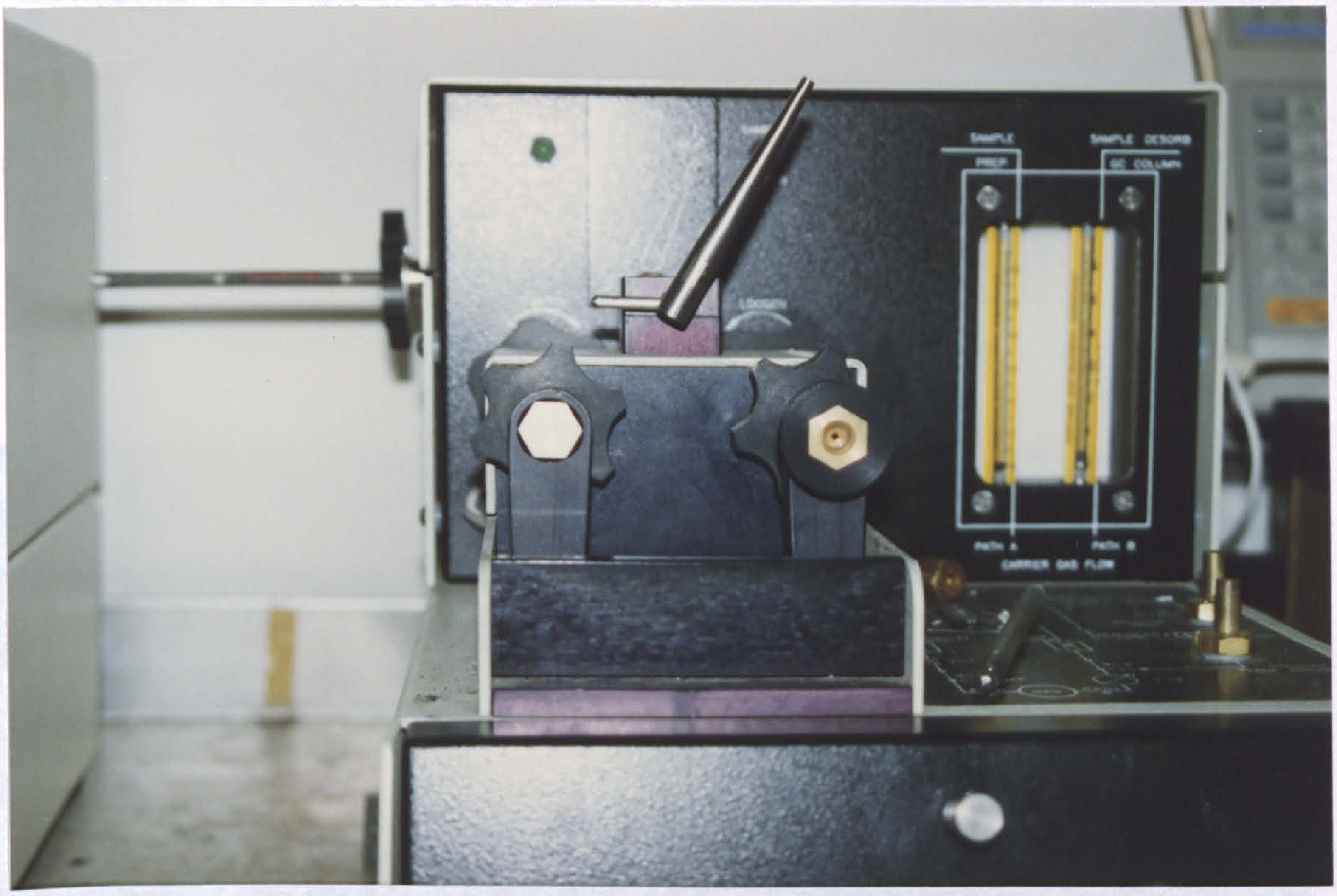


**Fig. 4.9 Carbotrap in trapping part of Thermal Desorption Unit**

#### 4.3.6.2 Desorption of sample to GC-MS

The Carbotrap 300 was placed in the desorption chamber to transfer PAHs to GC-MS. The GC-MS was set at a temperature program which started at 70 °C and increased temperature to 300°C at the rate of 7°C/min with a gas flow 2-3.5 ml/minute (described in section 4.3.1). All compounds in the Carbotrap were transferred to the GC under these conditions and components eluting from the column were identified and quantified by mass-spectrometry.

### 4.3.6.3 Qualitative analysis of samples

The chromatogram of each sample was saved in the computer which was connected to the GC-MS. Figure 4.11 (a,b) shows the gas chromatogram of a sample from PAHs in car exhaust. The number of the scan is show above each peak. The software in the system can compare each peak in the spectrum with the spectra of fifty thousand compounds that are in the library of the computer. Figure 4.12 shows the mass spectrum of scan number 1376 of the chromatogram in Fig. 4.11 (b). Figure 4.13 identified the spectrum of number 1376 as fluoranthene. Similarly, Figure 4.14 shows number 1112 in the gas chromatogram Fig. 4.11 (b) is anthracene.

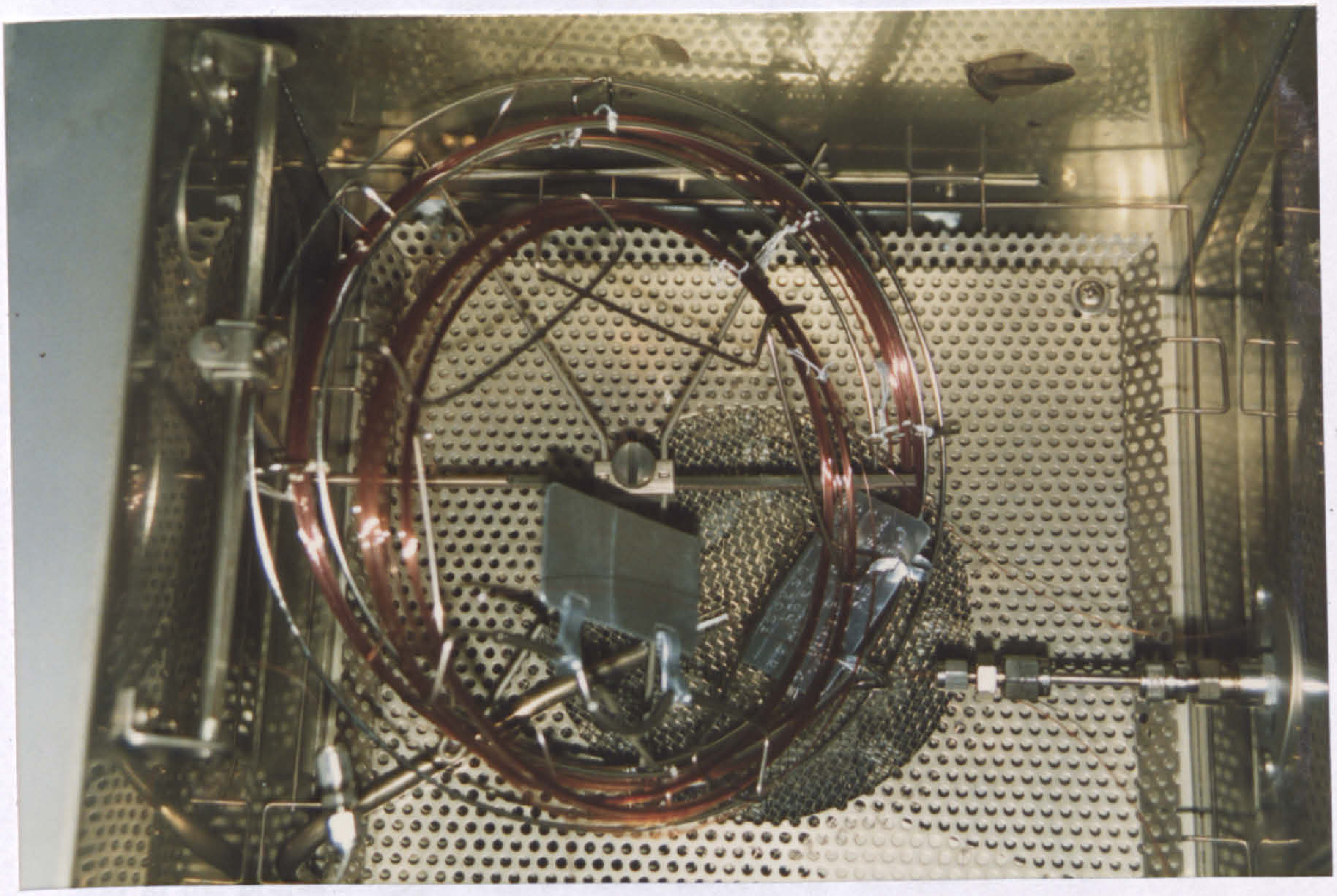


**Fig 4.10 30 metre capillary column into GC-MS**

In some of the samples, compounds that have similar mass spectra and GC retention times, mutually interfere. The most commonly encountered interferences are structural isomers. If a column longer than 30m is used, however, this problem decreases. The column used in the present work could not be lengthened, therefore the following ways have been used to solve the problem:

1. Using the software in the computer, the base peak (the strongest peak in the measurement of a compound) chromatogram was searched to determine which compound has the base peak. For example the base peak for benzo(a)pyrene and benzo(e)pyrene is 252 or for phenanthrene and anthracene is 178 etc. The base peak for each compound is to be found in a reference book. Figure 4.15 shows two chromatograms of the same sample, (a) the total ion current and (b) chromatogram of peak 202 which shows the presence of fluoranthene and pyrene. This method was used determined of samples of ambient air when low concentration of PAHs were present.

2. The use of retention time derived by the injection of a pure solution of each compound.

3. Decreasing the temperature of the column or changing the flow rate of inert gas (helium) in GC-MS so that compounds emerge over a longer time.

#### 4.3.6.4 Quantitative analysis of samples

The software in the computer determines the area of each peak in the chromatogram. Figure 4.16 shows the chromatogram of a sample from car exhaust where the area of each peak was determined. A standard solution recommended by EPA and obtained from Supelco was used to calibrate standard peaks. This solution includes 12 polycyclic aromatic hydrocarbons. 0.2-1 µl of the standard solution was transferred to a Carbotrap 300 in the preparation part of the Thermal Desorption Unit. When this Carbotrap is placed in the desorption chamber, the standard compounds are transferred to the GC-MS (similar to samples from air pollution). The sample conditions in preparation and desorption in Thermal Desorption Unit and GC-MS were similar to those for standard samples. Blank samples were also analysed to determine whether any impurity peaks were obtained from unused filters. The following equations were used to relate peak area to the weight of compound in the sample.

$$\frac{W_1}{W_2}=\frac{A_1}{A_2}$$

$$W_2=\frac{W_1 \times A_2}{A_1}$$

$W_1$ = Weight of compound in standard solvent (µg/µl)
$W_2$ = Weight of compound in sample (µg)
$A_1$= Area of compound in standard sample (Arbitrary units)
$A_2$=Area of compound in sample (Arbitrary units)

The concentration of each compound in air is calculated with the following equation:

$$\frac{W_2}{C}=\frac{V_S}{1}$$

$W_2$ = weight of compounds in the samples
$V_S$ = Volume of samples at standard conditions (STP) (described in section 4.3.5)
C = concentration of compound in 1 litre air

### 4.3.7 Determination of percentage recovery of PAHs under optimum conditions

To determine the recovery of PAHs under optimum conditions 1 µl of the standard solution was transferred to Carbotrap 300 and the results were compared with 1 µl direct injection. This analysis was performed in triplicate. The results in Table 4.6 indicate the recoveries are between 98 ± 4%.

Table 4.6 Recovery of PAHs in optimum condition

| Component | Concentration at direct injection (µg/µl) | Recovery with Carbotrap | Mean | Recovery (%) |
|---|---|---|---|---|
| Phenanthrene | 0.5 | 0.485<br>0.467<br>0.498 | 0.483 | 97 |
| Anthracene | 0.5 | 0.4825<br>0.492<br>0.479 | 0.484 | 97 |
| Fluoranthrene | 0.5 | 0.509<br>0.508<br>0.507 | 0.508 | 102 |
| Pyrene | 0.5 | 0.488<br>0.496<br>0.502 | 0.495 | 99 |
| Benzo(a)anthracene | 0.5 | 0.438<br>0.489<br>0.504 | 0.477 | 95 |
| Chrysene | 0.5 | 0.503<br>0.501<br>0.496 | 0.491 | 98 |
| Benzo(a)pyrene | 0.5 | 0.501<br>0.489<br>0.504 | 0.498 | 100 |
| Benzo(e)pyrene | 0.5 | 0.463<br>0.472<br>0.493 | 0.476 | 95 |

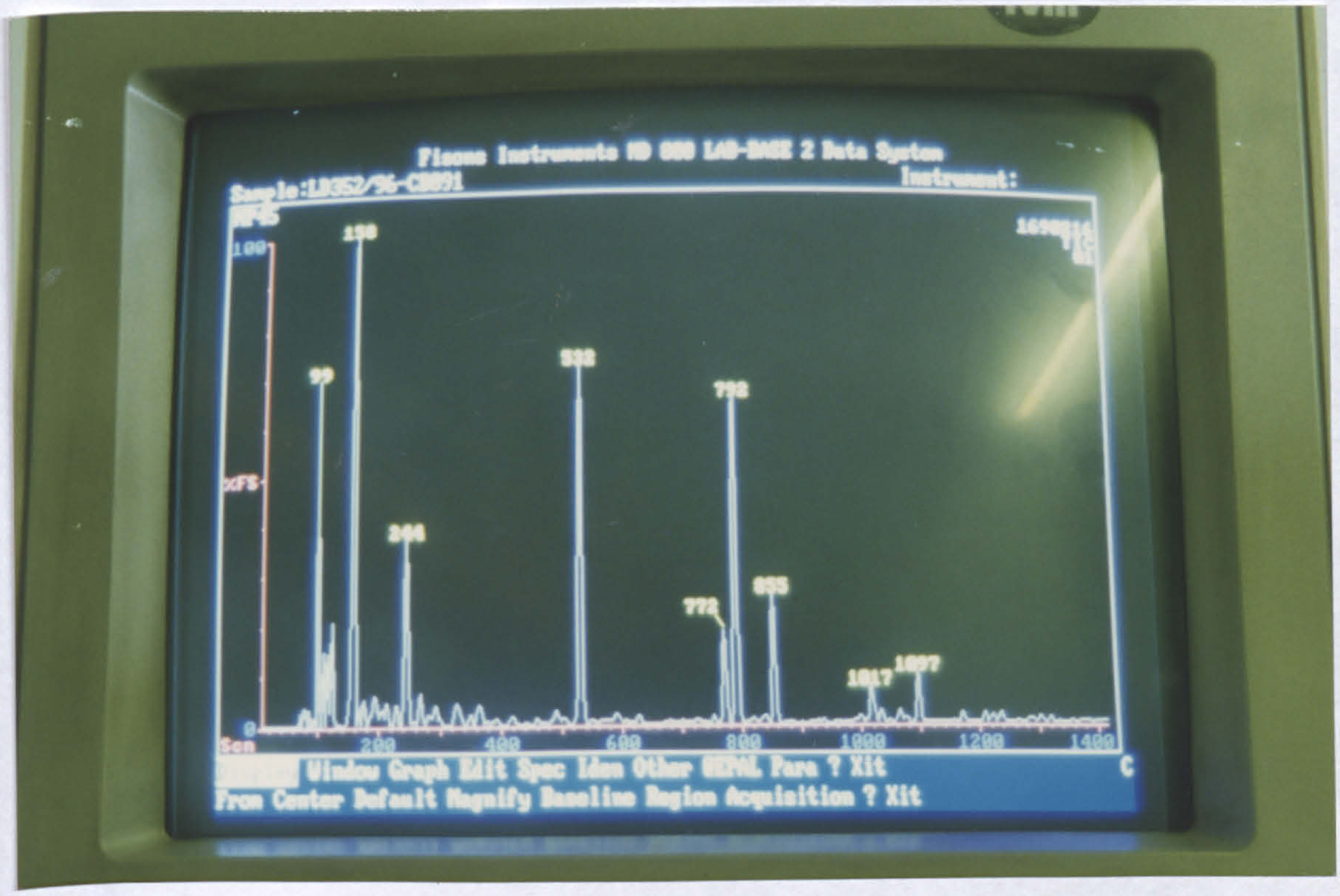


Figure 4.11 (a) Gas chromatogram of a sample in computer.

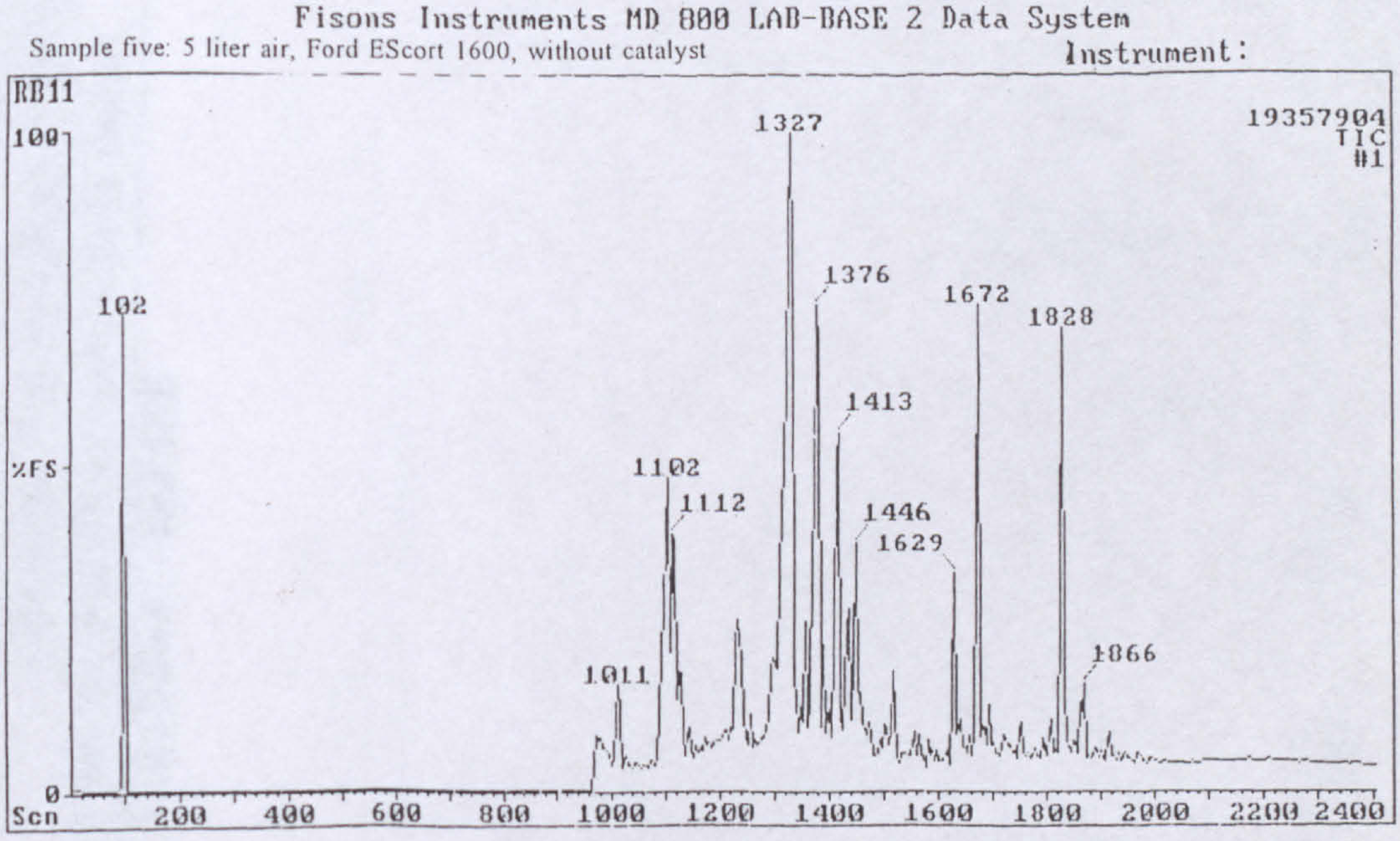


Figure 4.11 (b) Gas chromatogram of a sample from the car exhaust.

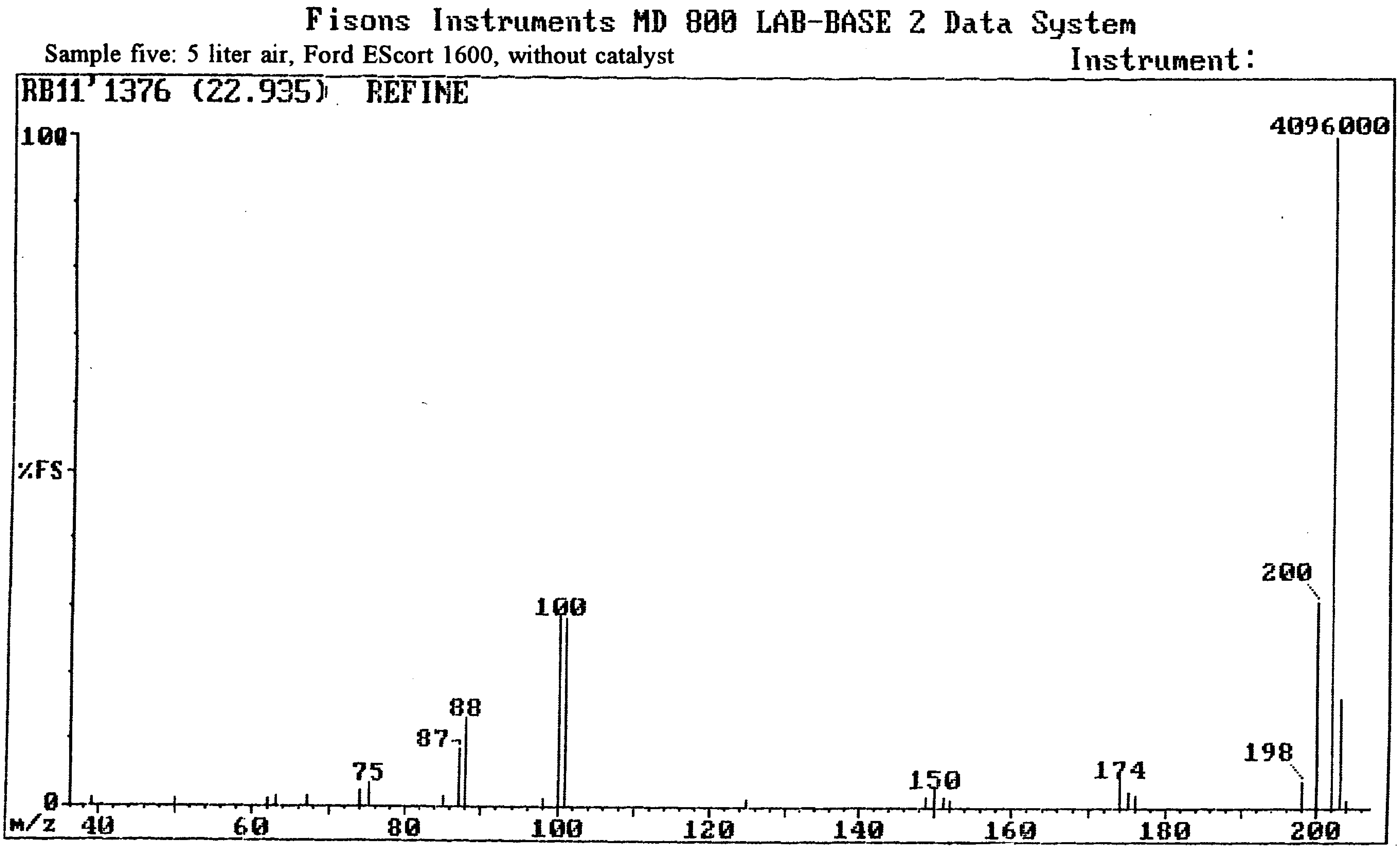
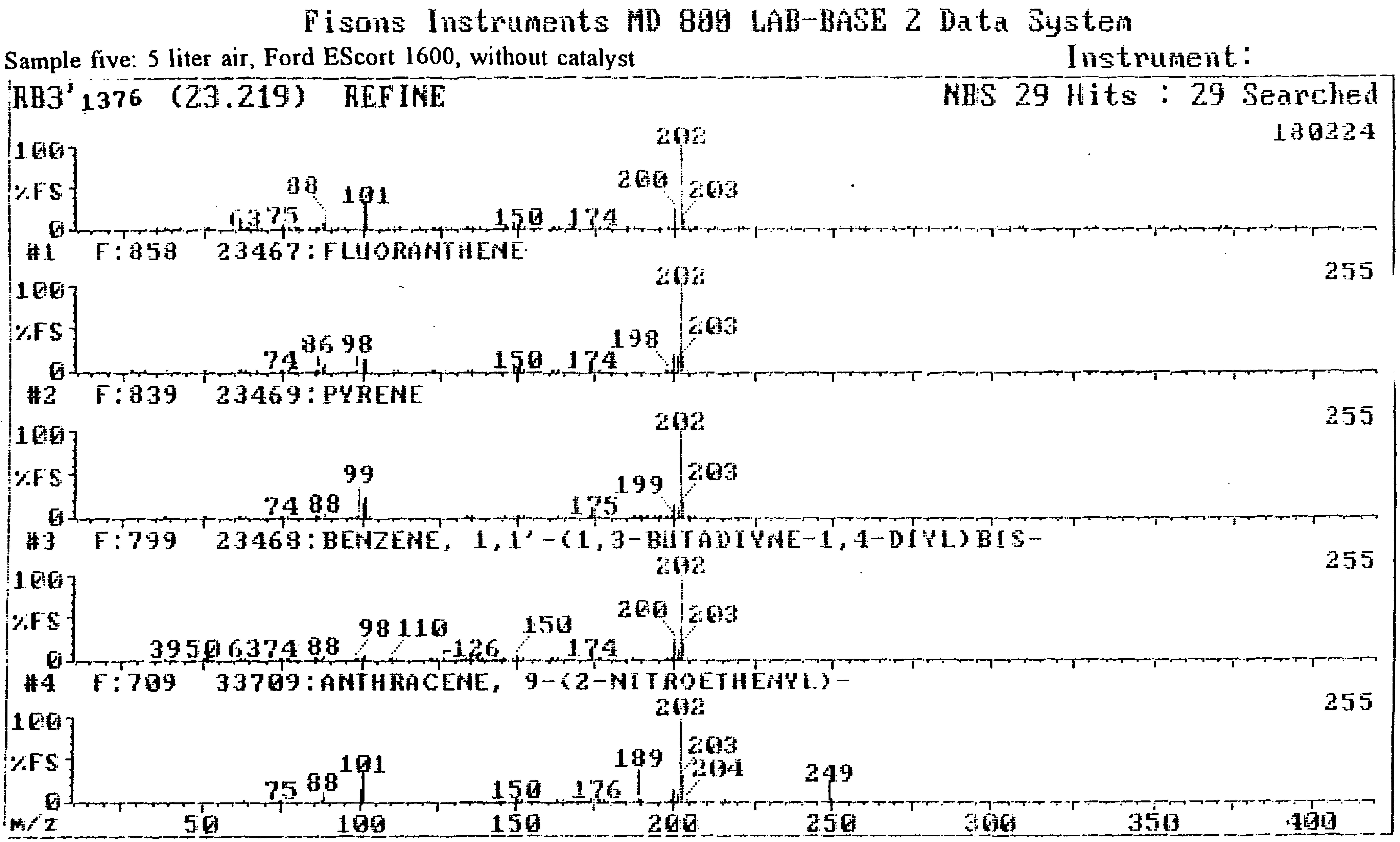


Figure 4.12 Mass spectrum of scan number 1376 from Fig. 4.11 (b)



Sample five: 5 liter air, Ford EScort 1600, without catalyst

Figure 4.13 Determination of mass spectrum 1376 from Fig. 4.11(b) by the software.

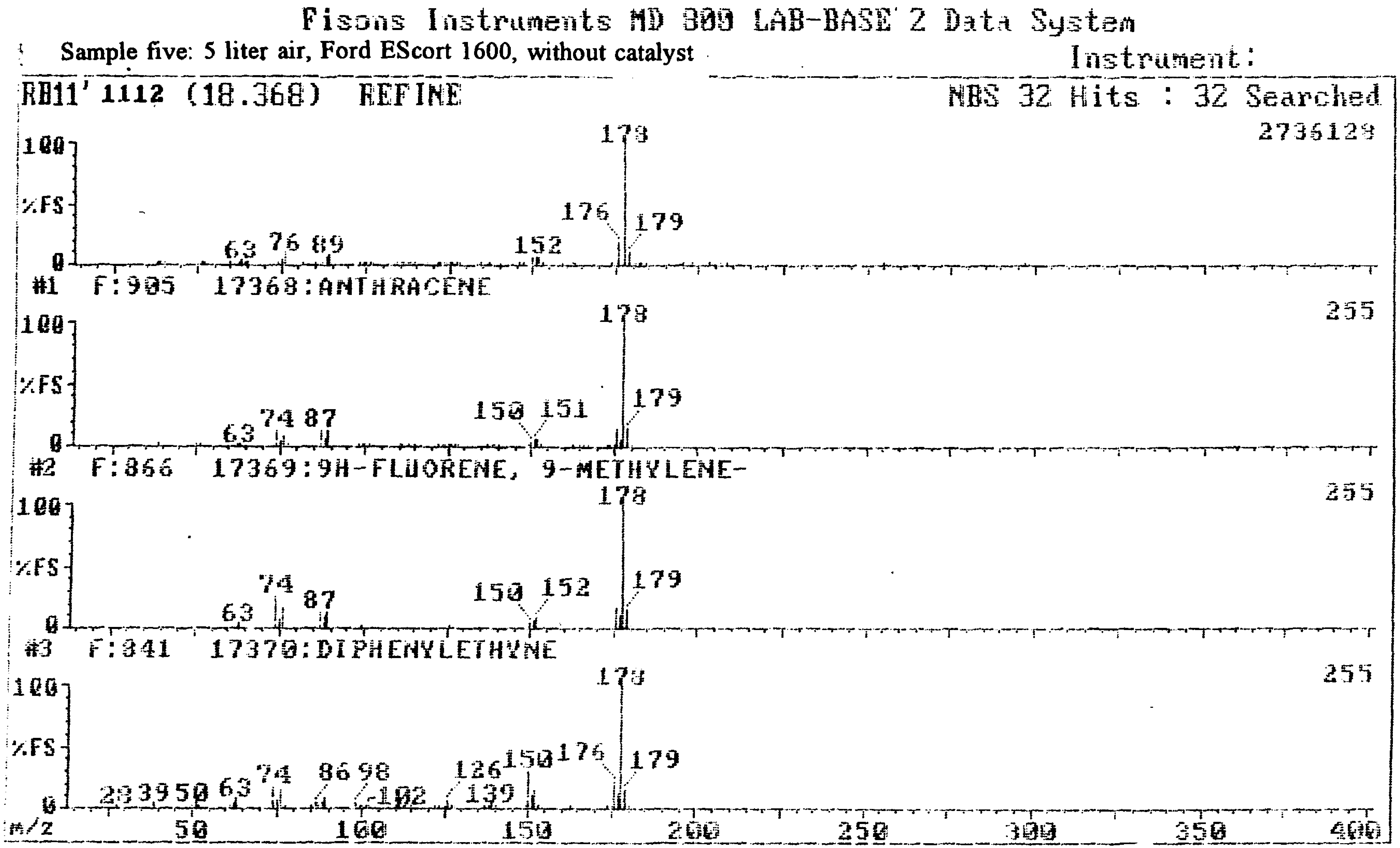


Figure 4.14 Determination of mass spectrum 1112 from Fig. 4.11 (b) by the software

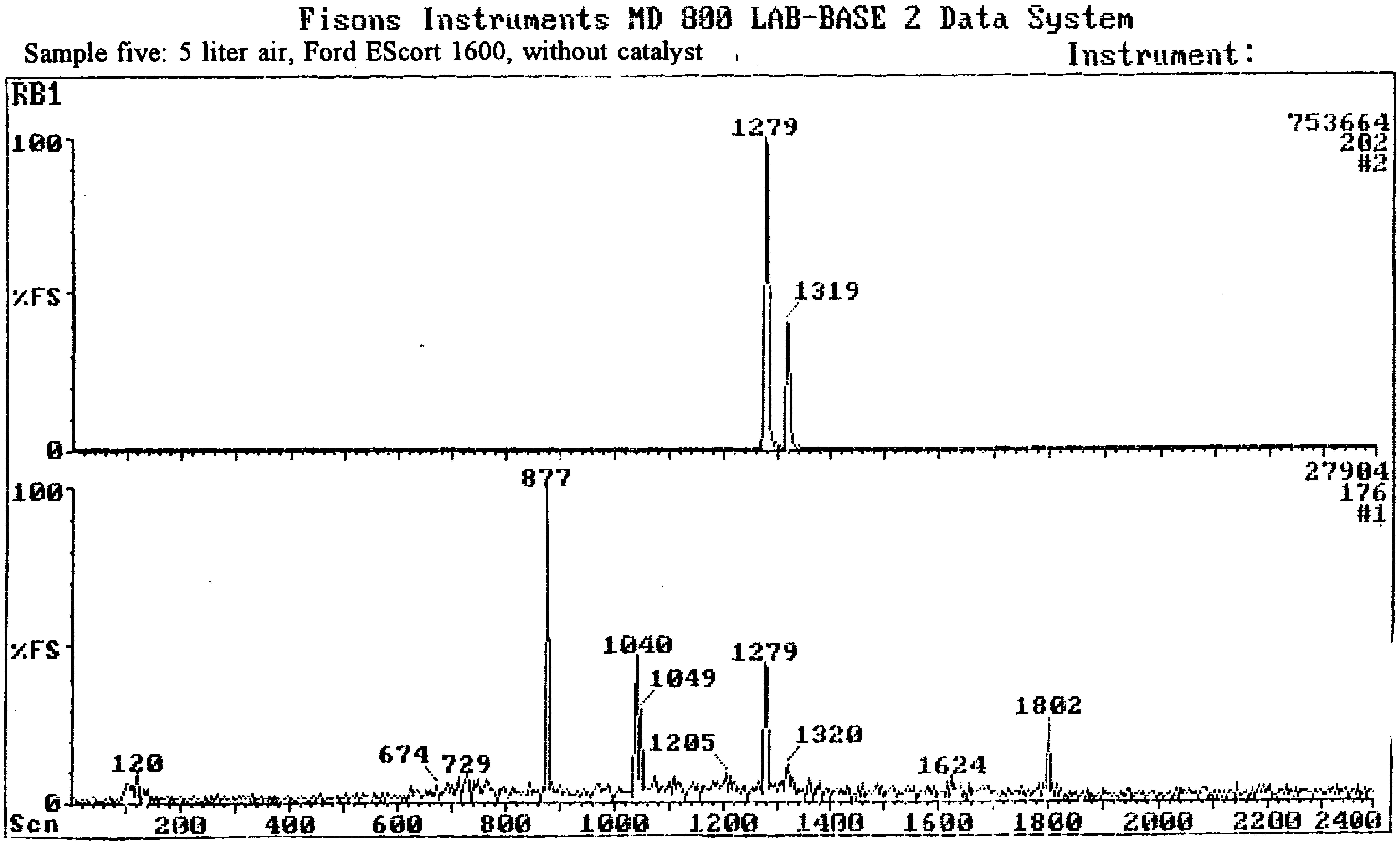
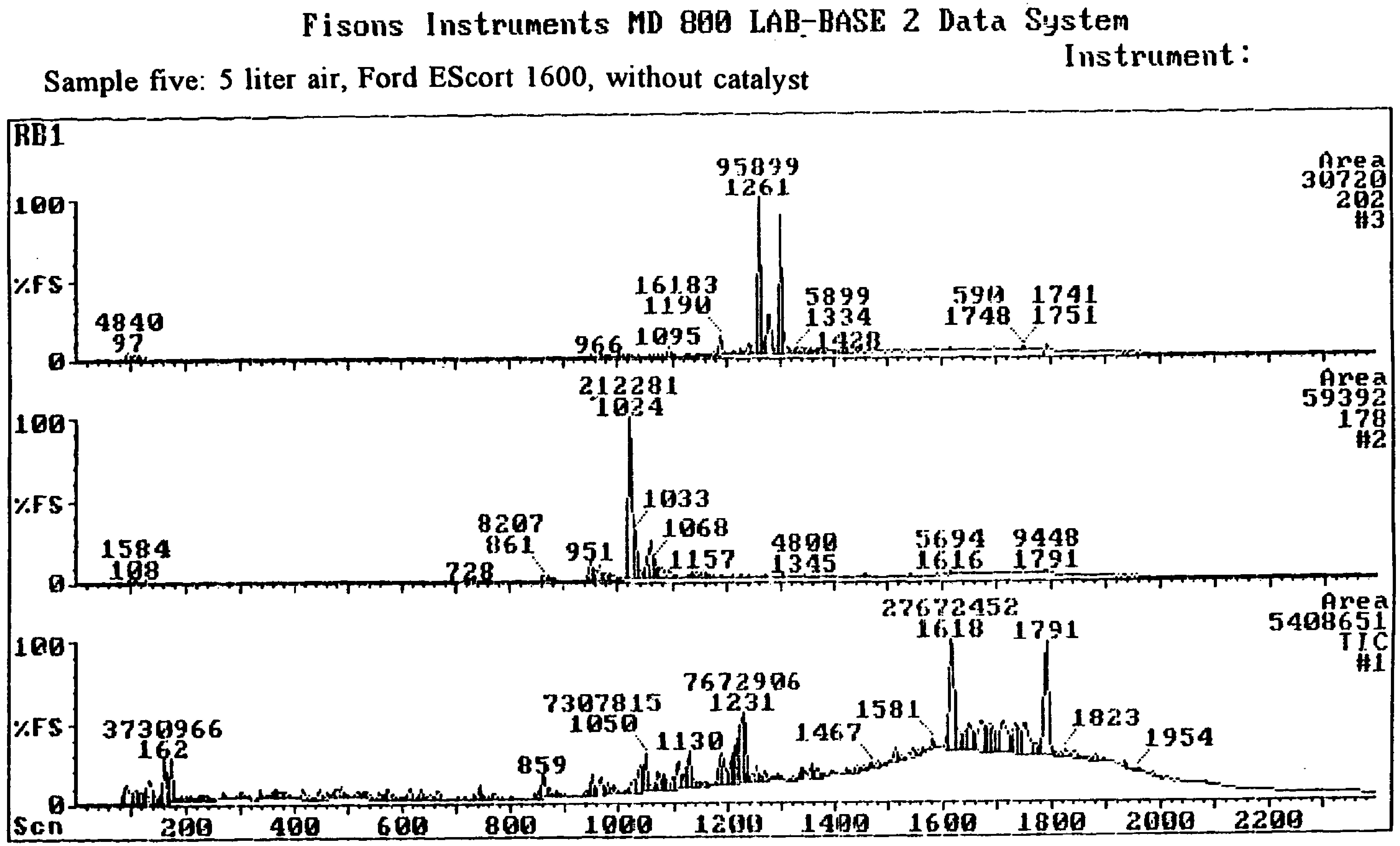


Figure 4.15 Gas chromatogram of a sample from PAHs in air, chromatogram (1) from compounds with base peak 176 (1279: fluoranthene , 1319:pyrene), chromatogram (2) from compounds with base peak 202 (1040: phenanthrene 1049:anthracene).



Sample five: 5 liter air, Ford EScort 1600, without catalyst

Figure 4.16 Gas chromatogram of a sample from car exhaust (area of each peak recorded above peaks ), chromatogram (1) TIC (Total ion chromatogram): whole of chromatogram determined by mass spectrometry. Chromatogram (2) chromatogram of compounds with base peak 178. Chromatogram (3) compounds with base peak 202 .

### 4.4 PAHs in ambient air

For the qualitative and quantitative analysis of polycyclic aromatic hydrocarbons (PAHs) and to determine the reproducibility of the method , 55 samples were obtained from the beginning of April 1996 until end of July 1996. A few filters were selected as blanks (i.e. not exposed to ambient air conditions). Most of the samples were obtained during the working day with a few collected during weekends. Sampling was concentrated on the busy period, 0900-1700 hours, but was extended in a few instances over a 24 hour period.

For the measurement of PAHs the samples were obtained at Cowley Road, Uxbridge, West London at a height 3 metres outside a flat. The sampling pump was connected to the tube of a filter holder which was located outside a window via a vent. The location of sampling is indicated in Fig. 4.17.

Samples were transferred to the laboratory immediately and analyzed on the same day. On some days, analysis of samples was delayed so they were stored in a freezer at low temperature.

The density of traffic in Cowley Road is indicated at Table 4.7.

Table 4.7 Flow of traffic in Cowley Road

| Day | Time (hour) | Traffic flow per hour Vehicles |
|---|---|---|
| Monday-Friday | 07:00-09:00 | 1700 |
| | 09:00-15:00 | 1250 |
| | 15:00-19:00 | 1900 |
| | 19:00-24:00 | 800 |
| Saturday | 07:00-19:00 | 1200 |
| | 19:00-24:00 | 600 |
| Sunday | 07:00-22:00 | 350 |

### 4.4.1 Results and discussion

#### 4.4.1.1 Quantitative analysis of samples

Eight polycyclic aromatic hydrocarbons including anthracene, phenanthrene, fluoranthrene, pyrene, benzo(a)anthracene, chrysene, benzo(a)pyrene and benzo(e)pyrene are the most important PAHs found in the chromatogram of ambient air. They were characterised using the gas chromatography- mass spectrometry system. Retention times

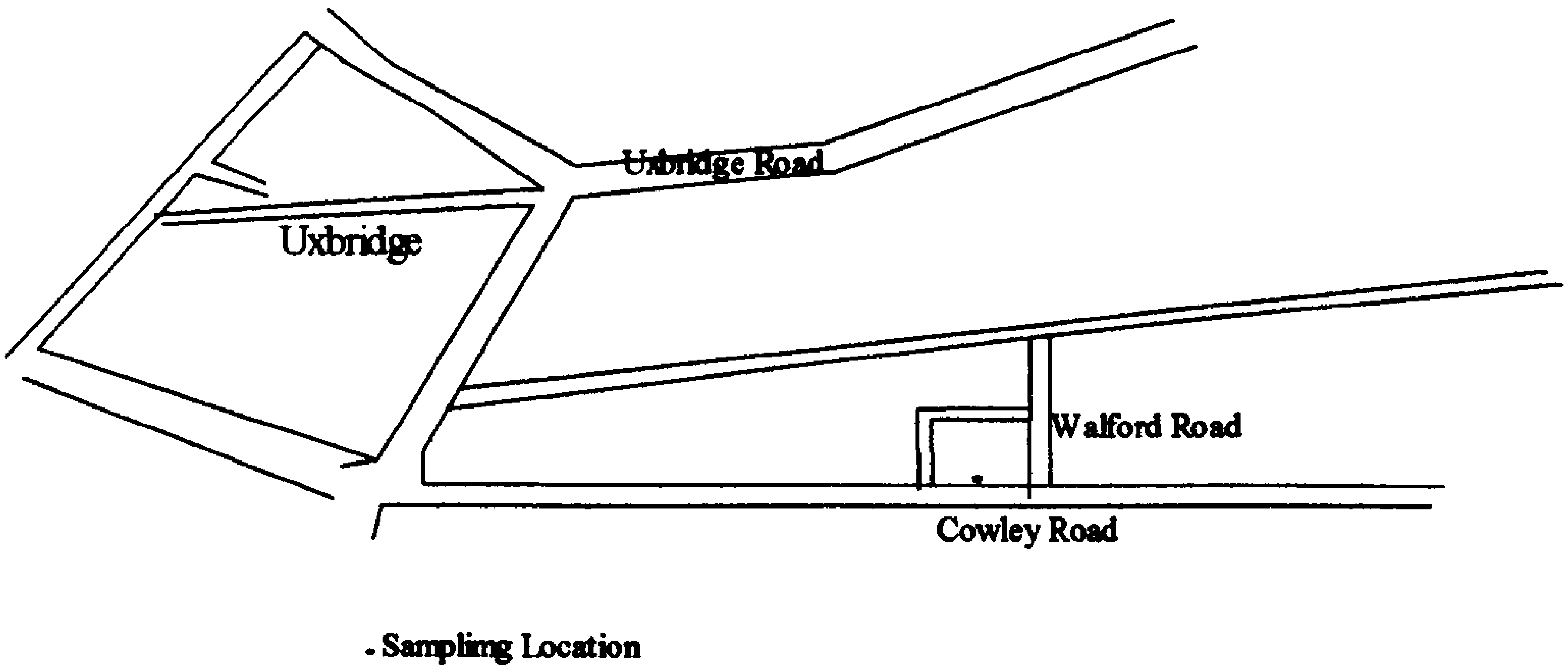


Figure 4.17 Site of sampling at Uxbridge Site

and mass spectra for standards were compared with the data obtained for the particulate fractions. All the determined hydrocarbons were found in the majority of the airborne particulate matter samples taken in April-July 1996.

### 4.4.1.2 Day and night variation

The day and night variation in the concentrations of eight polycyclic aromatic hydrocarbons cited in 4.4.1.1 measured on 22.07.96, is shown in Fig. 4.18. The temperature was between 20-29°C and the wind speed lower than 1m/s.

The data clearly indicate an increase in the concentrations of the eight hydrocarbons during the morning and afternoon rush hour periods, the concentration decreased over night when density of traffic is low.

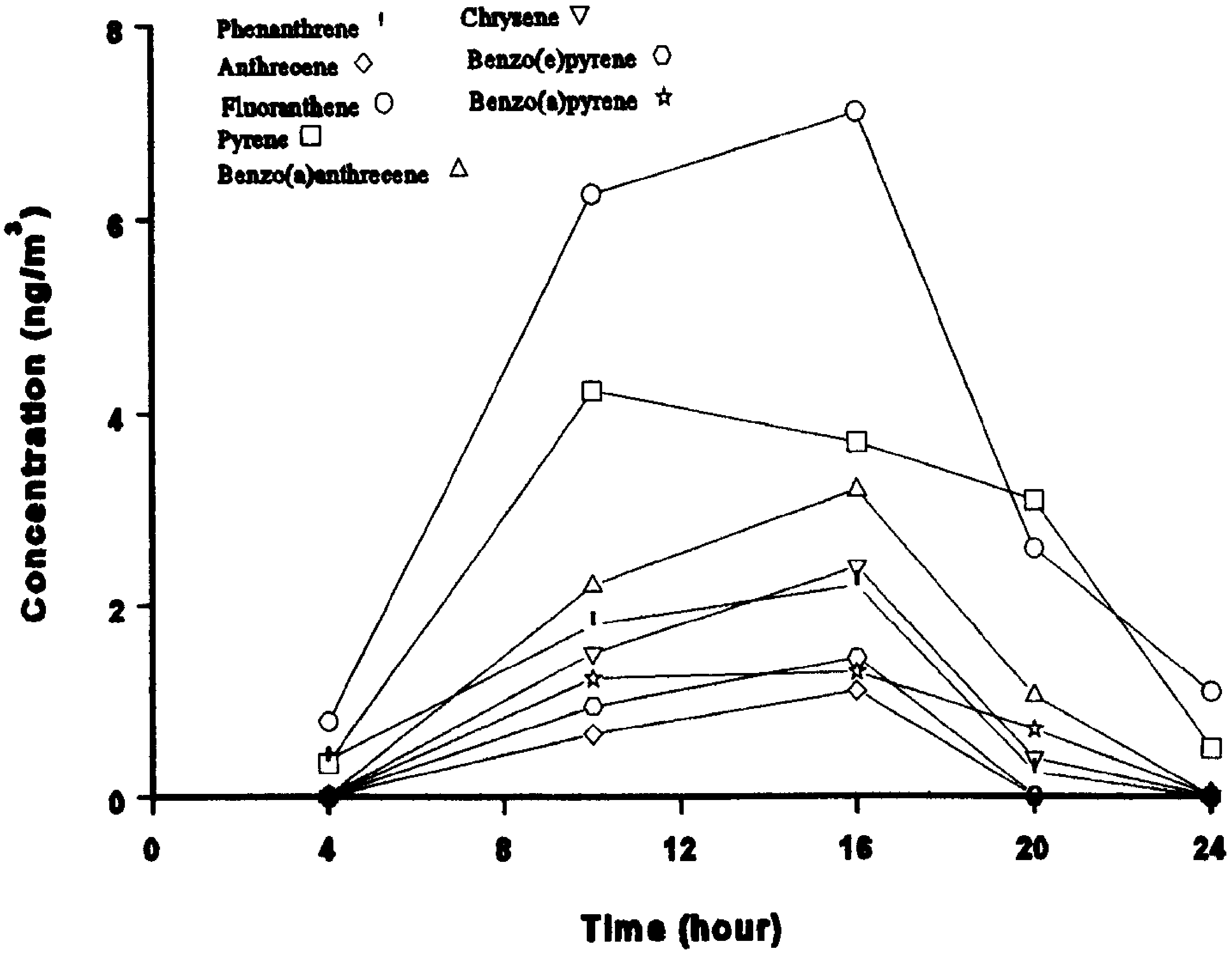


Fig. 4.18 Concentration of PAHs over 24 hour in Cowley Road at 22.07.1996

### 4.4.1.3 Monthly variation of PAHs

The monthly variation of the eight polycyclic aromatic hydrocarbons for the period 1st of April until 30th July shown in Table 4.8 (a, b, c, d) and indicate that fluoranthrene and pyrene concentrations are greater than all other compounds. The highest concentrations are 40.31 and 33.23 for pyrene and fluoranthene respectively which were observed on 13.04.96. The lowest concentrations for benzo(a)pyrene and benzo(e)pyrene, 0.01 ng/m$^3$, were found on 20th June.

All measured hydrocarbons in Cowley Road gave for the four months period concentrations between 0 and 40.31 ng/m$^3$. Wind speed over four months was between 0-4.4m/s.

Table 4.8 (a) Concentration of polycyclic aromatic hydrocarbons (ng/m$^3$ ) in ambient air over April 1996

| Compounds | Mean | S.D | Maximum | Minimum |
|---|---|---|---|---|
| Phenanthrene | 17.56 | 4.10 | 25.12 | 11.23 |
| Anthracene | 4.64 | 0.76 | 9.30 | 2.61 |
| Fluoranthrene | 21.53 | 5.16 | 33.23 | 12.34 |
| Pyrene | 19.21 | 3.64 | 40.31 | 9.37 |
| Benzo(a)anthracene | 6.41 | 2.31 | 12.60 | 3.11 |
| Chrysene | 5.36 | 2.64 | 14.37 | 7.61 |
| Benzo(a)pyrene | 2.43 | 1.34 | 4.11 | 0.95 |
| Benzo(e)pyrene | 2.14 | 0.78 | 5.13 | 0.45 |

Table 4.8 (b) Concentration of polycyclic aromatic hydrocarbons (ng/m$^3$ ) in ambient air over May 1996

| Compounds | Mean | S.D | Maximum | Minimum |
|---|---|---|---|---|
| Phenanthrene | 10.24 | 3.35 | 18.97 | 7.69 |
| Anthracene | 2.43 | 1.44 | 5.27 | 1.01 |
| Fluoranthrene | 15.17 | 4.31 | 27.96 | 4.44 |
| Pyrene | 13.24 | 3.97 | 22.65 | 4.63 |
| Benzo(a)anthracene | 6.34 | 2.61 | 12.35 | 3.12 |
| Chrysene | 4.34 | 2.11 | 5.41 | 1.29 |
| Benzo(a)pyrene | 2.10 | 0.95 | 3.31 | 0.91 |
| Benzo(e)pyrene | 1.80 | 1.311 | 2.80 | 0.58 |

Table 4.8 (c) Concentration of polycyclic aromatic hydrocarbons (ng/m$^3$ ) in ambient air over June 1996

| Compounds | Mean | S.D. | Maximum | Minimum |
|---|---|---|---|---|
| Phenanthrene | 5.34 | 2.34 | 8.17 | 3.10 |
| Anthracene | 1.71 | 1.12 | 3.10 | 0.02 |
| Fluoranthrene | 14.70 | 5.12 | 17.31 | 3.12 |
| Pyrene | 8.38 | 2.29 | 11.65 | 5.64 |
| Benzo(a)anthracene | 3.97 | 2.12 | 6.11 | 0.98 |
| Chrysene | 3.40 | 1.34 | 5.17 | 1.30 |
| Benzo(a)pyrene | 1.78 | 0.67 | 2.67 | 0.01 |
| Benzo(e)pyrene | 1.96 | 0.96 | 2.98 | 0.01 |

Table 4.8 (d) Concentration of polycyclic aromatic hydrocarbons (ng/m$^3$) in ambient air over July 1996

| Compounds | Mean | S.D. | Maximum | Minimum |
|---|---|---|---|---|
| Phenanthrene | 5.61 | 2.97 | 7.39 | 1.12 |
| Anthracene | 1.17 | 2.41 | 5.20 | 0.02 |
| Fluoranthrene | 9.64 | 3.80 | 17.60 | 2.13 |
| Pyrene | 5.76 | 4.21 | 13.34 | 1.96 |
| Benzo(a)anthracene | 2.91 | 2.61 | 5.30 | 0.02 |
| Chrysene | 2.49 | 0.69 | 5.98 | 0.34 |
| Benzo(a)pyrene | 1.35 | 2.98 | 5.31 | 0.1 |
| Benzo(e)pyrene | 1.22 | 1.86 | 3.12 | 0.03 |

Comparing the PAH contents determined during April-July, a significant drop in the amount of the hydrocarbons determined in June and July was found.

On the basis of the calculated ratio of the hydrocarbon content in April to the content in June-July, it has been found that the concentrations of April samples are 2-3 times higher than June-July. It is evident Table 4.8 (a-d) that concentrations of anthracene, phenanthrene, fluoranthrene, pyrene, benzo(a)anthracene, chrysene benzo(a)pyrene and benzo(e)pyrene from April being, 3.13, 3.96, 2.23, 3.33, 2.20, 2.15, 1.80, 1.75 times higher respectively than the concentrations measured in July. The higher amount of the more volatile PAHs determined in April samples result from the presence of these low molecular-weight PAHs (MW $\leq$ 250) in the particle phase (adsorbed in particles), while in the summer, these hydrocarbons are dominant in a vapour phase (Bidleman (4), 1988; Arey (3) et al., 1987). This was not investigated by our analytical procedure.

As expected, the amount of PAH in the gas phase increase with decreasing molecular weight and increasing vapour pressure of the compounds (18).

According to a study by Westerholm (18) et al., gas phase distribution is decreased with increase of molecular weight. Therefore collection of PAHs using a filter in summer decreases based on reduction in particle phase and increase in gas phase. This is confirmed in Table 4.9.

Ratio of each a PAHs from April to July were increased due to reduction of particulate phase and this be confirmed by Table 4.9.

Table 4.9 The concentration ratio of PAHs in April to other months

| Compounds | April/April | April/May | April/June | April/July |
|---|---|---|---|---|
| Phenanthrene | 1 | **1.71** | **3.28** | **3.13** |
| Anthracene | 1 | **1.90** | **4.29** | **3.60** |
| Fluoranthrene | 1 | **1.41** | **1.46** | **2.23** |
| Pyrene | 1 | **1.45** | **2.29** | **3.33** |
| Benzo(a)anthracene | 1 | **1.09** | **1.61** | **2.20** |
| Chrysene | 1 | **1.23** | **1.57** | **2.15** |
| Benzo(a)pyrene | 1 | **1.15** | **1.36** | **1.80** |
| Benzo(e)pyrene | 1 | **1.18** | **1.09** | **1.75** |

#### 4.4.1.3 Statistical correlation

A negative correlation (-67%) was seen between temperature of ambient air and concentration of PAHs. This is indicated in Table 4.8 (a, b, c, d); when the concentration recorded in June and July are lower than in April and May.

About 25 samples were obtained from inside a room of an apartment. None of the residents were smokers and the door of the room was closed to exclude pollution from the kitchen. Only the window of the room was opened. The results are given Table 4.11 and indicate the concentrations of the PAHs are low but correlation between concentration of pyrene and fluoranthene inside and outside of flat were 65% and 71%, respectively, which indicates that polycyclic aromatic hydrocarbons were emitted by vehicles which pollute the ambient air as well as the inside of house.

Table 4.10 Concentration of polycyclic aromatic hydrocarbons (ng/m$^3$) in ambient air over April-March outside of house, 1996

| Compounds | Mean | S.D | Maximum | Minimum |
|---|---|---|---|---|
| Phenanthrene | 9.31 | 4.26 | 25.12 | 1.12 |
| Anthracene | 2.50 | 2.67 | 9.30 | 0.02 |
| Fluoranthrene | 15.50 | 7.25 | 33.23 | 2.13 |
| Pyrene | 11.80 | 4.10 | 40.31 | 1.96 |
| Benzo(a)anthracene | 4.75 | 3.10 | 12.60 | 0.02 |
| Chrysene | 3.90 | 2.94 | 14.37 | 0.34 |
| Benzo(a)pyrene | 1.75 | 1.73 | 4.11 | 0.01 |
| Benzo(e)pyrene | 1.60 | 1.35 | 5.13 | 0.01 |

Table 4.11 Concentration of polycyclic aromatic hydrocarbons (ng/m$^3$) in ambient air over April-July inside room, 1996

| Compounds | Mean | S.D. | Maximum | Minimum |
|---|---|---|---|---|
| Phenanthrene | 2.10 | 1.89 | 4.12 | 0.4 |
| Anthracene | 1.10 | 1.40 | 3.10 | 0.3 |
| Fluoranthrene | 4.31 | 3.01 | 7.21 | 0.9 |
| Pyrene | 3.10 | 2.70 | 6.43 | 0.2 |
| Benzo(a)anthracene | 0.94 | 1.31 | 3.67 | 0.07 |
| Chrysene | 0.87 | 1.42 | 3.74 | 0.08 |
| Benzo(a)pyrene | 0.35 | 0.97 | 1.70 | 0.001 |
| Benzo(e)pyrene | 0.21 | 0.85 | 0.85 | 0.003 |

Results of some other studies on atmospheric PAH concentrations in Australia, Europe, Asia and America are shown in Table 4.12. The levels in Europe and Asia are, in most cases, at least an order of magnitude above any found in this study. This is probably due to the higher population density and greater use of solid fuels for heating and cooking in these areas.

In a 1994 study, Halsall (22) et al., quoted levels of PAH found in parts of the UK. They measured PAH is in the cities of London, Manchester, and Cardiff and in the light industrial town of Stevenage. Both the particulate and vapour phase of 15 PAHs were sampled using high-volume air samplers at roof top level. London, the largest urban centre, had the highest annual mean PAHs concentrations of 166 ng/m$^3$ in 1991. Phenanthrene and fluorene dominated the total PAH at each site and were present predominantly in the vapour phase throughout the year. The higher PAHs (MW > 250) were present on the collected particulate and showed a distinct seasonal variation (winter > summer) (22).

Table 4.12 Some PAH levels (ng/m$^3$) from other studies

| Location | Year | Season | BaP | Comments | Reference |
|---|---|---|---|---|---|
| Poland,Upper Silesia | 1991 | summer<br>winter | 35<br>50 | Industrial | D. Bodzek (20) et al |
| London, UK | 1972/73 | All Year | 5-10 | City | Commins and Hampton (30) |
| London, UK | 1991-92 | summer<br>winter | 1.2<br>2.1 | City | J.R Brown (19) et al |
| Antony, France | 1979<br>1980 | summer<br>winter | 0.02<br>4.6 | Residential | Muel and Saguem (13) |
| St. Denis, France | 1979<br>1980 | summer<br>winter | 0.07<br>150 | Industrial | Muel and Saguem (13) |
| Nuremberg FRG | 1981 | All year | 3.47 | Urban | Steinmetzer (14) et al. |
| Tehran, Iran | 1981 | summer<br>winter | 1.27<br>8.29 | Urban | Aghdaie and Abid (5) |
| Los Angeles, USA | 1971-72 | All year | 0.03 | Rural | Gordon and Bryan(16) |
| Los Angeles, USA | 1974 | summer<br>autumn<br>winter<br>spring | 0.17<br>0.26<br>1.27<br>0.77 | Urban | Gordon(15) |
| Melbourne, Australia | 1979 | winter | 0.99 | Urban | Mainwaring and Stirling(17) |

## 4.5 PAHs in vehicle emission

High molecular weight hydrocarbons emitted from car exhaust were identified under varying conditions of engine load and the concentrations of the eight polycyclic aromatic hydrocarbons found in the chromatogram were measured.

To obtain samples, a 40 cm length of metal tube was placed in the car exhaust, and the outlet of the tube connected to a filter holder. The pump was adjusted at a flow rate of 2.5 l/min., so that the volume of each sample was 5-10 litre as sampling time varied from 2 to 4 minutes. The glass fibre filters were weighed before and after sampling to determine the amount of particulate collected. Glass fibre filters were transported from the field in a dried plastic container which was sealed with tape.

Seven types of cars were tested;

1.Toyota Carina without catalyst, unleaded petrol from Sainsbury

2.Toyota Corolla, petrol injection with catalyst, unleaded petrol from Sainsbury

3.Ford Escort 1600, without catalyst, unleaded petrol from Esso

4.Rover 218SDT, without catalyst, diesel fuel from Sainsbury

5.Vauxhall Corsa, with catalyst, unleaded petrol

6. Passatt, with catalyst, unleaded petrol.

7.Vauxhall Cavalier, Turbo diesel, without catalyst

### 4.5.1 Identification of pollutant

About 40 high molecule weight hydrocarbons were identified by GC-Mass Spectrometry Table 4.13. All of the compounds formed in car exhaust are mostly aromatic hydrocarbons. Details of the formation of high molecular weight hydrocarbons during pyrosynthesis and under oxygen-deficient conditions or cracking of organic compounds is explained in chapter one. The concentrations of some hydrocarbons are low, e.g. perylene, methylfluorane and some are high, e.g. fluoranthene, pyrene.

### 4.5.2 Results

Data relating to the eight individual compounds studied, obtained from the exhausts of seven different cars under different tests conditions, are included in Table 4.14-4.18. The amounts of PAH in internal combustion with hot and cold starts are shown in Table 4.14 and 4.15 and indicate level of PAHs follows hot start are higher than for cold start conditions.

Amounts of aromatic hydrocarbons in unleaded fuel for internal combustion cars were between 29 and 35%.According to studies by Blumer (31) in 1976 and westerholm (18), et al. in 1988 the amount and range of PAH produced from any pyrolytic process varies widely, being dependent upon the fuel type and combustion conditions. The aromatic hydrocarbon contents of fuel has been the main focus of concern and is directed at the composition of fuels, since benzene and its derivatives produce more PAH than aliphatic hydrocarbons (Hoffman et al., 1965)(10). A number of investigations have shown that PAH emission increases as the aromatic content increases (Candeli et al., 1974; Begeman and Colucci, 1970; Gross 1972,) (6,11,12). Not all aromatic compounds have the same

Table 4.13 Compounds found in chromatograph of diesel exhaust particulates with GC-MS

| No | Compounds | No | Compounds |
|---|---|---|---|
| 1. | Naphthalene | 22 | $C_4$-fluorenes |
| 2. | acenaphthylene | 23 | pyrene |
| 3. | 2-naphthaldehyde | 24 | methylphenylnaphthalenes |
| 4. | 1-naphthaldehyde | 25 | $C_3$-phenanthrenes |
| 5. | methylnaphthaldehyde | 26 | methylfluoranthenes |
| 6. | methylfluorenes | 27 | methylpyrenes |
| 7. | 6-methyl-2-naphthaldehyde | 28 | $C_4$-phenanthrenes |
| 8. | fluorenone | 29 | $C_3$-phenylnaphthalenes |
| 9. | 2-methylfluorenes | 30 | $C_5$-fluorenones |
| 10 | 9,10-anthracenedione | 31 | benzo (ghi)fluoranthene |
| 11 | dibenzothiophene | 32 | benzo(a)anthrecene |
| 12 | $C_4$-naphthaldehyde | 33 | chrysene |
| 13 | phenanthrene | 34 | nitropyrene |
| 14 | 3-methylphenanthrene | 35 | benzofluoranthene |
| 15 | 2-methylphenamthrene | 36 | benzo(a)pyrene |
| 16 | 2-phenanthrenecarboxaldehyde | 37 | benzo(e)pyrene |
| 17 | 1. and 4-methylphenanthrene | 38 | perylene |
| 18 | 1-methylphenanthrene | 39 | dibenzo(a,h)anthrecene |
| 19 | phenylnaphthalene | 40 | 2,2 -Binaphthyl |
| 20 | $C_2$-Phenanthrenes | | **C10-C25 Aliphatic Hydrocarbons** |
| 21 | fluoranthene | | |

effect, suggesting the importance of the individual aromatic constituents in a fuel (Candeli et al. 1974, 1983)(7). The aromatic fraction in fuel, for either petrol or diesel engine, generally contains a broad spectrum of aromatic compounds, ranging from $C_6$ to $C_{10}$ or $>C_{10}$ , although the heavier compounds ($>C_{10}$ ) are present only in a low percentage (Candeli et al. 1974)(6). It was found that benzene derivatives, such as ethyl benzene and xylene, were better precursors for PAH formation than benzene itself (Candeli et al. 1974, 1983)(6,7). In general, the greater the content of high-boiling aromatic compounds in fuels, the higher the PAH content (Hall et al., 1982; Pedersen et al., 1980)(8,9), therefore the total atmospheric particulates found in internal combustion engines exhaust are lower than for diesel engines. But concentration of PAHs is still high when there are more aromatic hydrocarbons present in the fuel. Table 4.14 and Table 4.18 shown PAHs concentration in internal combustion and diesel engines under hot start conditions. Results indicate that emission of anthracene, phenanthrene, fluoranthrene, pyrene, benzo(a)anthracene chrysene, benzo(a)pyrene and benzo(e)pyrene from diesel engines are 1.5,1.57, 1.14, 1.12, 1.29, 1.11, 1.11, 2.16 respectively higher than for internal combustion engines. Catalytic converters cause a decrease in the emissions of polycyclic aromatic hydrocarbons from car exhaust. Table 4.15 and Table 4.16 show the PAHs concentration with and without catalyst internal combustion under hot start conditions. Results indicate that emission of anthracene, phenanthrene, fluoranthrene, pyrene, benzo(a)anthracene chrysene, benzo(a)pyrene and benzo(e)pyrene without catalyst are 3.82, 4.80, 3.94, 3.33, 2.34, 2.5, 3.29, 4.91 respectively higher than with catalyst for internal combustion engines.

The fuel for diesel engines has large molecules of aliphatic hydrocarbons and aromatic hydrocarbons. PAHs are not only produced from pyrosynthesis of aromatic hydrocarbons but are also made from large molecular weight aliphatic hydrocarbons. Consequently concentrations of PAHs in diesel engines are high as indicated in Tables 4.17 and 4.18. The concentration depends on the condition of the car, temperature, e.g. cold start burning of hydrocarbons is incomplete and PAHs are increased due to an increase in unburned hydrocarbons.

Table 4.14 Concentration of polycyclic aromatic hydrocarbons ( $\mu g/m^3$ ) in hot start internal combustion without catalyst

| Compounds | Mean | S.D | Max. | Min. |
|---|---|---|---|---|
| Phenanthrene | 3.2 | 2.10 | 10.21 | 0.10 |
| Anthracene | 1.33 | 1.05 | 5.66 | 0.02 |
| Fluoranthrene | 7.5 | 3.41 | 17.66 | 1.34 |
| Pyrene | 6.44 | 3.04 | 12.33 | 0.98 |
| Benzo(a)anthracene | 2.12 | 1.7 | 5.23 | 1.12 |
| Chrysene | 1.70 | 1.43 | 4.70 | 0.01 |
| Benzo(a)pyrene | 1.44 | 2.20 | 5.70 | 0.07 |
| Benzo(e)pyrene | 0.97 | 1.23 | 3.89 | 0.09 |

Table 4.15 Concentration of polycyclic aromatic hydrocarbons ( µg/m$^3$ ) in cold start internal combustion without catalyst

| Compounds | Mean | S.D. | Max. | Min. |
|---|---|---|---|---|
| Phenanthrene | 4.7 | 3.18 | 8.21 | 0.10 |
| Anthracene | 2.26 | 1.73 | 5.66 | 0.02 |
| Fluoranthrene | 12.23 | 4.13 | 17.66 | 1.34 |
| Pyrene | 5.94 | 6.80 | 11.33 | 0.98 |
| Benzo(a)anthracene | 1.76 | 2.5 | 5.23 | 1.12 |
| Chrysene | 2.35 | 2.1 | 4.70 | 0.01 |
| Benzo(a)pyrene | 1.78 | 2.20 | 5.70 | 0.07 |
| enzo(e)pyrene | 1.13 | 1.69 | 3.89 | 0.09 |

Table 4.16 Concentration of polycyclic aromatic hydrocarbons (µg/m$^3$ ) in hot start internal combustion with catalyst

| Compounds | Mean | S.D. | Max. | Min. |
|---|---|---|---|---|
| Phenanthrene | 1.23 | 2.66 | 3.2 | 0.07 |
| Anthracene | 0.47 | 1.33 | 2.7 | 0.01 |
| Fluoranthrene | 2.11 | 2.1 | 4.28 | 0.21 |
| Pyrene | 1.78 | 2.5 | 5.13 | 0.12 |
| Benzo(a)anthracene | 0.75 | 1.2 | 2.12 | 0.05 |
| Chrysene | 0.94 | 0.70 | 2.70 | 0.06 |
| Benzo(a)pyrene | 0.87 | 1.44 | 2.10 | 0.009 |
| Benzo(e)pyrene | 0..23 | 0.97 | 1.70 | 0.002 |

Table 4.17 Concentration of polycyclic aromatic hydrocarbons (µg/m$^3$ ) in cold start diesel engine

| Compounds | Mean | S.D | Max. | Min. |
|---|---|---|---|---|
| Phenanthrene | 5.18 | 2.65 | 11.23 | 1.24 |
| Anthracene | 3.27 | 2.84 | 6.48 | 0.34 |
| Fluoranthrene | 8.10 | 3.10 | 13.89 | 1.34 |
| Pyrene | 6.23 | 2.95 | 11.67 | 0.45 |
| Benzo(a)anthracene | 3.10 | 1.19 | 4.19 | 0.04 |
| Chrysene | 1.70 | 0.90 | 3.12 | 0.04 |
| Benzo(a)pyrene | 1.21 | 1.84 | 3.20 | 0.001 |
| Benzo(e)pyrene | 0.92 | 1.23 | 2.80 | 0.04 |

Table 4.18 Concentration of polycyclic aromatic hydrocarbons ( μg/m$^3$ ) in hot start diesel engine

| Compounds | Mean | S.D | Max. | Min. |
|---|---|---|---|---|
| Phenanthrene | 4.8 | 2.21 | 7.16 | 1.10 |
| Anthracene | 2.10 | 1.80 | 6.45 | 0.23 |
| Fluoranthrene | 8.6 | 4.32 | 14.45 | 1.60 |
| Pyrene | 7.2 | 4.10 | 10.70 | 0.60 |
| Benzo(a)anthracene | 2.75 | 2.21 | 6.41 | 0.43 |
| Chrysene | 1.90 | 1.97 | 4.10 | 0.30 |
| Benzo(a)pyrene | 1.60 | 2.23 | 6.50 | 0.60 |
| Benzo(e)pyrene | 2.10 | 2.54 | 8.69 | 0.45 |

## 4.6 Summary

A method has been developed to analyse polycyclic aromatic hydrocarbons (PAHs) in airborne particulate by Thermal Desorption and GC-Mass Spectrometry. Samples were obtained from ambient air using fibre glass filters with a flow rate 2 litre/minute over a period between 1 to 5 hour. The filters were placed in an empty tube and the pollutants transferred to a Carbotrap using Thermal Desorption with helium flow rate of 12-16 ml/minute at temperature of 340°C over 15 minutes. Thermal Desorption was also used to transfer compounds from the Carbotrap to GC-Mass Spectrometer. A 30 metre capillary column was used to separate the hydrocarbons. Results show PAHs associated with particle phase decrease in summer and emission of PAHs depends on density of vehicles, types of engine, fuels and catalyst in exhaust.

## 4.7 Conclusion

1.A new method has been achieved to transfer of PAHs from a filter to a Carbotrap 370 by Thermal Desorption. The recovery of extracted PAHs to Carbotrap was 95 to 102% indicating that the efficiency of the Carbotrap is high. A wide range of PAHs can transfer from the filter to the Carbotrap in 15 minutes indicating high efficiency in a short time. The PAHs can be removed from the Carbotrap by heating. The Carbotrap also has good thermal stability and does not absorb CO, $NO_X$ and $SO_2$. It is good for focussing the sample and injection gives a well resolved chromatogram.

2. The new analytical method was used to study:

a) the amount of PAHs in ambient air.
b) the concentration of PAHs inside a building
c) identification of PAHs in vehicle emission
d) the effect of catalytic converters on PAHs emission
e) the difference in emission between diesel and petrol engine

The results of these studies show the particulate phase of PAHs decreases in summer due to high temperature; the concentration of fluoranthene and pyrene are higher than other PAHs; PAHs emitted to air from vehicles contribute to the pollution inside houses especially in the summer season; 40 high molecules of PAHs and other hydrocarbons were identified in the soot of diesel emissions; the effect of catalytic converters on PAHs emissions from diesel and internal combustion engines is that a fresh catalyst was capable of removing approximately 70-90% of PAH emission from car exhaust; there is an additional tendency that a diesel car without catalyst emits more PAHs than an internal combustion car.

## 4.8 References

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# Chapter Five: Concentrations of Volatile Organic Compounds in Ambient Air Conditions at Brunel University and in Vehicle Emissions

## 5.1 Introduction

Volatile organic compounds which are being emitted from car exhausts to ambient air in urban sites and are known to affect human health. Benzene, a component of petrol, is known to be a carcinogen and a link between benzene and leukaemia has been shown in some epidemiological studies. The control of benzene is important and new legislation by Air Quality Standards in the UK recommend 5 ppb for permitted levels of benzene (2). An increase in the concentration of volatile organic compounds can also cause an increasing amount of secondary pollution associated with ozone, peroxyacetyl nitrate (PAN) and aldehydes (described in chapter one). Secondary pollution causes irritation in eye and lung which are increased in air when inversion (pollution to be trapped under a dense layer of air) occurs (5,6).

Measurement and control of monocyclic aromatic hydrocarbons related to the production of polycyclic aromatic hydrocarbons (PAHs) in air is important because, according to some studies, an increase in aromatic hydrocarbons in fuel increases the PAHs in air (14,15).

Because of the importance of control of hydrocarbons and other pollutants in air, the European Community Directive (91/441/EEC) requires that all new light duty motor vehicles be fitted with catalytic converters (21). For these reasons, therefore, it is important to know the concentration of volatile organic compounds in air and in vehicle emissions.

Two international methods from EPA and NIOSH use T*enax* and charcoal for sampling benzene and other alkyl derivatives but there is not a internationally recognized method for the measurement of hydrocarbons used a Carbotrap. For this reason the use of Carbotrap as a sampler was also evaluated in the present work (3,4).

The objectives of the work described in this chapter are:

1. to determine the optimum conditions for sampling and analysis of volatile organic compounds with a Carbotrap in ambient air.
2. to identify the volatile organic compounds in ambient Uxbridge air and vehicle emissions.
3. to obtain quantitative measurement of the principal hydrocarbons in ambient Uxbridge

air and vehicle emissions under different conditions.

## 5.2 Instrumentation

To analyse the volatile organic compounds in ambient air the following pieces of apparatus were used:

### 1. Sampling pump

A sampling pump from Negretti Company, Model NR700, was used to obtain samples of volatile organic compounds. The pump was connected to the Carbotrap holder with a Teflon tube. Calibration and adjustment of the sampling flow rate was achieved by using a flow meter connected between the sampler and pump. The flow rate of the pump was 0-5 litre/minute.

**Fig. 5.1 Sampling pumps and Calibration System**

### 2. Flow meter

The calibration of the sampling pump was performed by a flow meter with capacity 0-500 ml/minute. For high performance, the flow meter was calibrated with a soap bubble (soap bubble was described in chapter 4 section 4.2.2).

### 3. Carbotrap 300

The Carbotrap was described in chapter four section 4.2.4. Two sizes of Carbotrap 300 were used in the study: 4 and 2mm diameter. Carbotrap with 4 mm diameter was used for sampling of volatile organic compounds from air and Carbotrap with 2mm diameter was used in studies of Thermal Desorption methods. The Carbotrap 300 has three parts;

I) Carbopack C
ii) Carbopack B
iii)Carbosieve S-III Carbon Molecular Sieve

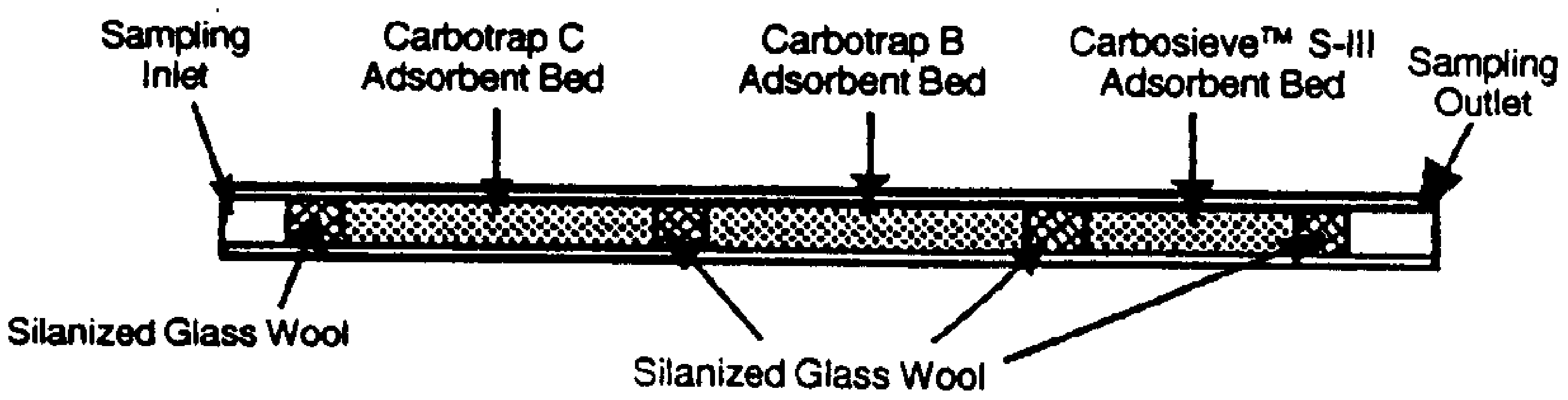


**Fig. 5.2 Carbotrap 300 for focussing of PAHs from filter**

Carbopack B and C are similar to Carbotrap 370 (described in section 4.2.4.1 of chapter four )

Carbosieve S-III is a spherical carbon molecular sieve which has a large surface area (about 800m$^2$/gram) and 15 to 40Å pores. This structure makes the Carbosieve S-III adsorbent very useful for trapping small molecules such as vinyl chloride.

**4. Thermal Desorption Unit** (described in chapter 4 section 4.2.5)

**5. Gas chromatography-Mass Spectrometry**(described in chapter 4 section 4.2.6 but a 60m × 0.25mm, 1.50 µm film, VOCOL capillary column was used to separate volatile organic compounds.)

**6. Weather Monitor** (described in chapter 4 section 4.2.7)

**7. Gas Chromatograph**

A gas chromatograph, Varian 3700, equipped with a Flame Ionization Detector (FID) was used for the analysis of the volatile organic compounds. Separation of the volatile organic compounds was achieved on a 60m × 0.25mm, 1.50 µm film VOCOL capillary column. This column typically has a thicker stationary phase film that ensures greater retention and resolution of the more volatile compounds. Nitrogen or helium was used as carrier gas at a flow rate of 2 ml/minute. The temperature of the column was held at 35°C for 4 minutes and then increased to 200°C at a rate of 4° C/minute and held for 4 minutes.

### 5.3 Determination of optimum conditions for sampling volatile organic compounds with a Carbotrap in ambient air

Long sampling times and high flow rates may cause some compounds to breakthrough the Carbotrap, therefore, both factors were evaluated as follows:

(a) Effects of flow rates on adsorbent capacity when sampling air

(b) Effect of time duration on adsorption capacity of a Carbotrap tube

### 5.3.1 Effect of flow rates on adsorbent capacity when sampling air

The compatibility of the pumping system associated with the Carbotrap tubes was investigated using different flow rates namely : 50, 80, 100, 150 and 200 ml min$^{-1}$. A tube was connected between the pump and a flow meter and the observed fall off in flow rate particularly at the higher values (at 200 ml min$^{-1}$) was noted. Table 5.1 is a summary of the data obtained for the collection of five different compounds under different flow rate conditions. It is clear, as is also demonstrated in Fig.5.3, that a higher flow rate has a negative effect on the trapping efficiency of the Carbotrap. The above experimental work indicates a flow rate of 80-100 ml/minute and that a sampling volume 1-4 litre is acceptable for street air samples. A flow rate of more than 100 ml/min causes compounds to breakthrough the Carbotrap ( Data from Figure 5.3 was obtained over one day under the same condition with one sampling pump so there is no error bar in the figure).

Table 5.1 Concentration of individual hydrocarbons in air at different flow rate

| Time (min.) | Flow Rate (ml/min) | Concentration μg/m$^3$ | | | | |
|---|---|---|---|---|---|---|
| | | Benzene | Toluene | Ethyl benzene | m- and p-xylene | o-xylene |
| 30 | 50 | 9.7 | 13.3 | 2 | 8.1 | 4.3 |
| 30 | 80 | 10.4 | 13.9 | 2.1 | 8.3 | 3.8 |
| 30 | 100 | 10.1 | 13.1 | 1.9 | 8.2 | 3.9 |
| 30 | 150 | 8.2 | 12.7 | 1.2 | 6.2 | 2.5 |
| 30 | 200 | 7.2 | 10.2 | 1.1 | 4.8 | 2.8 |

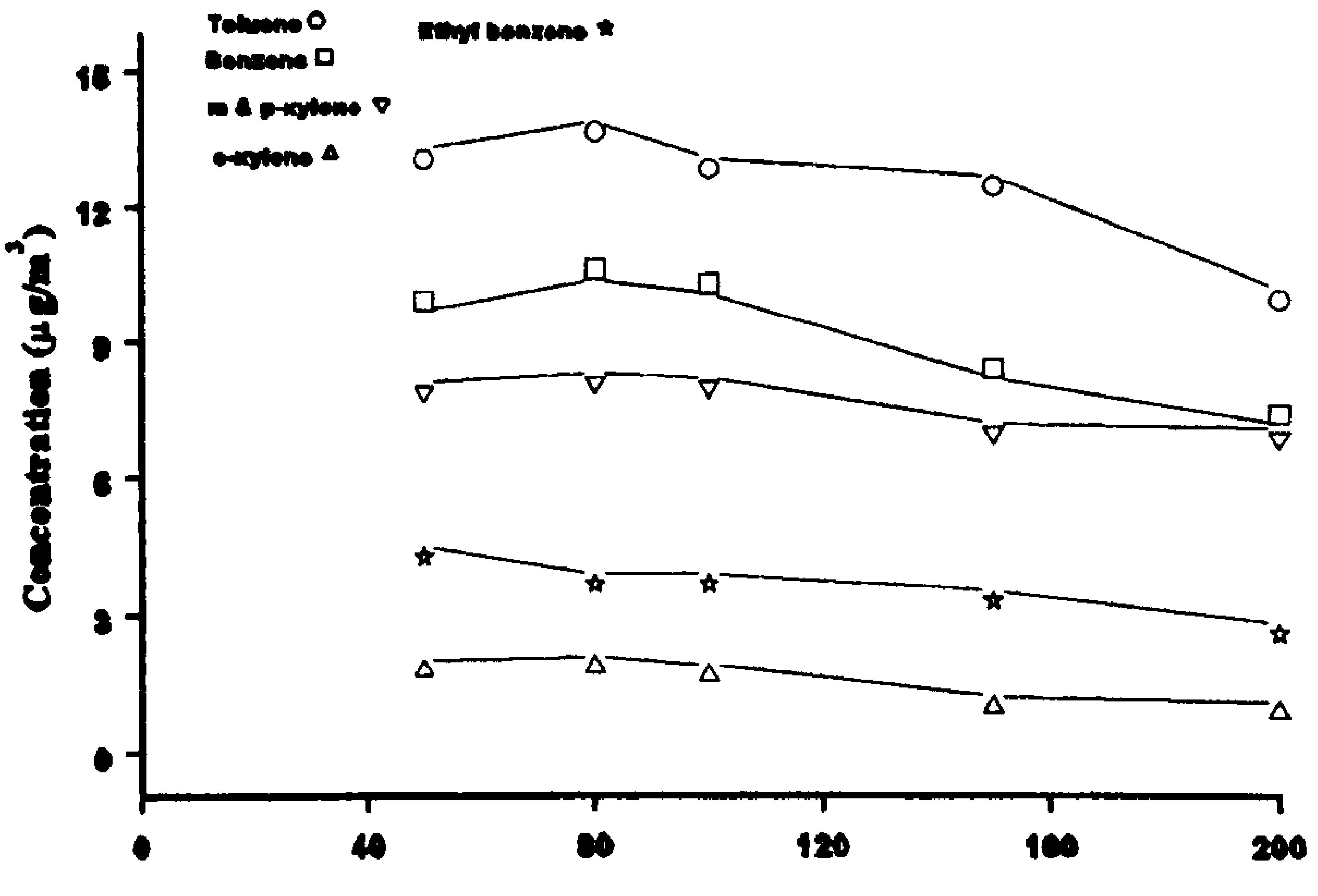


Fig. 5.3 Effect of flow rate on sampling of individual hydrocarbons with Carbotrap(300) on campus of Brunel university

### 5.3.2 Effect of time duration on adsorption capacity of a Carbotrap tube

The time taken for sampling air was evaluated by sampling under similar conditions (temperature, humidity, wind speed).Table 5.2 is a summary of data obtained for the collection of five different compounds at different time periods at the optimum flow rate of 100 ml/min (see 5.3.1). The data in Fig. 5.4 show that increasing the time period had a negative effect on the trapping efficiency (data from Figure 5.4 was obtained over one day under the same condition with one sampling pump so there is no error bar in the figure).

Table 5.2 The effect of time upon trapping capacity of Carbotrap

| Flow rates (ml/min) | Time (min.) | Benzene | Toluene | Ethyl benzene | m + p xylene | o-xylene |
|---|---|---|---|---|---|---|
| 100 | 10 | 9.3 | 12.6 | 2.1 | 5.7 | 2.7 |
| 100 | 30 | 9.7 | 13.4 | 2.6 | 6.1 | 3.1 |
| 100 | 45 | 9.4 | 13.1 | 2.3 | 5.2 | 2.6 |
| 100 | 60 | 8.7 | 11.7 | 2.0 | 4.8 | 2.4 |
| 100 | 120 | 7.6 | 9.4 | 1.6 | 4.3 | 1.8 |
| 100 | 180 | 6.6 | 9.1 | 1.3 | 4.1 | 1.7 |

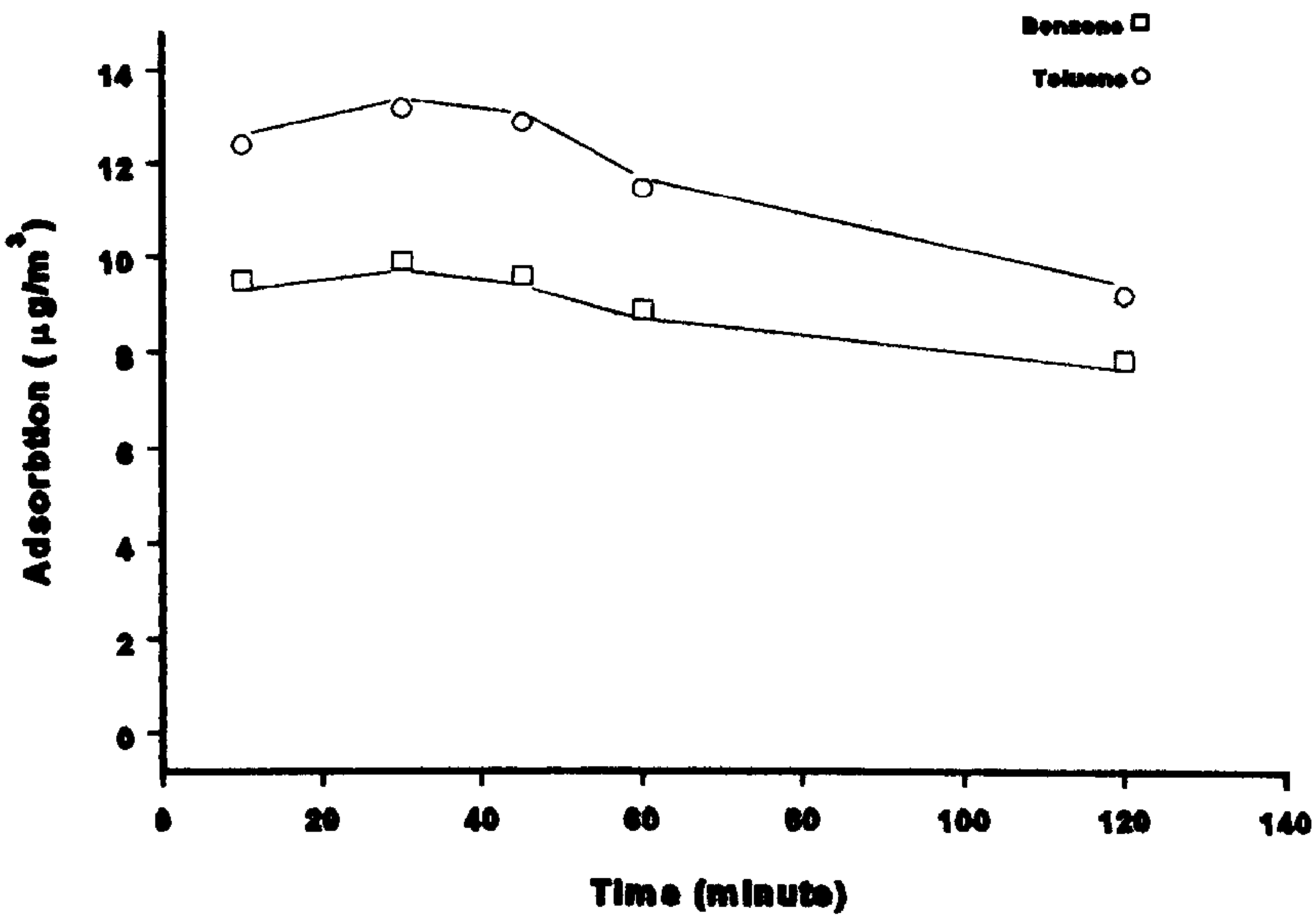


Fig. 5.4 Effect of time on sampling of toluene and benzene with Carbotrap(300) on campus of Brunel university

### 5.3.3 Calibration of Gas Chromatograph with Thermal Desorption

The GC was calibrated using the Thermal Desorption apparatus by the injection of specified amounts of compounds under different pressures of inert gas and temperature programmes for the GC column.

The results have shown that the optimum pressure is between 40-60 psi and the best temperature program for the column is initially 35°C which is increased up to 200°C at a rate of 4° C/minute. The detector temperature was maintained at 250°C.

To specify the optimum conditions for temperature, time and flow rate to focus a sample in the Thermal Desorption Unit, the following experiments were performed.

(1) Measurement of preparation (focussing) in Thermal Desorption

(2)Measurement of time taken to focus a sample to a 2mm Carbotrap 300 tube

(3) Measurement of a suitable flow rate to focus a sample to a 2mm Carbotrap 300 tube

#### 5.3.3.1 Measurement of temperature for preparation of samples

The effect of increasing temperature was evaluated by injecting 1 μl of benzene standard into an empty tube on the Thermal Desorption apparatus. The volatile contents of the tube were then transferred to a 2 mm Carbotrap 300 located in the focussing position. The temperature was fixed and the time of transfer was 9 minutes. The collected sample was passed to the GC column for benzene analysis. This experiment was performed over the temperature range 200- 400°C. The results were compared with those obtained when 1 μl of benzene standard was injected directly into the GC column. Results in Fig. 5.5 and Table 5.3 indicated that optimum temperature range is 280-320°C for a good recovery of benzene.

Table 5.3 Recovery of benzene at different temperature for focussing

| Temperature (°C) | Data of recovery (μg) | Recovery (%)★ | Mean of recovery (%) |
|---|---|---|---|
| 200 | 0.251, 0.267, 0.268 | 57, 60.8, 61 | 59.6 |
| 250 | 0.364, 0.348, 0.344 | 82.9, 79.2, 78.5 | 80.2 |
| 275 | 0.413, 0.437, 0.401 | 94.0, 99.5, 91.3 | 94.9 |
| 280 | 0.453, 0.445, 0.431 | 103.1, 101.3,98.1 | 100.8 |
| 300 | 0.463, 0.453, 0.419 | 105.4, 103.1,95.4 | 101.3 |
| 320 | 0.458, 0.431, 0.452 | 104.3, 97.9,102.7 | 101.4 |
| 360 | 0.453, 0.433, 0.449 | 102.9,98.6,102.0 | 101.2 |

★Weight of benzene in 1 μl standard solution was 0.439 μg and recovery(%) calculated according to the following equation:

$$Recovery = \frac{Average\ of\ recovery}{0.439} \times 100$$

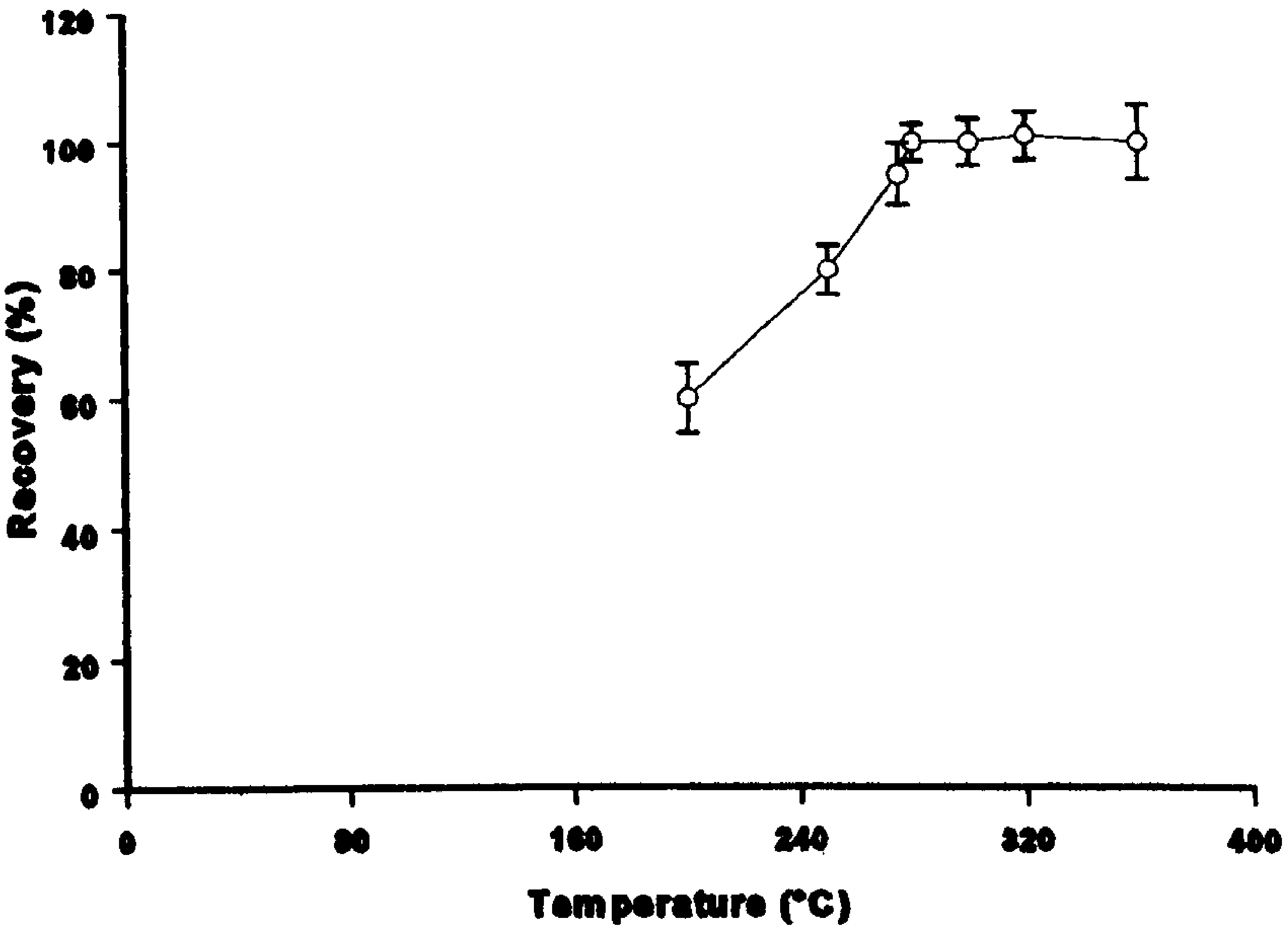


Fig. 5.5 Effect of changes of temperature for focussing benzene by Thermal Desorption

### 5.3.3.2 Measurement of time taken to focus a sample to a 2mm Carbotrap 300 tube

To determine the optimum time for preparation of focussed samples when the helium flow rates are 5-10 ml/minute a 1µl standard benzene sample was injected into an empty tube on the Thermal Desorption Unit. The focused sample was then transferred to the desorption part (procedure 5.3.3.1) and the amount of benzene was measured by the GC column. A range of transfer times, 4-20 minutes, was used and the results compared with those obtained by direct injection on the GC column. From Fig. 5.6 it appears that transfer times greater than 9 minutes do not affect the recovery of benzene.

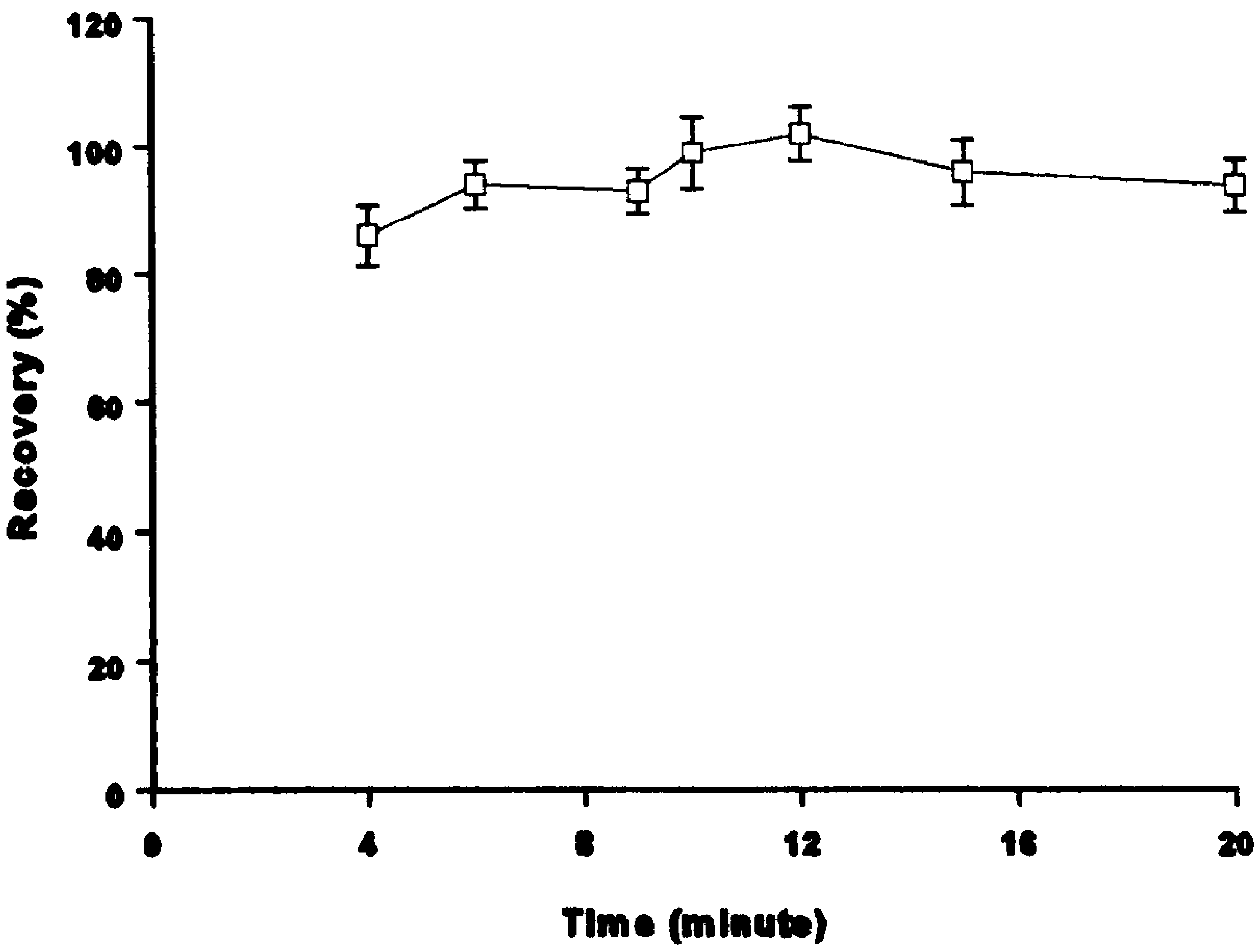


Fig. 5.6 Effects of period of time on focussing of benzene in Thermal Desorption

### 5.3.3.3 Measurement of a suitable flow rate to focus a sample to a 2mm Carbotrap 300 tube

The flow rate for the preparation of samples (focussing from a 4 mm to 2 mm tube) was evaluated by injection of 1 µl of benzene standard, using procedure 5.3.3.1. This procedure was performed in triplicate at different flow rates and the results were compared with the direct injection of similar size samples to the GC column. The results are shown in Figure 5.7 and indicate that a suitable flow rate is 5-10ml/min. An increase in the flow rate to more than 10 ml/min caused a decrease in recovery because of benzene breakthrough from the Carbotrap

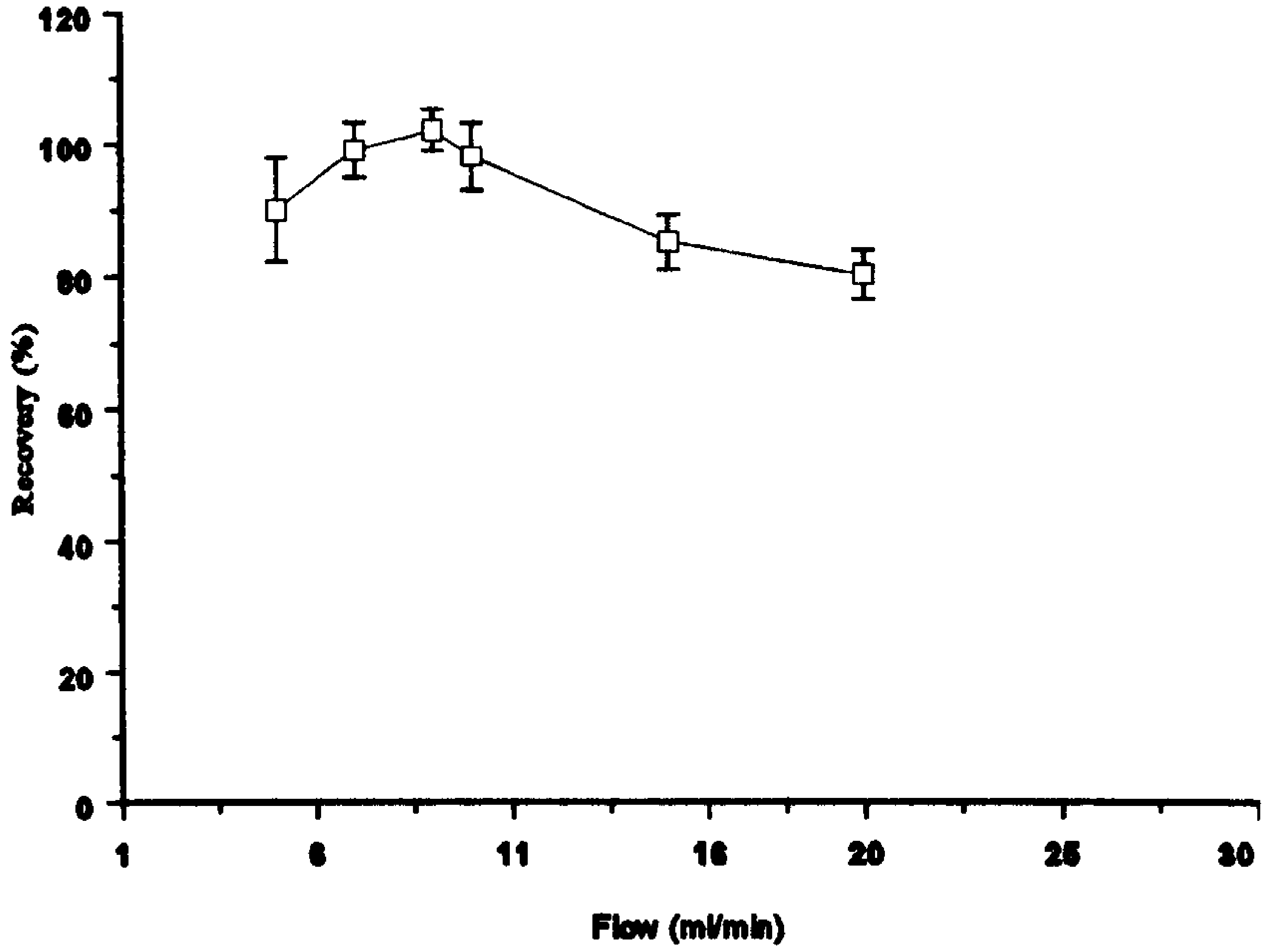


Fig. 5.7 Effect of changing flow rate for focussing of benzene in Thermal Desorption

### 5.3.3.4 Summary of conditions for sampling and analysis

1.The best conditions for focussing and desorption of compounds in a Thermal Desorption Unit are as follows;

a) Valve compartment; 230°C (recommended by the manufacturer ).

b) Tube desorption chamber when sample in transferred to focussing position (sample preparation); 320°C

c) Transfer line from TDU to GC or GC/MS; 230°C (recommended by the manufacturer).

d) Time for transfer to focussing portion; 9 minute.

e) Flow of inert gas for preparation sample (focussing); 5-10 ml/minute.

f) Flow of inert gas to transfer ( desorption) compounds to GC or GC-MS; 2-3.5ml/minute.

2.The best conditions for obtaining samples from air are as follows;

a) Time duration to obtain samples from air: 45 minutes..

b) Flow rates of pump sampling to obtain samples from air; 80-100 ml/min.

### 5.4 Sample collection

Samples were obtained from air with a sampling pump and the 4mm Carbotrap 300 (described in section 5.2 ). A flow meter was used to measure the flow rate of the pump (described in section 5.2). The flow of the pump was set 100 ml/minute (described in 5.3.1). This can change during sampling. Therefore the flow rate was checked after each sample collection. The length of time for sampling is 45 minutes (described in 5.3.2). After sampling, the Carbotrap 300 was transported in a holder which was sealed with tape.

Calculation of the volume of sample is the same for PAHs sampling (refer to 4.3.5 in chapter four)

### 5.5 Analysis of samples

A Thermal Desorption Unit (described in section 4.2.5) linked to a gas chromatograph (described in section 5.2) or GC-MS (described in section 4.2.6 in chapter four ) were used to analyse the samples. Thermal Desorption was used for focussing the samples and transfer of compounds to the GC or GC-MS.

#### 5.5.1 Preparation of sample

To prepare the sample, the 4 mm Carbotrap 300 was placed in the chamber of the Thermal Desorption Unit and a 2mm Carbotrap 300 placed in the trapping part of the apparatus to focus compounds. The Thermal Desorption Unit was set at optimum conditions of temperature, flow rate and length of time which are 280-320°C, 5-10 ml/minute and 9 minutes (described in section 5.3.3.1, 5.3.3.2, 5.3.3.3). All of the compounds were focussed from the 4mm Carbotrap to the 2 mm Carbotrap under these conditions.

#### 5.5.2 Desorption of sample to GC-MS

The 2mm Carbotrap300 was placed in the desorption chamber and the GC-MS or GC was set at a temperature program which started at 35°C and increased temperature to 200 °C at the rate of 4° C/minute. The flow rate of inert gas was set at 2-3.5 ml/minute (described in section 5.3.3). The GC column temperature was then increased according to the temperature programme and the components eluting from the column identified and quantified by mass spectrometry.

### 5.5.3 Qualitative analysis of samples

The qualitative determination of volatile organic compounds is similar to PAHs as described in chapter 4 section 4.3.6.3. Figure 5.8 shows the chromatogram of a sample of volatile organic compounds in car exhaust. Figures 5.9, 5.10, 5.11, 5.12, 5.13 show the mass spectra of peaks numbered 496, 841, 1146, 1169, 1258 of chromatogram Fig. 5.8 which are benzene, toluene, ethyl benzene, m- and p-xylene and o-xylene.

### 5.5.4 Quantitative analysis of samples

Gas chromatography and gas chromatography - mass spectrometry were used for the quantitative determination of volatile organic compounds. A standard solvent, recommended by EPA, from Supelco was used to determine standard peaks. This solvent includes benzene, toluene, ethyl benzene, m- and p-xylene and o-xylene. 0.2-1 μl of this standard solvent was transferred to a Carbotrap 300 in the preparation part of Thermal Desorption Unit. The Carbotrap placed in the desorption chamber transfers the standard compounds to the GC-MS or GC (same as samples from air pollution or car exhaust). The sample conditions for the preparation and desorption in Thermal Desorption Unit and GC-MS are the same as the standard samples. Blank samples were also analysed to determine whether any impurity could the transferred to the samples.

The calculation of the concentration of individual hydrocarbons is similar to that for polycyclic aromatic hydrocarbons as described in section 4.3.6.4.

### 5.5.5 Determination of the recovery of individual hydrocarbons under optimum conditions

To determine the recovery of individual hydrocarbons under optimum conditions, 1 μl of the standard solution was transferred to a Carbotrap 300 and the results compared with 1 μl direct injection. This experiment was performed in triplicate. The results in Table 5.4 indicate the recovery is 98.2-101.1%.

Table 5.4 Recovery of individual hydrocarbons in optimum condition.

| Component | Data of Recovery (μg) | Recovery (μg) | Mean of Recovery (%) |
|---|---|---|---|
| Benzene | 0.486 | 97.2 | 98.2 |
| | 0.496 | 99.2 | |
| | 0.502 | 100.4 | |
| Toluene | 0.501 | 100.2 | 100 |
| | 0.503 | 100.6 | |
| | 0.496 | 99.2 | |
| Ethyl benzene | 0.504 | 100.8 | 101.1 |
| | 0.503 | 100.6 | |
| | 0.510 | 102 | |
| m- and p-xylene | 0.498 | 99.6 | 98.7 |
| | 0.487 | 97.4 | |
| | 0.496 | 99.2 | |
| o-xylene | 0.503 | 100.6 | 98.5 |
| | 0.479 | 95.8 | |
| | 0.496 | 99.2 | |

★Weight of individual hydrocarbons in 1 μl EPA standard solution was 0.5 μg and recovery(%) calculated according to the following equation:

$$Recovery = \frac{Average\ of\ recovery}{0.5} \times 100$$

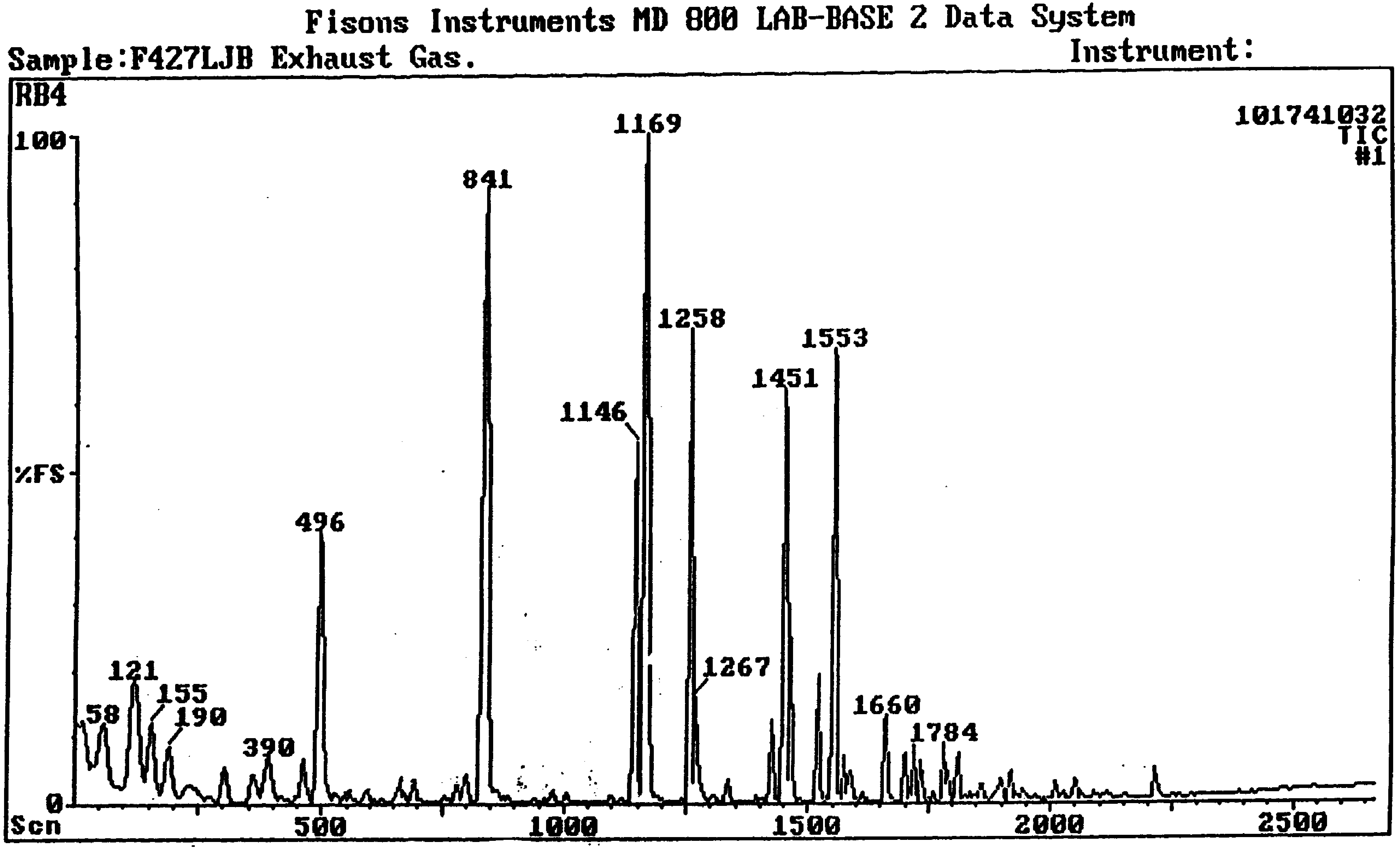


Figure 5.8 Gas chromatogram of a sample of volatile organic compounds from car exhaust.

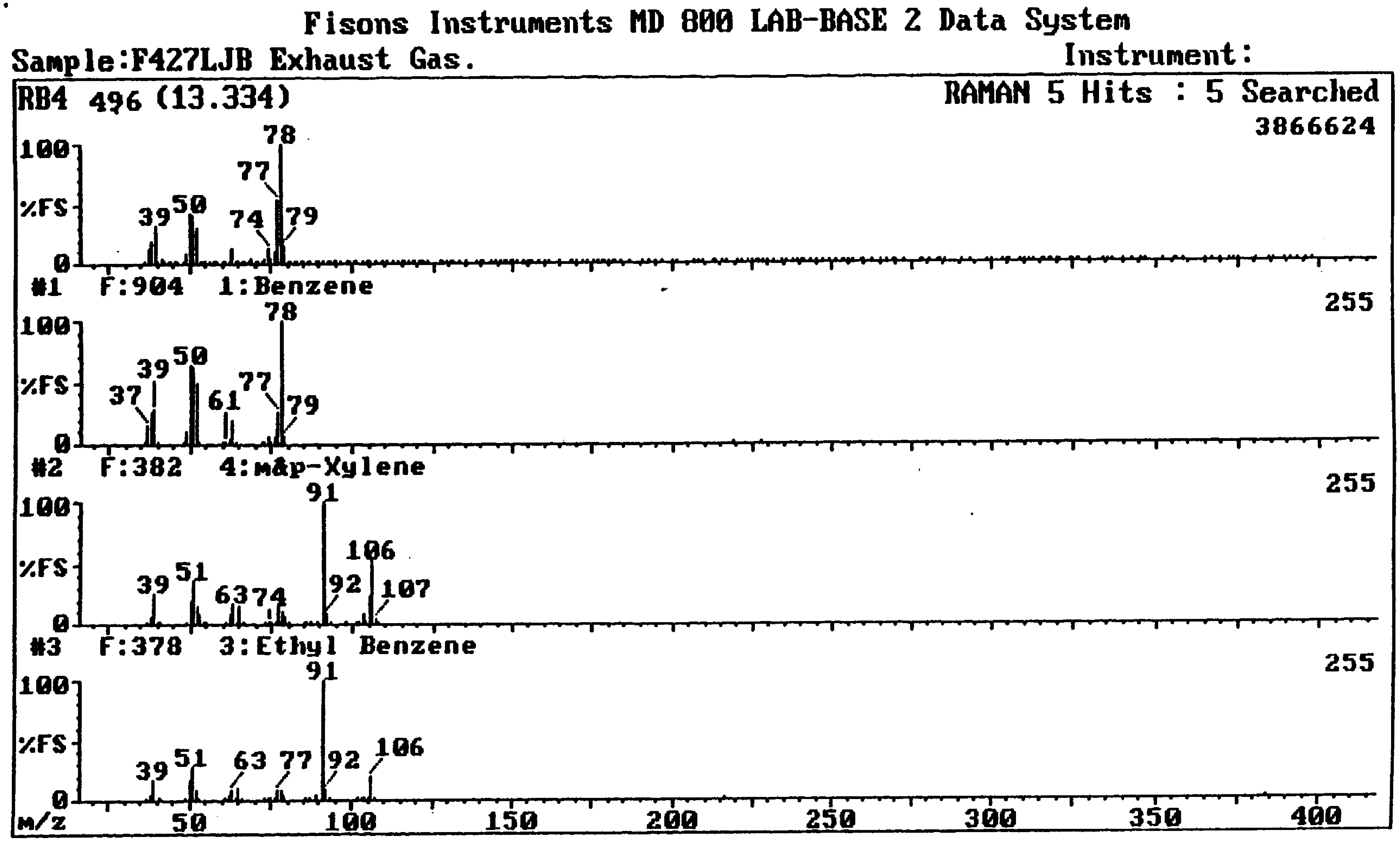


Figure 5.9 Identification of mass spectrum 496 of Fig 5.8 by the software.

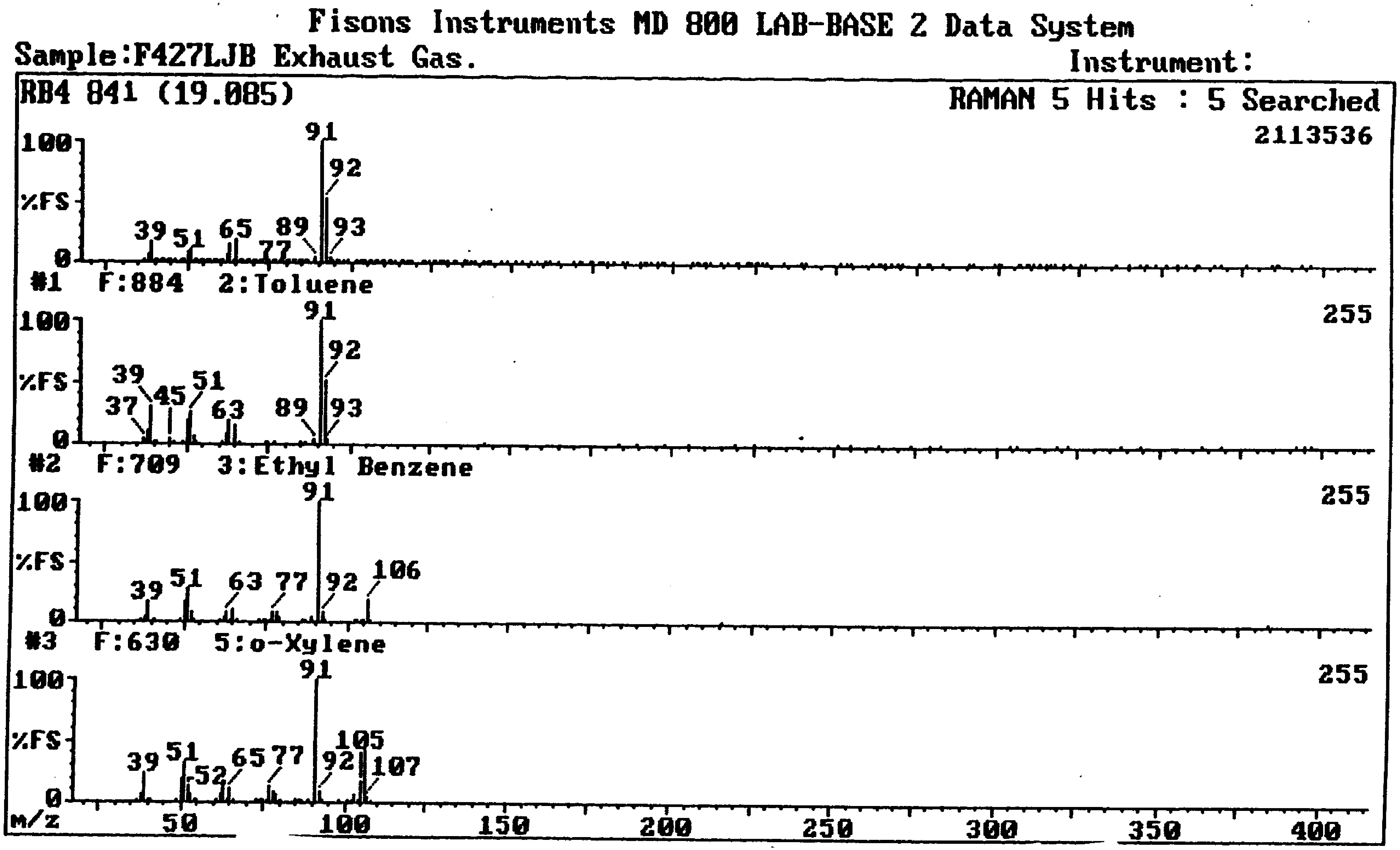


Figure 5.10 Identification of mass spectrum 841 of Fig 5.8 by the software.

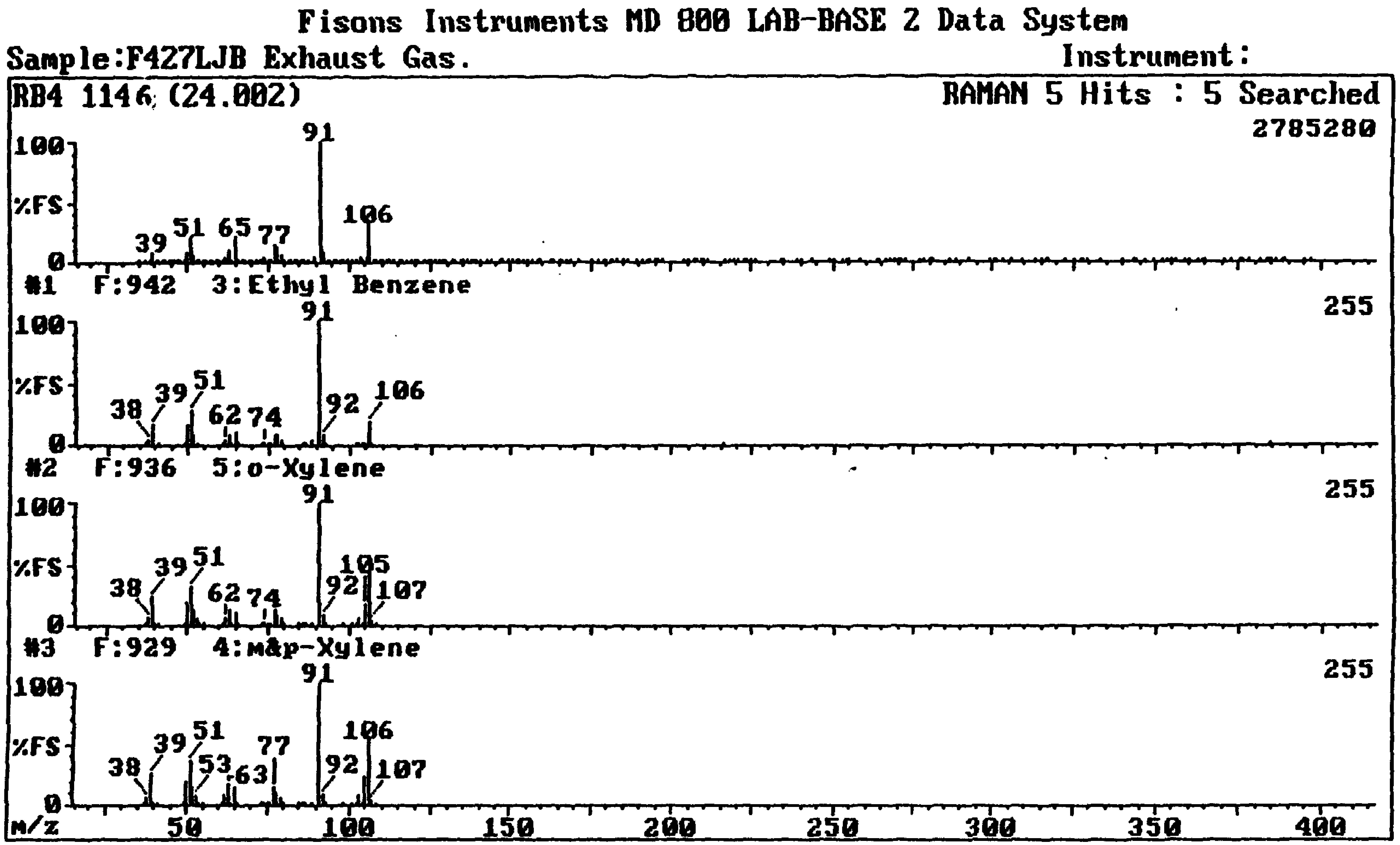


Figure 5.11 Identification of mass spectrum 1146 of Fig 5.8 by the software.

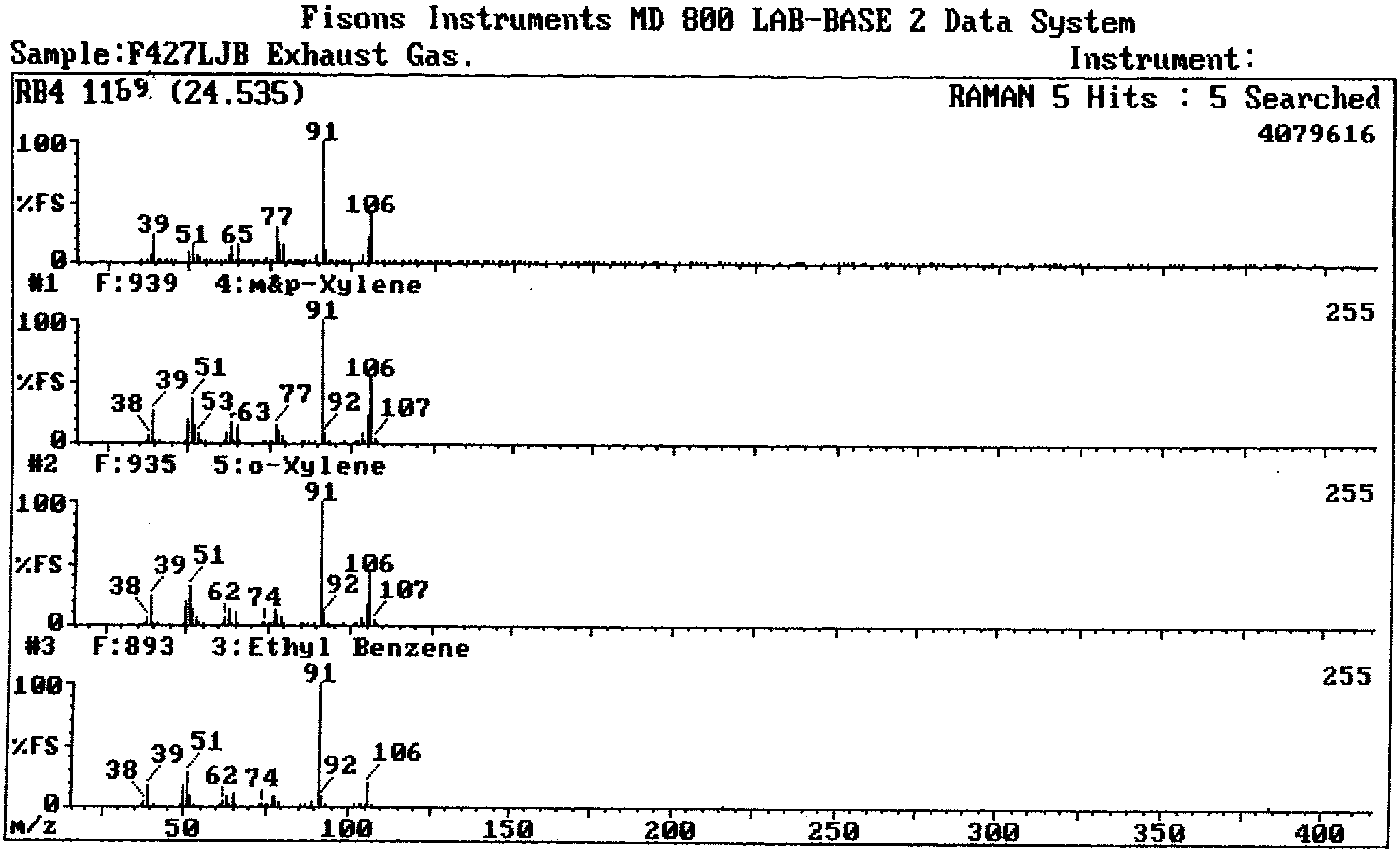
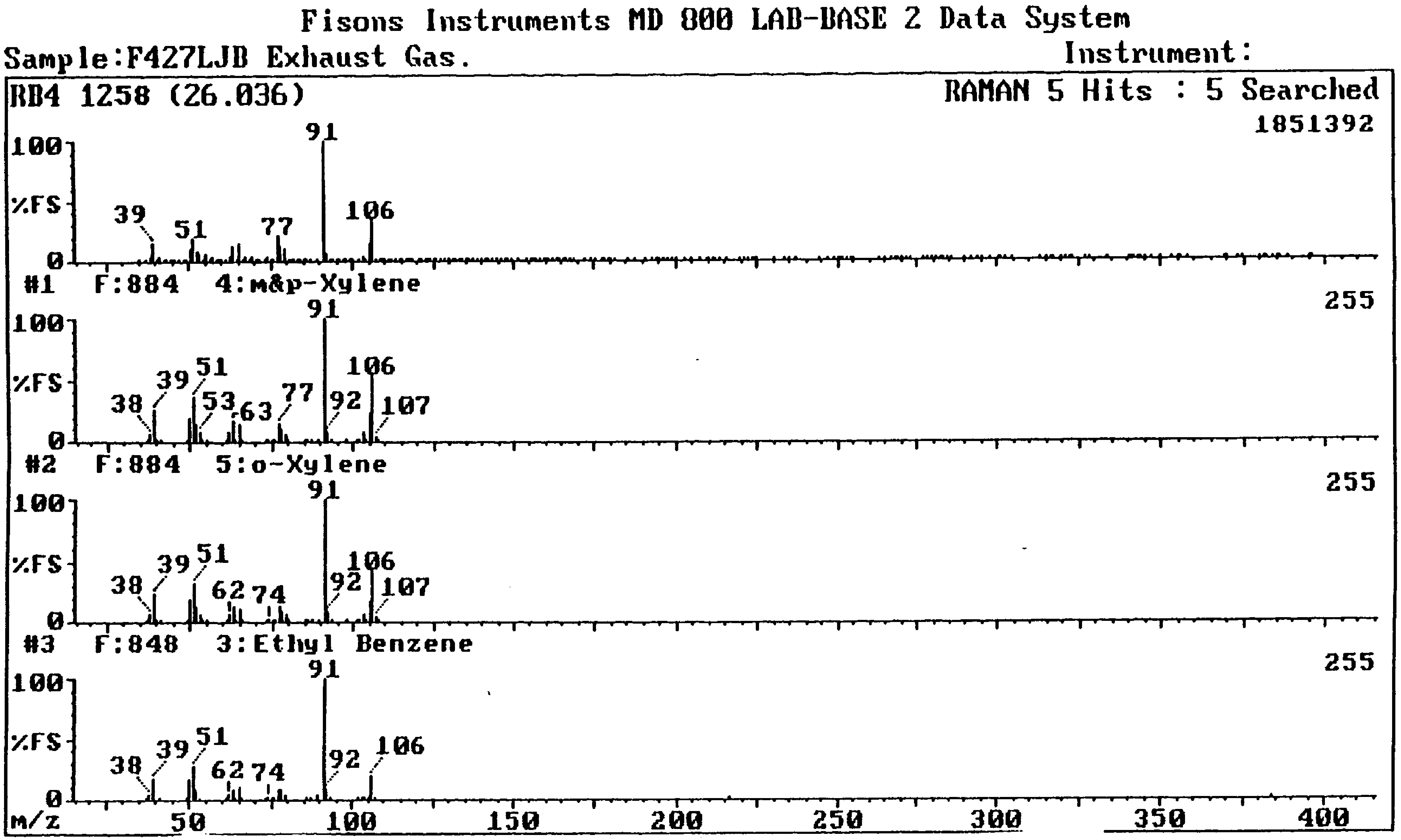


Figure 5.12 Identification of mass spectrum 1169 of Fig 5.8 by the software.



Fisons Instruments MD 800 LAB-BASE 2 Data System

Sample:F427LJB Exhaust Gas.

Instrument:

RB4 1258 (26.036)

RAMAN 5 Hits : 5 Searched

Figure 5.13 Identification of mass spectrum 1258 of Fig 5.8 by the software.

### 5.6 Sampling programs

Over a period of five months, January to August 1995, approximately 150 individual samples were taken at Cleveland Road, a public road which runs through the Brunel campus, and analysed for hydrocarbons, and 50 samples were obtained to measure individual hydrocarbons at car parks. Sampling stations were in three places at Brunel University;

1) Cleveland Road, near to Brunel University, was considered representative of a low traffic street. The approximate traffic density in this street is shown in Table 5.5.
2) A car park at the back of Chemistry Department
3) A car park beside the Engineering Department

Table 5.5 Hourly traffic in Cleveland Road

| Day | Hour | Approx. Hourly traffic |
|---|---|---|
| Saturday | 8:30-18 | 240 |
| Sunday | 8:30-17:30 | 170 |
| Monday-Friday | 8:30-9:30 | 600 |
| | 9:30-15:30 | 350 |
| | 15:30-16:30 | 400 |
| | 16:30-17:30 | 520 |

The positions of the sampling stations are shown in Fig. 5.14. Most of the samples were obtained during the working day with a few collected during weekends. Sampling was concentrated on the busy period, 09.00-17.00, but was extended in a few instances over a twelve-hour period (8.00-20.00 h).

The sampling points were at a distance of 2.0 m from the kerb at a height 1.5-2.0 m above ground level.

### 5.7 Results and discussion

#### 5.7.1 Analysis of samples

27 hydrocarbons were identified with GC-Mass Spectrometry and are listed in Table 5.6.

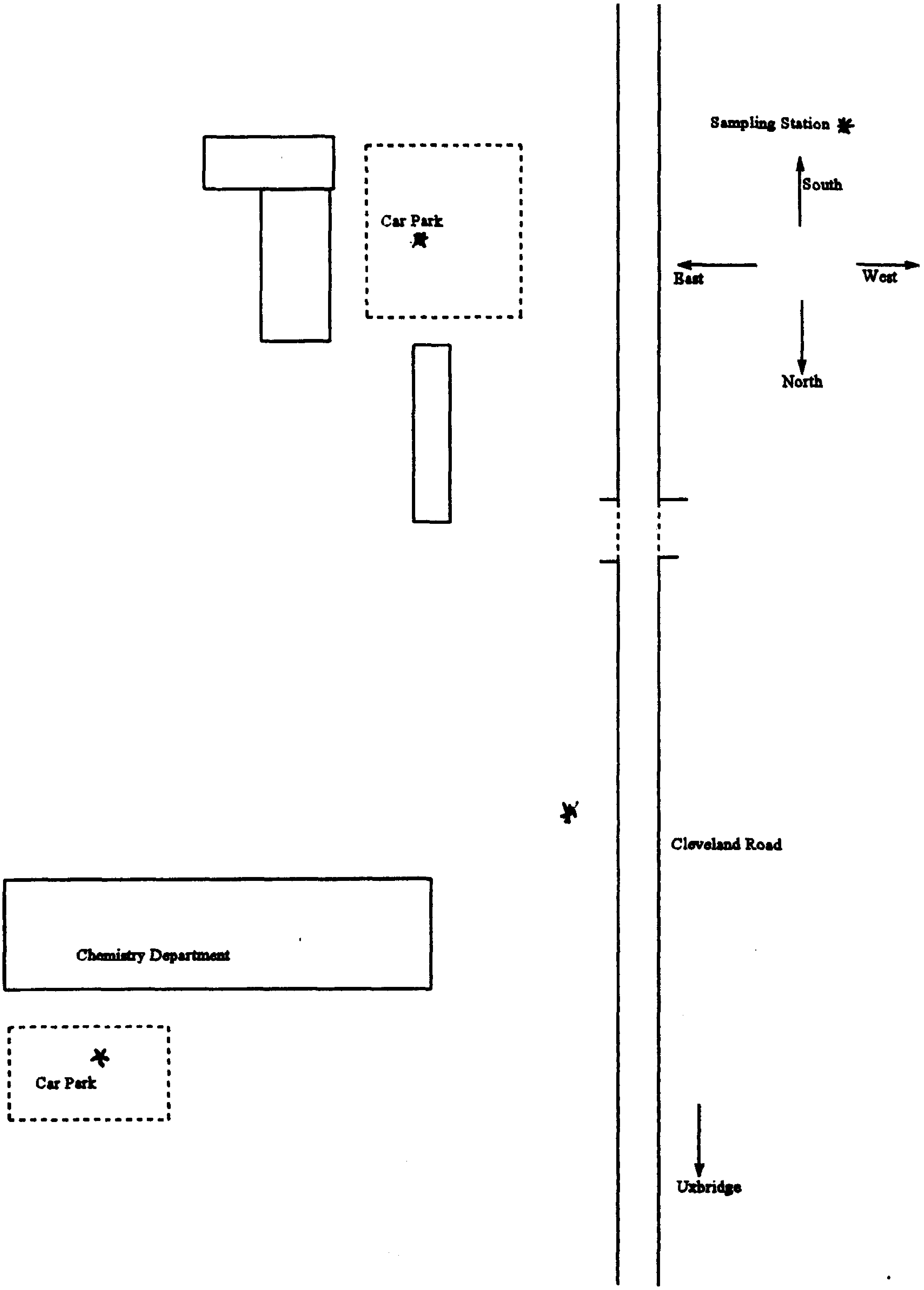


Figure 5.14 Map of sampling stations in Brunel University

The daily samples which were obtained under high wind speed conditions have few of the hydrocarbons but samples at low wind speed contain most of them.

Individual hydrocarbons including benzene, toluene, ethyl benzene, o-xylene and m- and p-xylene represent the main peaks on the chromatograms of ambient air samples and were characterised using the gas chromatography system.

### 5.7.2 Diurnal variation (8.00 to 20.00 h)

The diurnal variation in the concentrations of four aromatic hydrocarbons (benzene, toluene, m- and p-xylene, o-xylene) was measured on 16.04.1995 and is shown in Fig. 5.15.The data clearly indicate an increase in the concentrations of the four hydrocarbons during the morning and afternoon rush hour periods, with a recession between 10.00 and 14.00, a phenomenon that was commonly observed on weekdays

Exceptions were observed during weekends and Bank Holidays, when the diurnal variation was completely different but always related to traffic flow.

### 5.7.3 Daily variation

The daily variation of the same five hydrocarbons was determined for the period 4th January until 30th April and the results shown in Fig. 5-16(a, b, c, d). The highest concentrations are 17.00 and 19.00 $\mu g\ m^{-3}$ for benzene and toluene respectively observed on 19.03.95. The lowest concentrations were 0.78 and 1.20 $\mu g\ m^{-3}$ for benzene and toluene respectively, found on 24th January.

All measured hydrocarbons in Cleveland Road gave concentrations between 0 and 29 $\mu gm^{-3}$ over four months period. Wind speed over the four months, shown in Fig. 5.17, show that there is a negative correlation between the distribution of hydrocarbons and wind speed. Hourly distributions of benzene, toluene, m- and p-xylene and o-xylene measurements over the period 4th January until 30th April at this site are represented in Fig. 5.18 (a, b, c, d). Comparison of the data in Fig. 5.18 with those in Table 5.5 show that concentration of selected hydrocarbons depends upon traffic flow.

Table 5.6 Hydrocarbons determined in ambient air samples.

| No. | Hydrocarbons | No. | Hydrocarbons |
|---|---|---|---|
| 1 | iso butane | 15 | m- and p-xylene |
| 2 | Isobutane | 16 | o-xylene |
| 3 | Butane | 17 | Propyl benzene |
| 4 | Iso pentane | 18 | 1,3 Ethyl methyl benzene |
| 5 | n-pentane | 19 | 1,3,5 Trimethyl-benzene |
| 6 | 2,2-Dimethyl butane | 20 | 1,2,4 Trimethyl-benzene |
| 7 | 2,3-Dimethyl butane | 21 | 1,2,3 Trimethyl-benzene |
| 8 | 2-Methyl pentane | 22 | 1,3 Methyl propyl benzene |
| 9 | Hexane | 23 | 1,2,4,5-Tetramethyl-benzene |
| 10 | Benzene | 24 | 1,2,3,5-Tetramethyl-benzene |
| 11 | 2-methylhexane | 25 | 2,9 Dimethyl decane |
| 12 | Toluene | 26 | Naphthalene |
| 13 | 2,3-Dimethyl hexane | 27 | 2-Methyl naphthalene |
| 14 | Ethyl benzene | | |

### 5.7.4 Correlation between individual hydrocarbons

The mean ratio found between toluene concentration in air and other compounds and also correlation between toluene and other compounds over the four-month period are follows:

| Compounds | Ratio | Correlation |
|---|---|---|
| Benzene | 1.27 | 0.96 |
| Ethyl benzene | 3.10 | 0.84 |
| m & p-xylene | 1.50 | 0.87 |
| o-xylene | 2.80 | 0.86 |

The best correlation is for toluene and benzene with a standard deviation $\sigma_n$=0.21, which indicates is strong correlation. This can be confirmed by reference to Fig. 5.19, where data of benzene is plotted against toluene in a regression mode. The correlation between benzene and toluene in this normal distribution is as good as 93% and the linearity is expressed by the equation:

$$Y=0.24+0.76X$$

Ethyl benzene, o-xylene, m- and p-xylene have a good correlation with toluene and the lines are expressed by following equation:

| | |
|---|---|
| $Y=0.18+0.31X$ | Toluene and ethyl-benzene |
| $Y=-0.16+0.37X$ | Toluene and o-xylene |
| $Y=1.09+0.56X$ | Toluene and m- and p-xylene |

Referring back to the Fig. 5.19(a, b, c, d) it is also apparent that similarities exist between the distributions in (b) and (c), which indicate that m- and p-xylene and o-xylene concentrations correlate well with toluene concentrations.

Strong correlation between toluene and other compounds indicates the hydrocarbons in ambient air conditions are produced from motor vehicle exhausts.

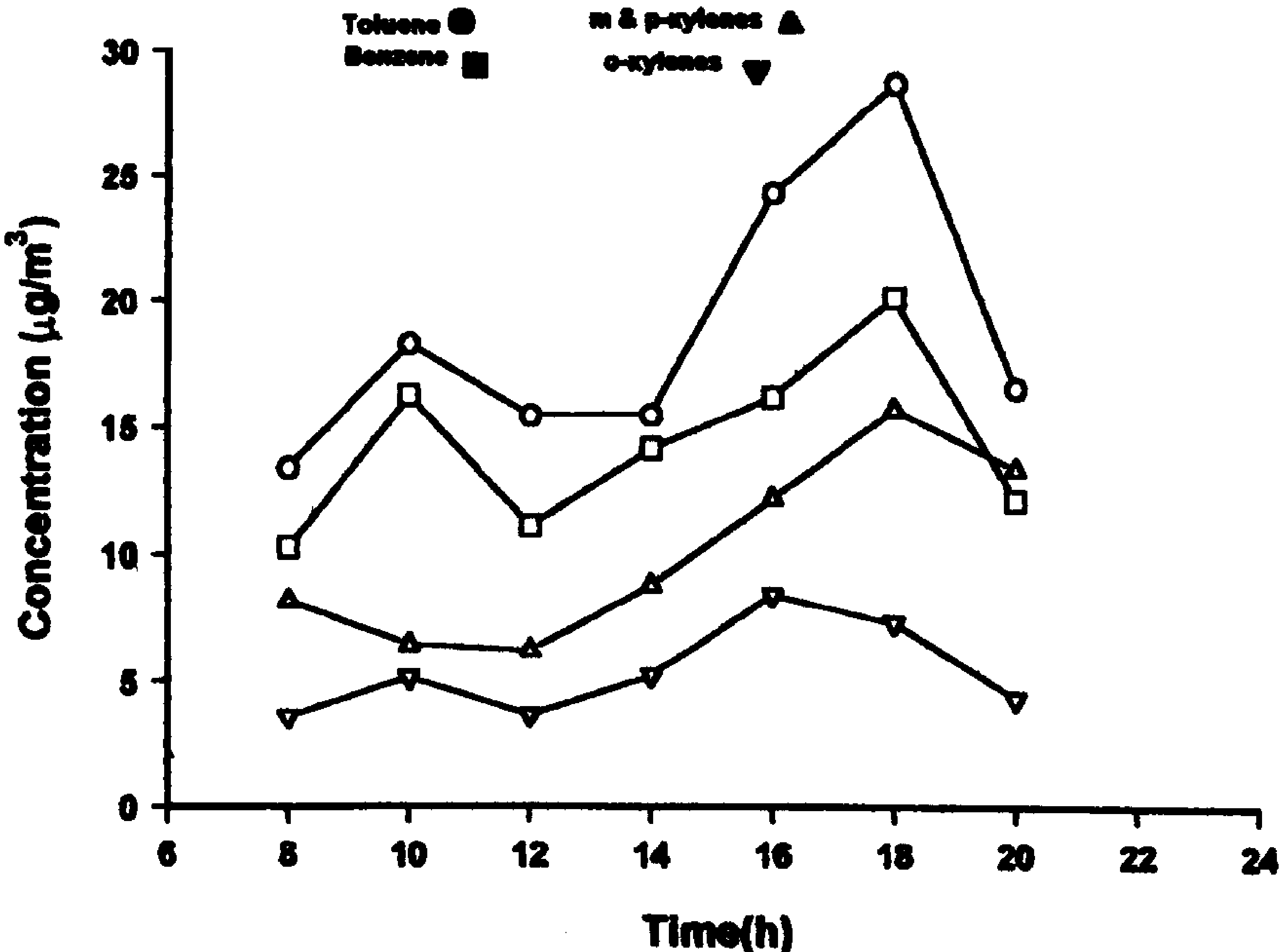


Fig. 5.15 Durnal variation of four hydrocarbons at exhibition road site on the 16.04.1995

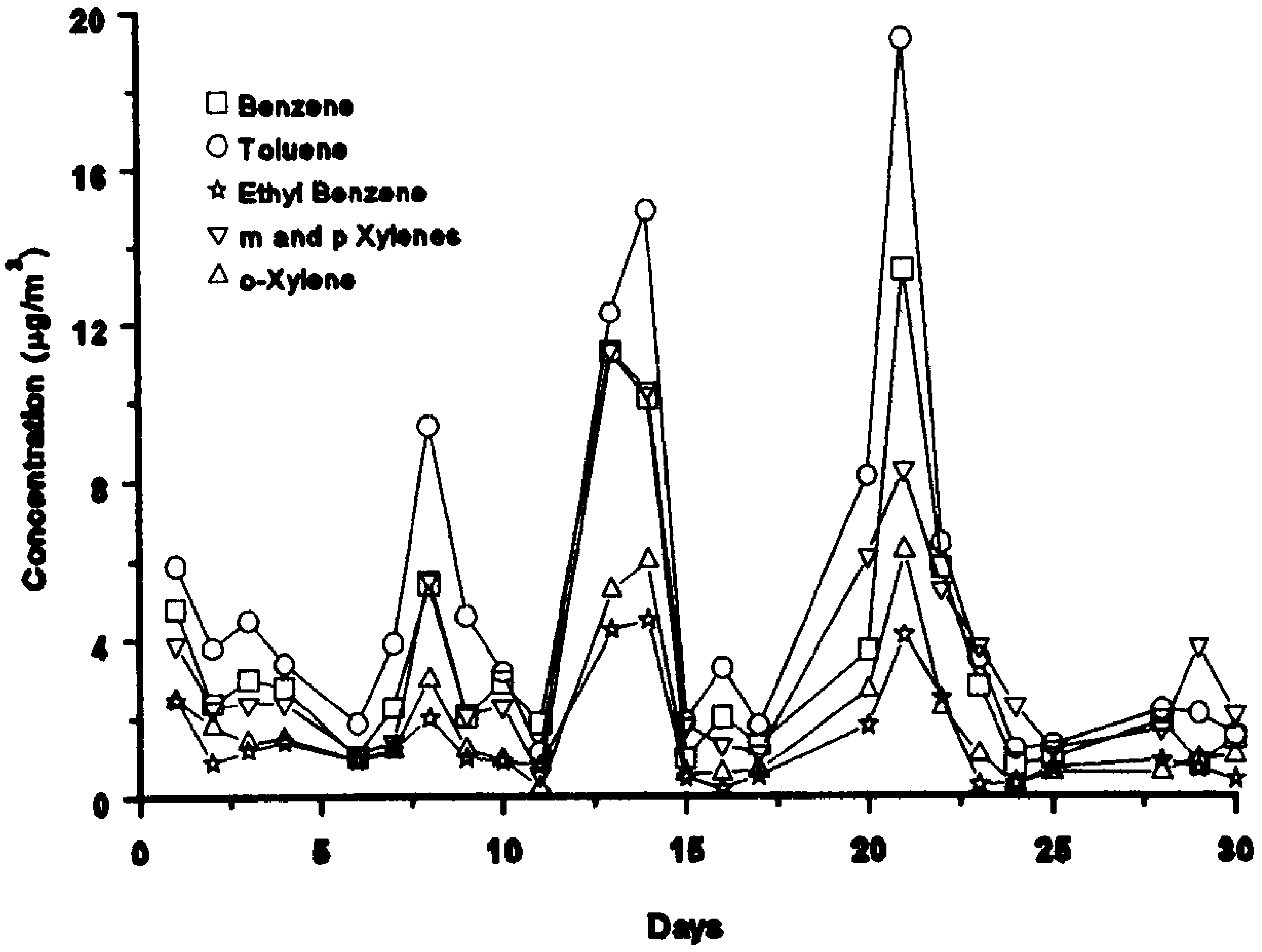


Fig.5.16(a) Concentration of benzene, toluene, ethyl benzene, m+p-xylenes and o-xylene in Cleveland Road over January 1995

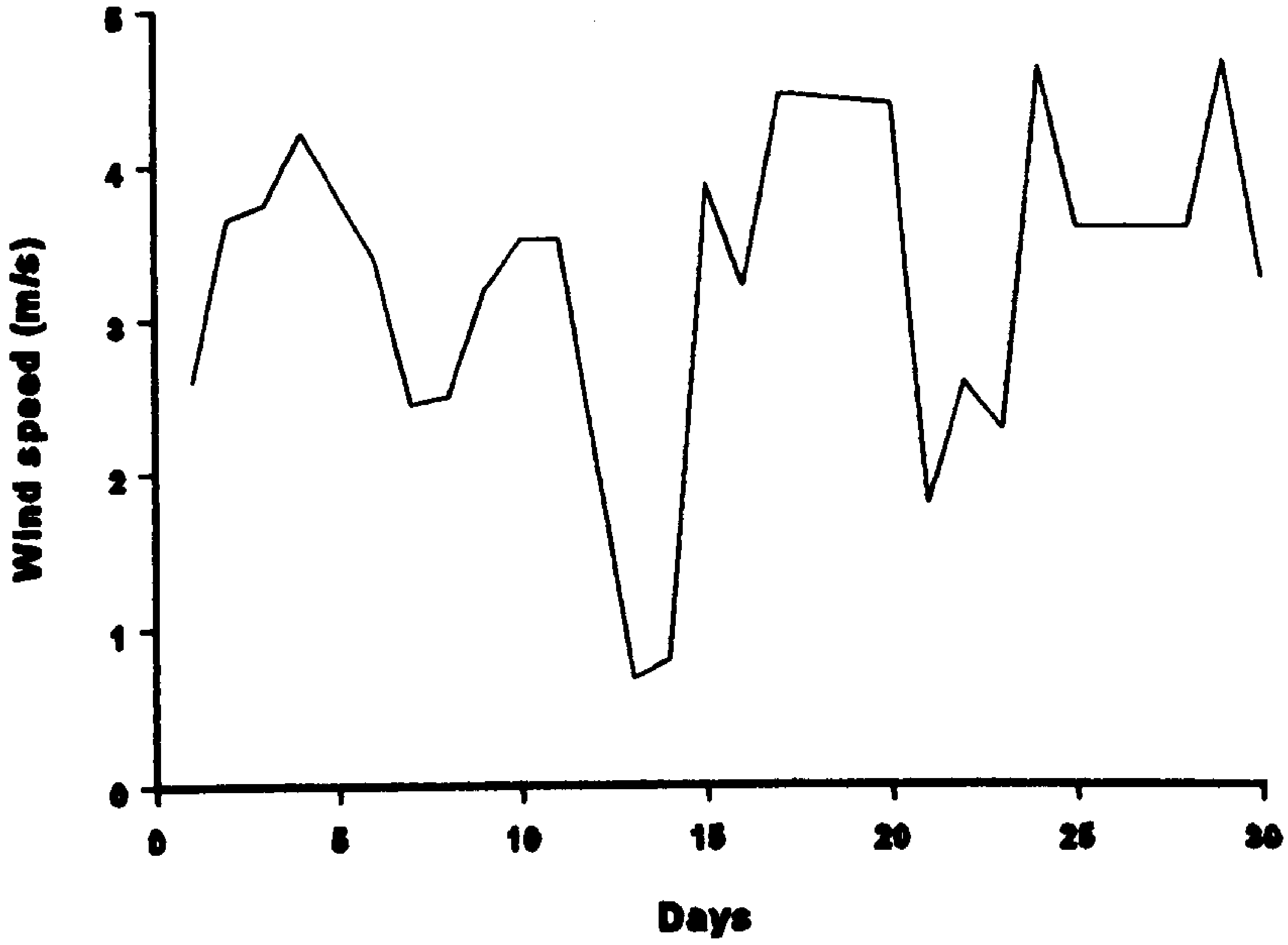


Fig. 5.17(a) Wind speed at campus of Brunel university over January 1995

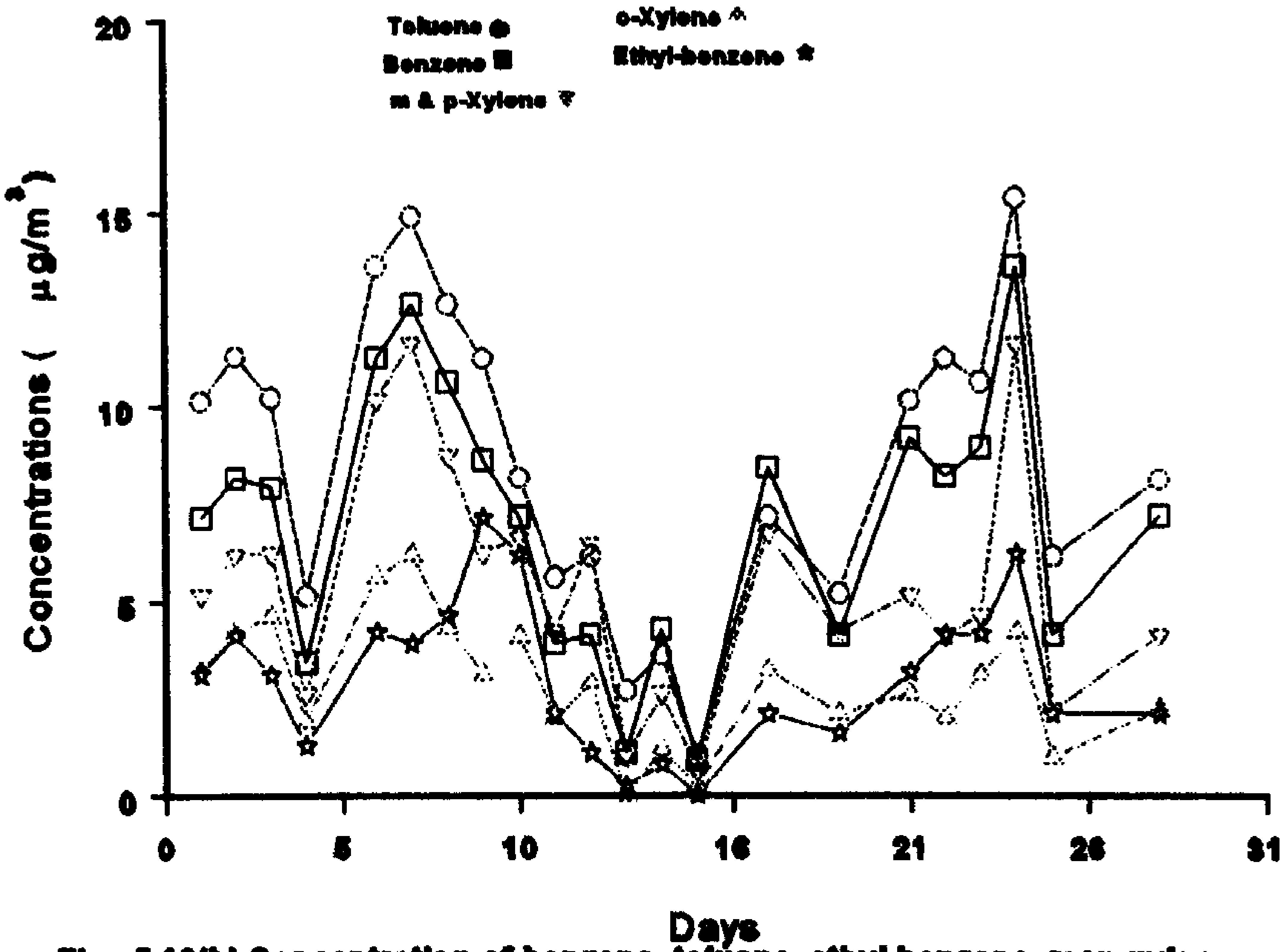


Fig. 5.16(b) Concentration of benzene, toluene, ethyl benzene, m+p-xylene and o-xylene in Cleveland Road over February 1996

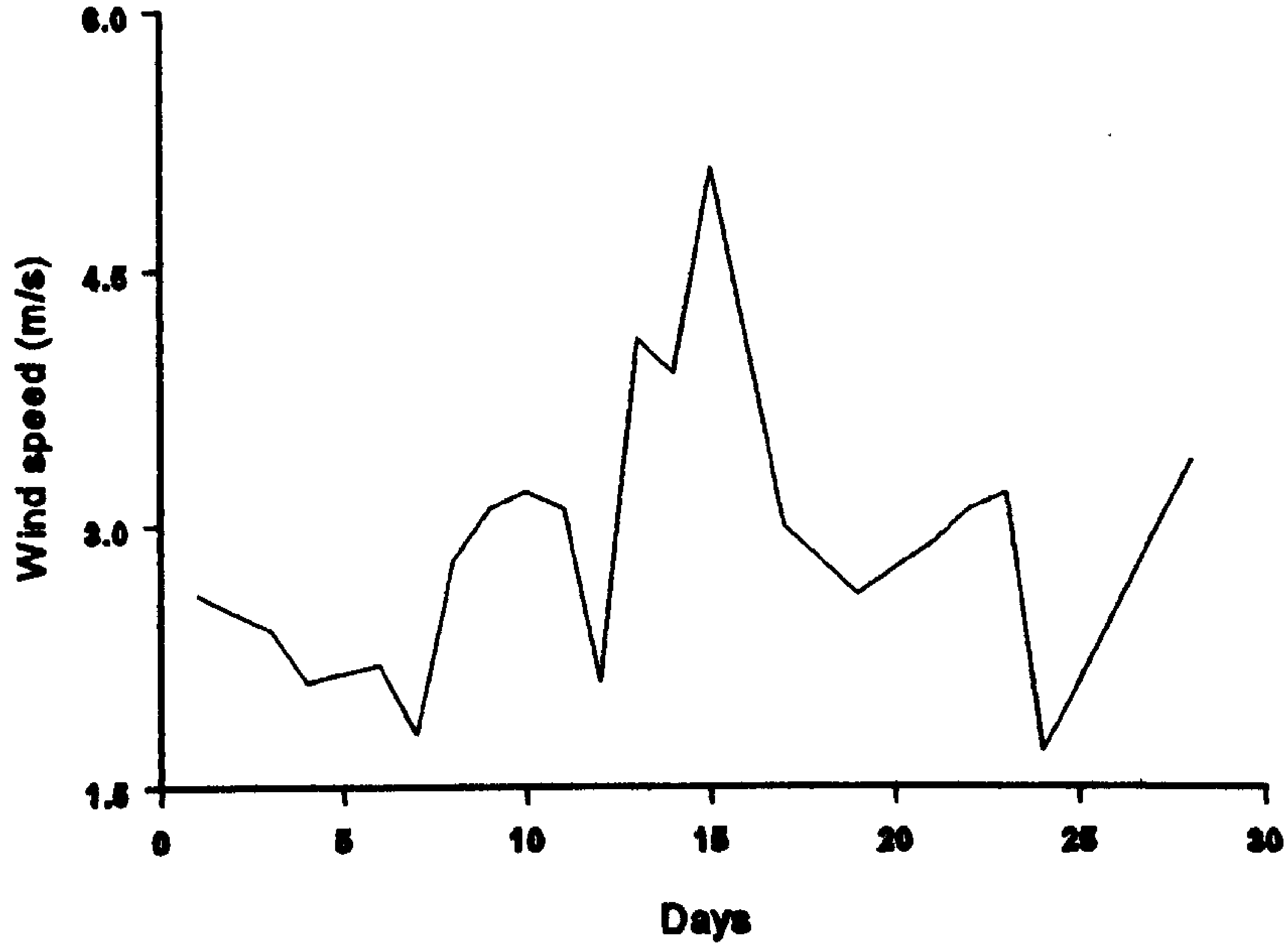


Fig. 5.17(b) Wind speed at Campus of Brunel university over Februry 1996

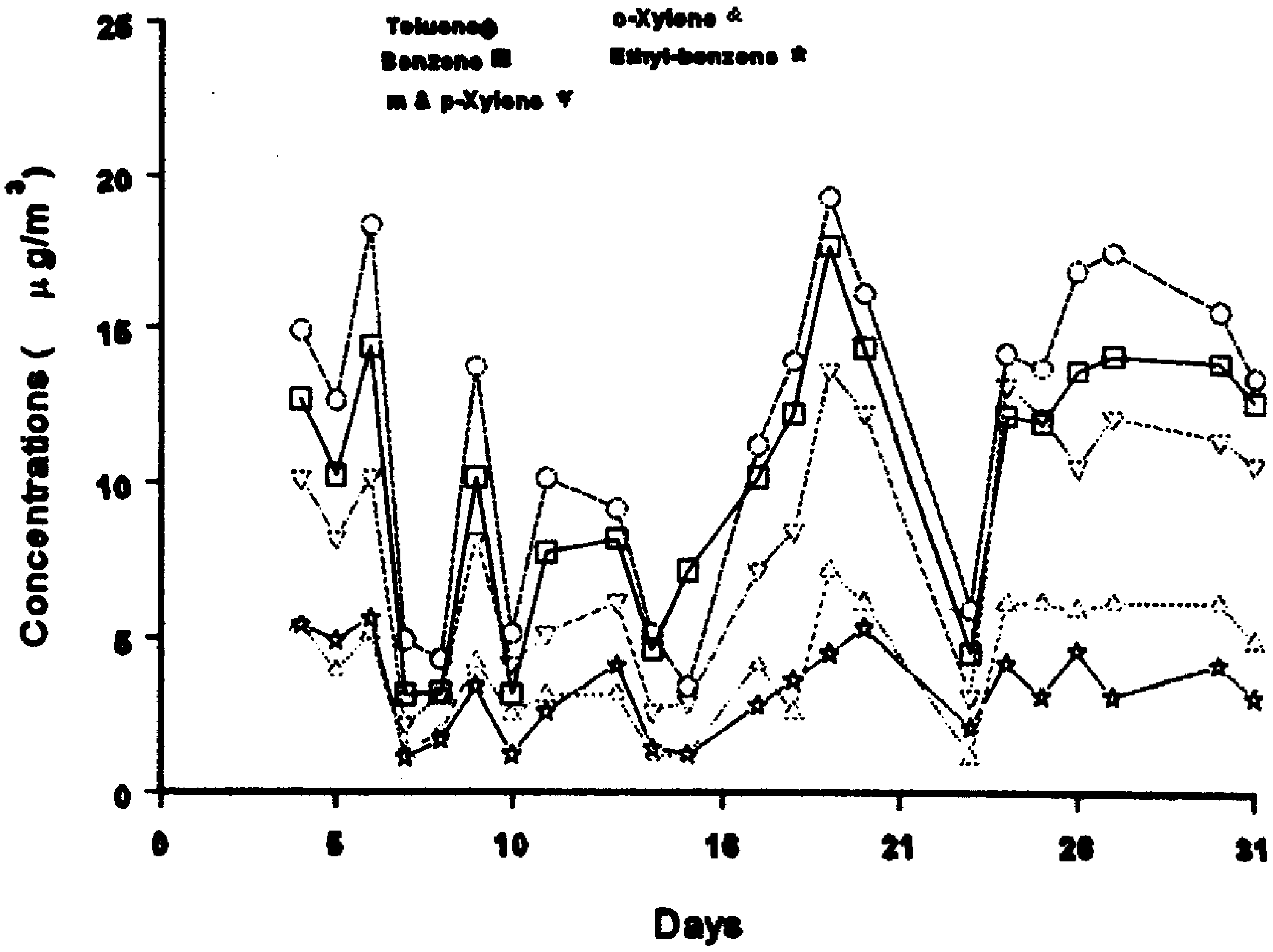


Fig. 5.16(c) Concentration of benzene, toluene, ethyl benzene, m+p-xylene and o-xylene in Cleveland Road over March 1995

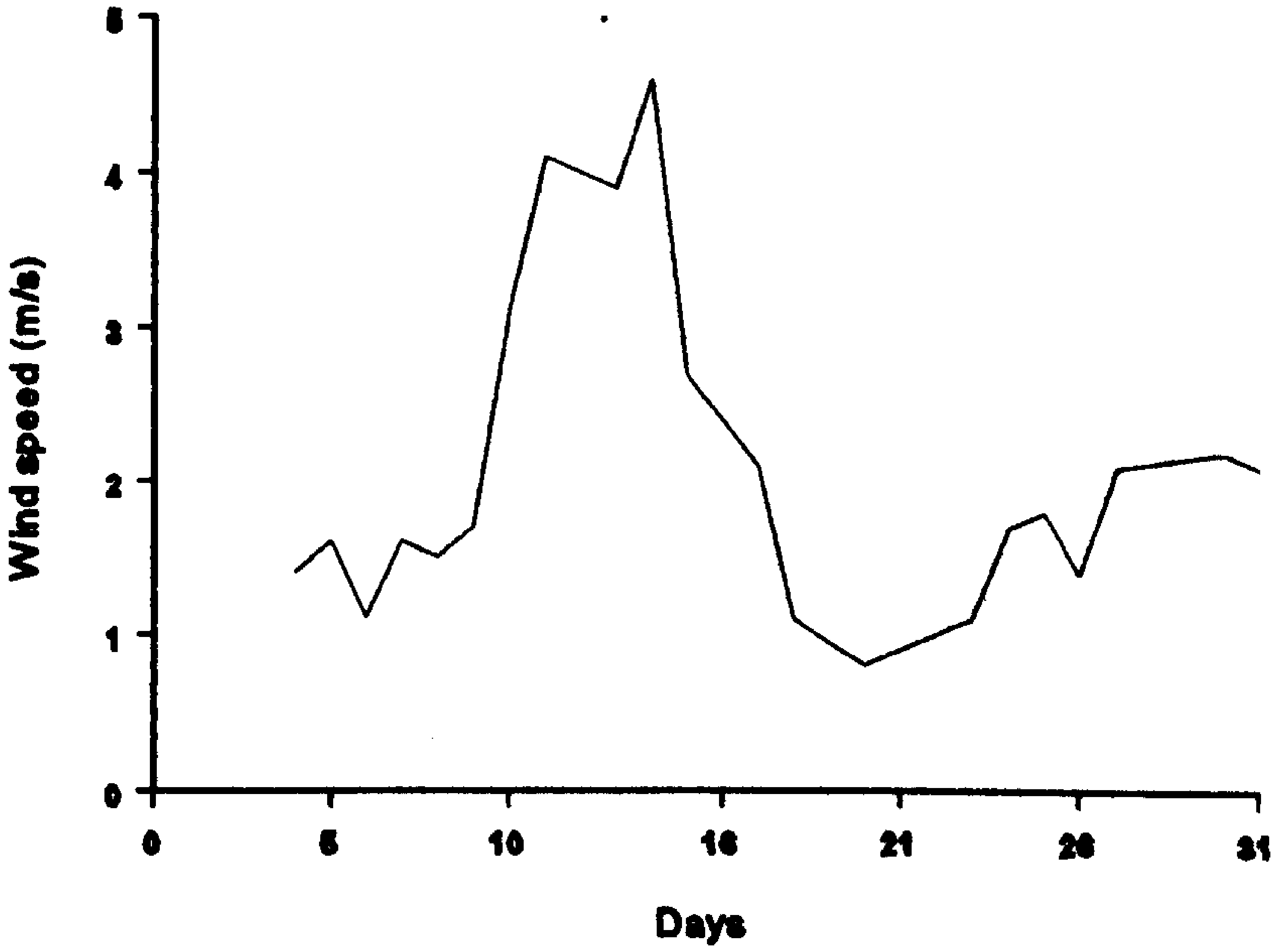


Fig. 5.17(c) Wind speed at campus of Brunel university over March 1996

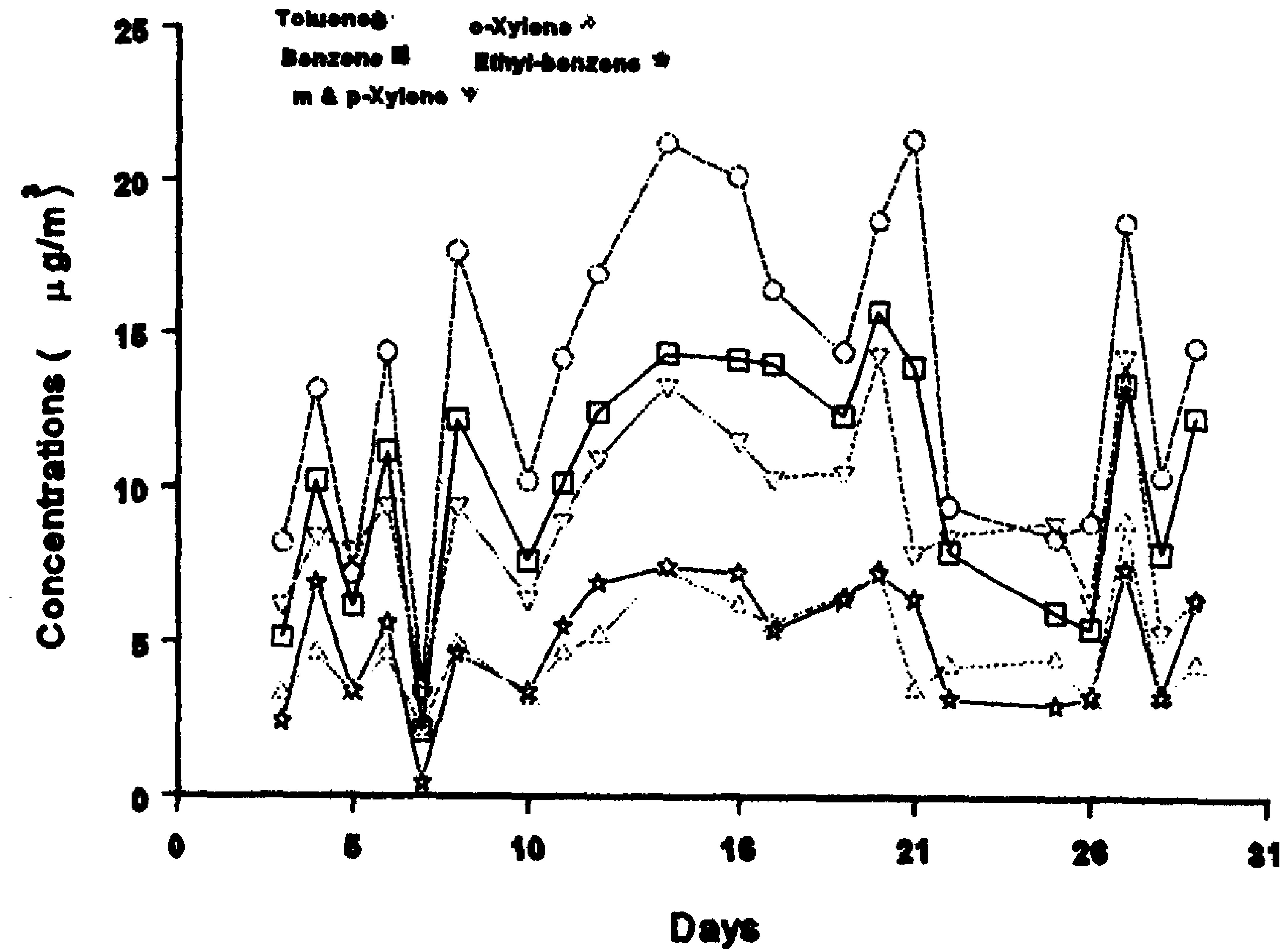


Fig. 5.16(d) Concentration of benzene, toluene, ethyl benzene, m & p-xylene and o-xylene near to Cleveland Road over April 1995

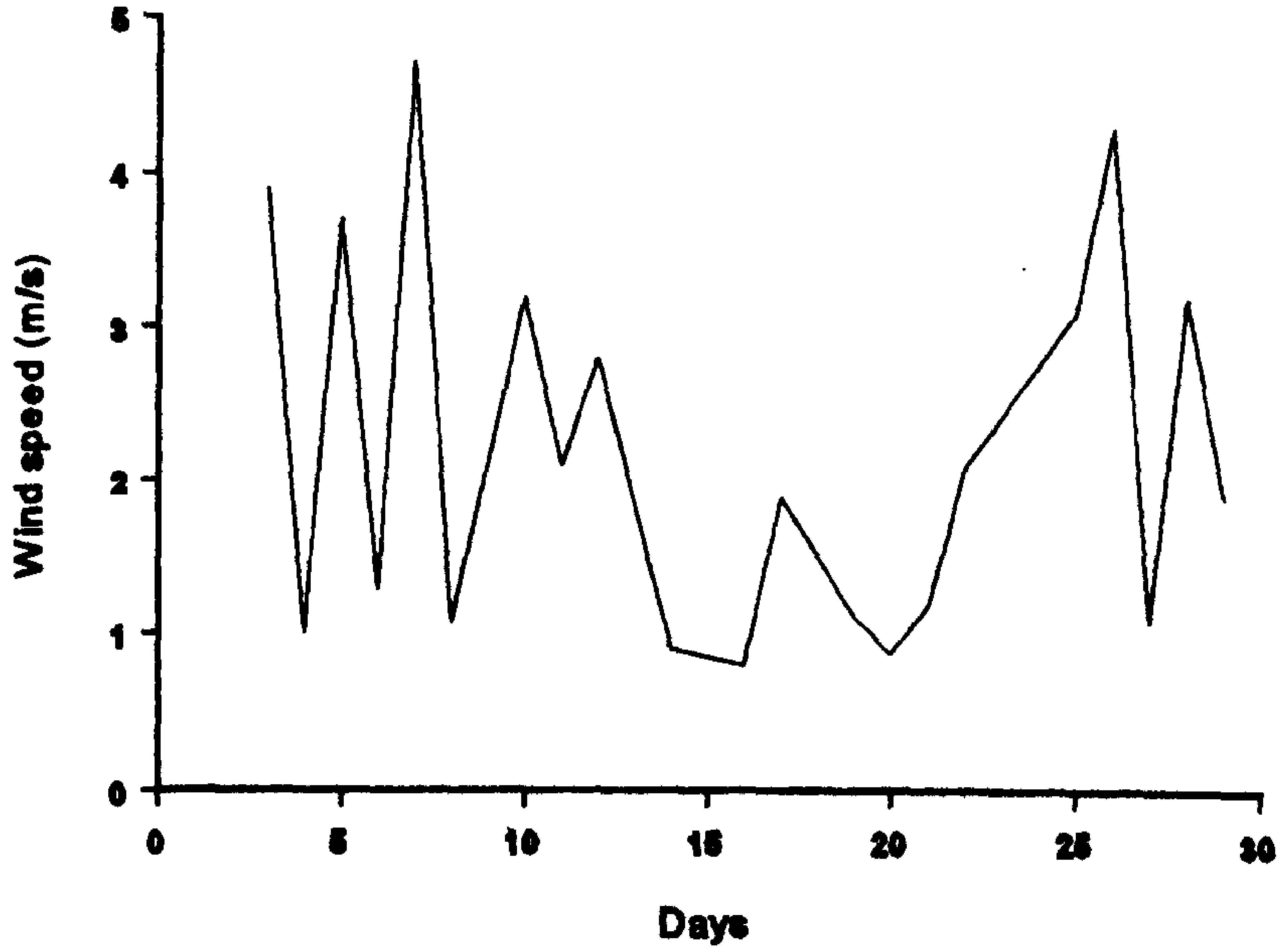


Fig. 5.17 (d) Wind speed in campus of Brunel university over April 1995

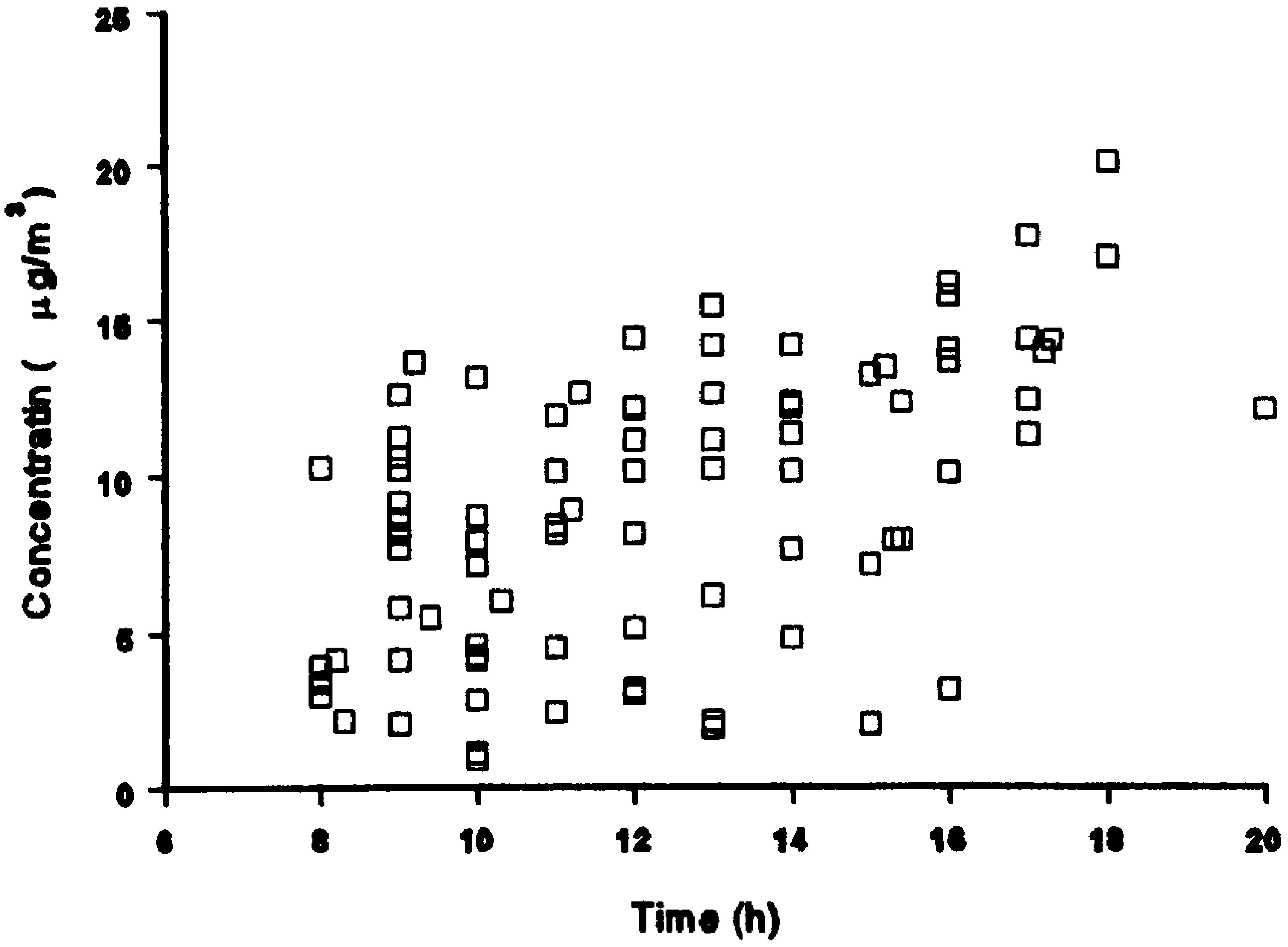


Fig.5.18 (a) Hourly distribution of benzene measurement in Cleveland Road (January-April 1995)

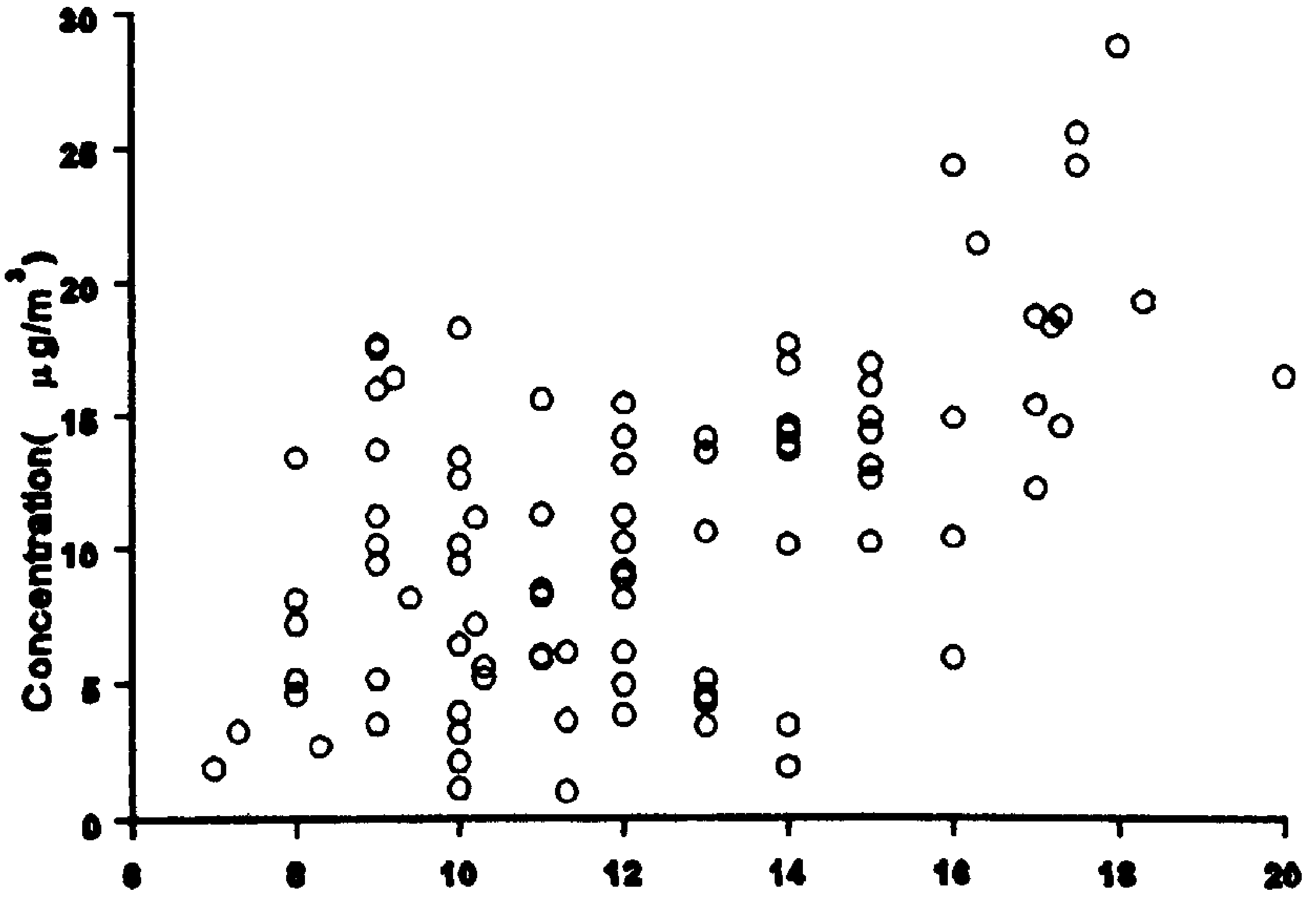


Fig. 5.18(b) Hourly distribution of toluene measurement in Cleveland Road over Jaunary-June 1995

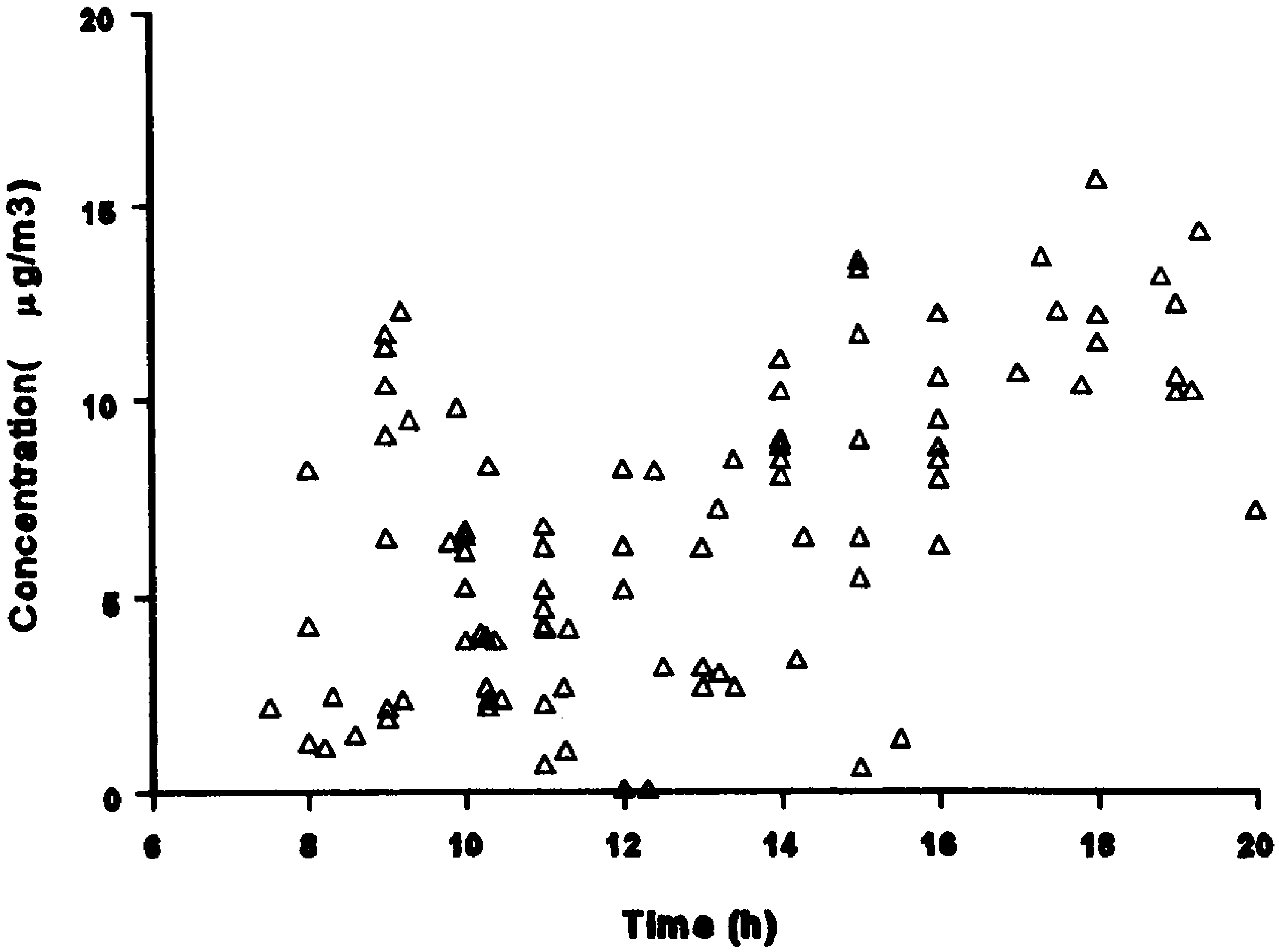


**Fig. 5.18(c) Hourly distribution of m&p-xylene measurement in Cleveland Road over Jaunary-June 1996**

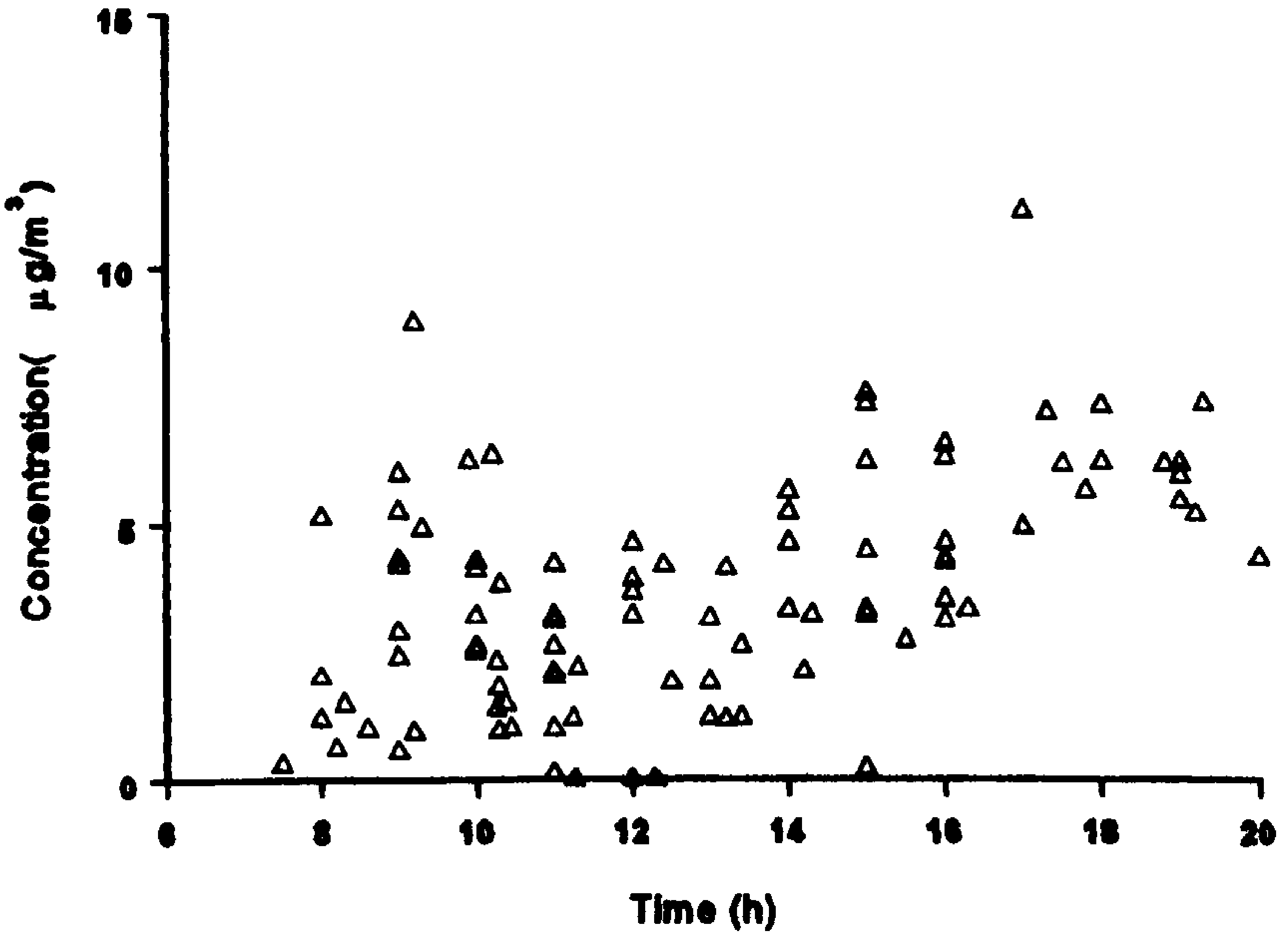


**Fig. 5.18 (d) Hourly distribution of o-xylene measurement in Cleveland Road over Jaunary-June 1996**

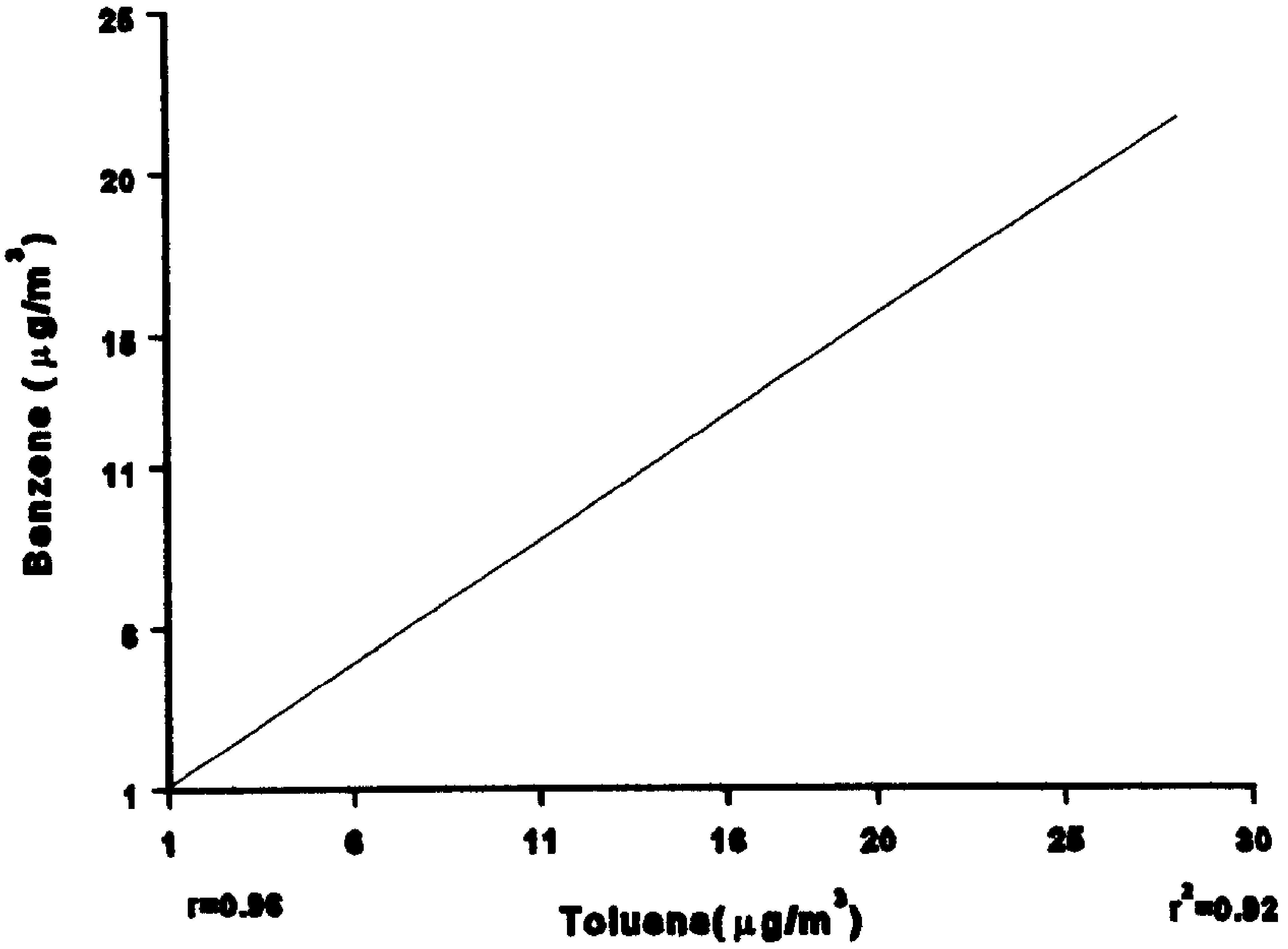


Fig. 5.19 (a) Correlation of toluene and benzene concentration

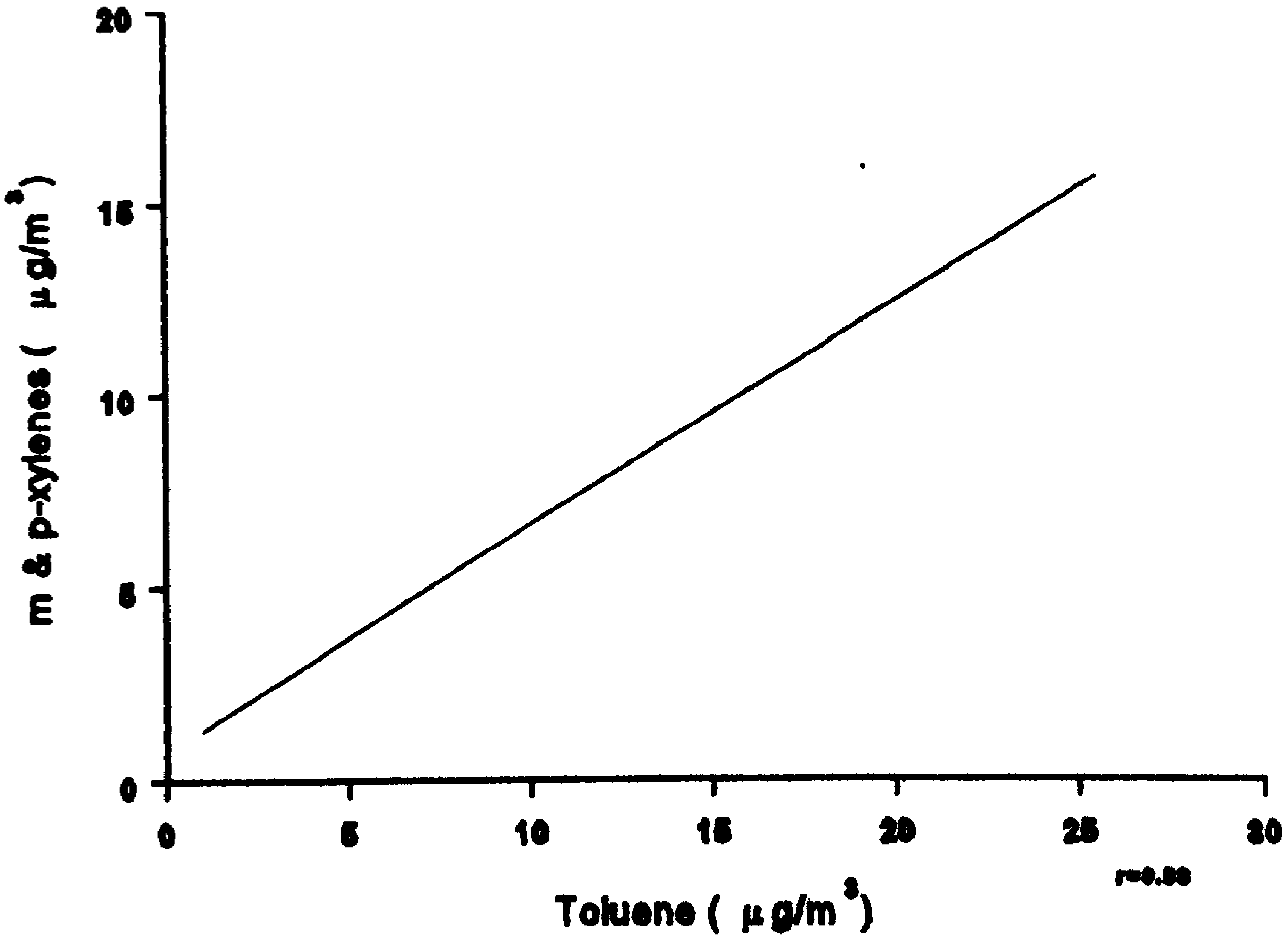


Fig. 5.19 (b) Correlation of toluene and m & p-xylenes concentration

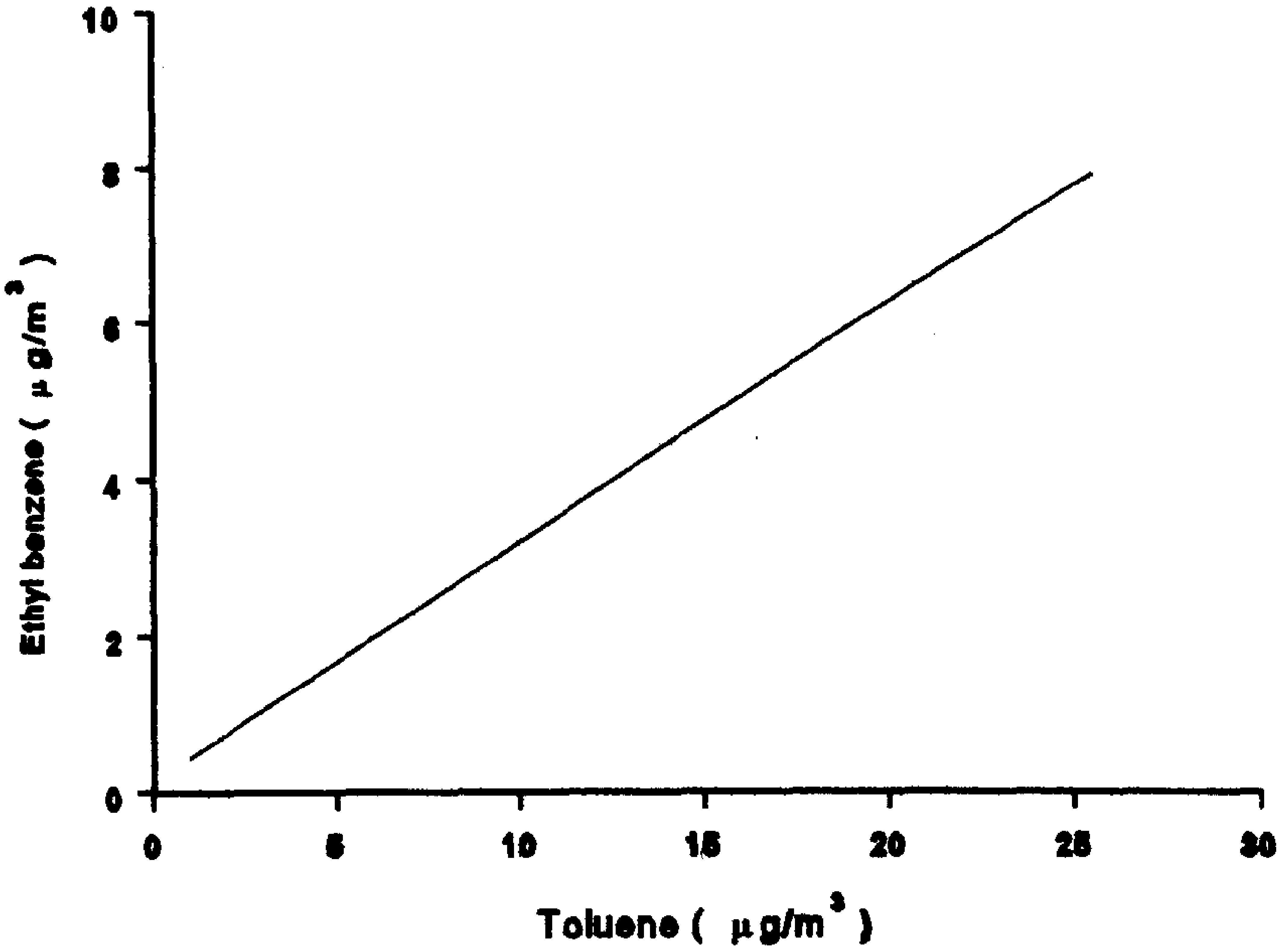


Fig. 5.19 (C) Correlation between toluene and ethyl-benzene

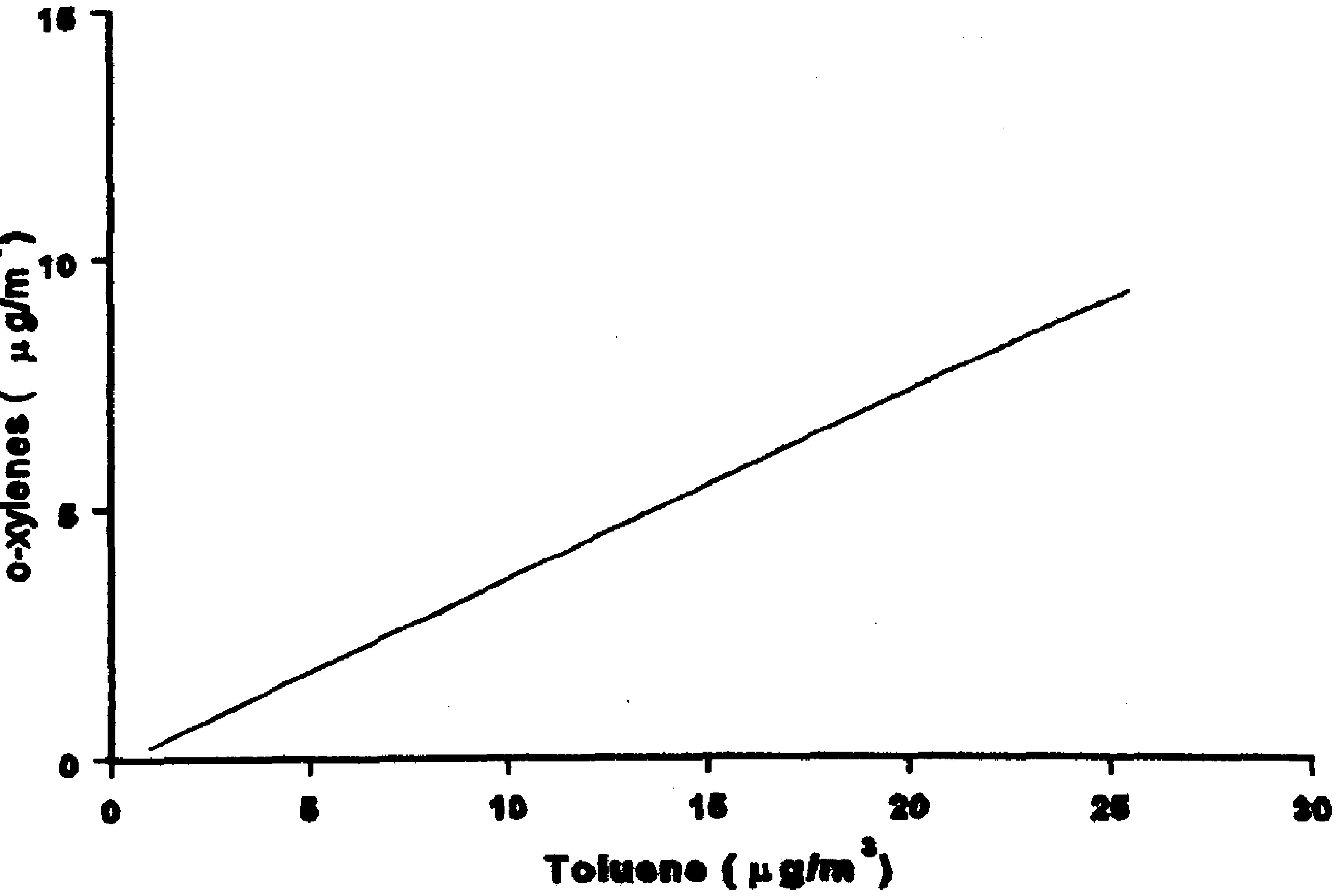


Fig. 5.19(d) Correlation of toluene and o-xylenes concentration

## 5.8 Variation in hydrocarbon concentration with months

The monthly variation in hydrocarbon concentration in air was investigated over a four month period. Referring again to Fig. 5.14 (a, b, c, d) the distribution of benzene, toluene, m- and p-xylene and o-xylene is recorded separately for each month with different symbols. The distribution shows the slight elevation in hydrocarbon concentrations in March and April and a decrease in January and February .

Table 5.7 Average temperature and wind speed over four months at Cleveland Road

| Months | Average of wind speed m/s | Average air temperature °C |
|---|---|---|
| January | 2.75 | 8.5 |
| February | 2.86 | 9 |
| March | 2.35 | 12 |
| April | 2.20 | 14.5 |

The air temperature in March and April is found to be higher than in January and February (Table 5.7). This causes the concentrations of individual hydrocarbons in March and April to be more than in January and February (Table 5.8).

A particular observation relates to the afternoon of 16th April, when there was no perceptible wind and a high temperature (15°C). During that afternoon, the highest concentration of benzene, 26.06 $\mu g/m^3$, was recorded, for the Cleveland Road measurements. This is an indication that high temperatures and still conditions give rise to elevated concentrations of less volatile pollutants in a given area.

## 5.9 The results from car parks

About 50 samples were obtained from two car parks on the university campus (map Fig. 5.15 ). Results are shown at Table 5.9.Concentration of the individual hydrocarbons in the car park are approximately one-third of Cleveland Road values (Table 5.9 and Table 5.8). As wind ,transfers pollutants from Cleveland Road to the car park, so, the origins of pollution in the car park is either evaporation from carburettors in the parked cars or from Cleveland Road.

Table 5.8 Monthly concentration of individual hydrocarbons in Cleveland Road at 1995

| Month | Sta. | Concentration μg/m³ | | | | |
|---|---|---|---|---|---|---|
| | | Benzene | Toluene | Ethyl Benzene | m- and p-xylene | o-xylene |
| January | Mean | 3.56 | 5.07 | 1.42 | 3.5 | 1.8 |
| | S.D. | 3.40 | 4.67 | 1.22 | 2.91 | 1.68 |
| | Max. | 13.35 | 19.30 | 4.48 | 11.27 | 6.20 |
| | Min. | 0.78 | 1.12 | 0.18 | 0.56 | 0.21 |
| February | Mean | 7.02 | 10.2 | 3.06 | 5.5 | 2.30 |
| | S.D. | 3.44 | 3.92 | 1.88 | 3.01 | 1.59 |
| | Max. | 13.60 | 15.40 | 7.11 | 11.60 | 6.17 |
| | Min. | 0.90 | 1 | 0 | 0.90 | 0 |
| March | Mean | 10.05 | 14.38 | 3.32 | 8.04 | 4.05 |
| | S.D. | 3.60 | 3.40 | 1.41 | 3.82 | 3.88 |
| | Max. | 17.66 | 19.26 | 5.60 | 3.60 | 7.13 |
| | Min. | 3.12 | 4.90 | 1.10 | 2.20 | 1.12 |
| April | Mean | 10.19 | 13.7 | 5.03 | 8.97 | 4.78 |
| | S.D. | 3.79 | 4.94 | 1.96 | 2.87 | 1.68 |
| | Max. | 18.70 | 21.40 | 7.40 | 14.29 | 8.90 |
| | Min. | 2.10 | 3.42 | 0.40 | 3.30 | 2.10 |

Table 5.9 Concentration of individual hydrocarbons in car park

| | Benzene | Toluene | Ethyl benzene | m- and p-xylene | o-xylene |
|---|---|---|---|---|---|
| Mean | 2.5 | 2.6 | 0.70 | 1.99 | 0.87 |
| Max. | 4.8 | 5.3 | 2.24 | 5.1 | 3.4 |
| Min. | 0 | 0.23 | 0 | 0.40 | 0 |
| S.D. | 1.83 | 2.10 | 0.90 | 1.23 | 0.64 |

The ratio of toluene to benzene is 1.07, which is lower than in Cleveland road. The reason for this phenomenon may be that more benzene evaporated than toluene or the photochemical reaction of the toluene during transfer from street to car park causes a decrease in the concentration of toluene.

### 5.10. Analysis of petrol and diesel fuel

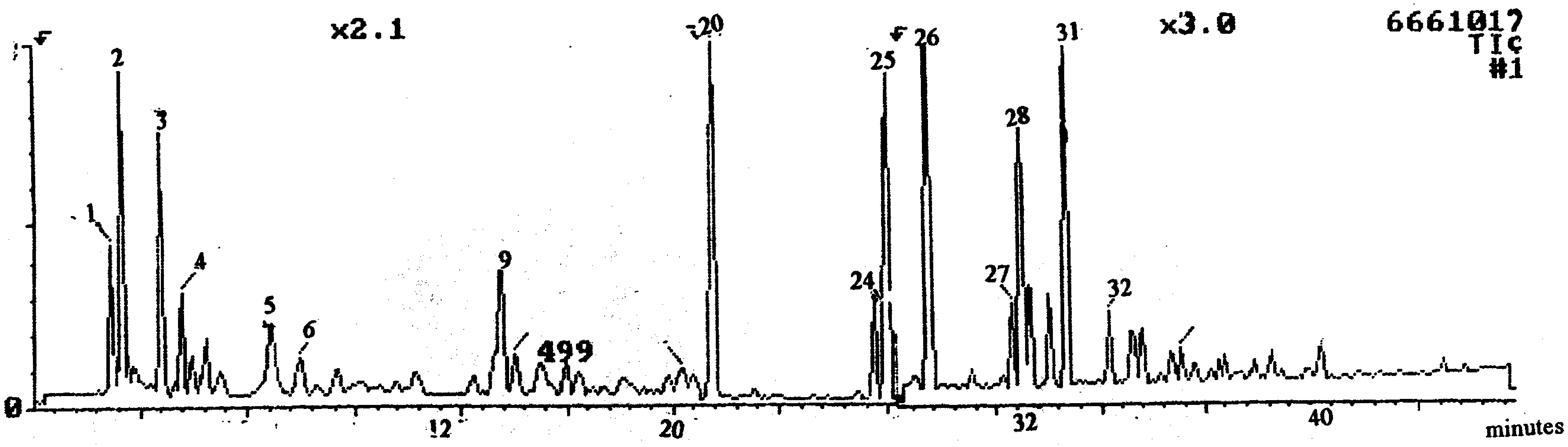
The hydrocarbons present in petrol and diesel fuel were identified and the concentrations of total aromatic hydrocarbons in 10 samples of unleaded petrol were found to be in range 29-34 percent in content to compared to rate of diesel fuel approximately 3-5 percent. A chromatogram of unleaded petrol is given in Figure 5.20 together with list of hydrocarbons whilst Table 5.10 lists some of the hydrocarbons in diesel fuel.

Table 5.10 Some of hydrocarbons from diesel fuel

| Number | Hydrocarbon | Number | Hydrocarbon |
|---|---|---|---|
| 1 | 3 Methyl hexane | 15 | Cyclopentyl-benzene |
| 2 | Methyl cyclohexane | 16 | 1,7 Dimethyl naphthalene |
| 3 | 2,3,4 trimethyl pentane | 17 | 1,8 Dimethyl naphthalene |
| 4 | toluene | 18 | 3-Methyl-hexadecane |
| 5 | Trans-1,2-dimethyl cyclohexane | 19 | 2,6 Dimethyl heptadecane |
| 6 | n-Octane | 20 | 6-Ethyl-2 Methyl decane |
| 7 | m- and p-xylene | 21 | 3 methyl undecane |
| 8 | Propyl-cyclohexane | 22 | 2,4,6 Trimethyl decane |
| 9 | 4-Methyl-Octane | 23 | 3,8 Dimethyl undecane |
| 10 | 2,2,6 Trimethyl hepatane | 24 | 2,3 Dimethyl undecane |
| 11 | 1,3,5-trimethyl benzene | 25 | 2,6,7 Trimethyl decane |
| 12 | 1,2,4- trimethyl benzene | 26 | Tricosane |
| 13 | n-Decane | 27 | 2 Methyl penta decane |
| 14 | n-Butyl benzene | 28 | 3 Methyl hexa decane |

### 5.11 Hydrocarbons in car exhaust

Hydrocarbons emitted from car exhausts were identified under varying conditions of engine load and the concentrations of five hydrocarbons (benzene, toluene, ethyl



1)Propane 2)n butane 3) 2-Methyl butane 4) 2,3-Dimethyl butane 5)2-Methyl pentane 6)3-Methyl pentane 7)Hexane 8)2-Methyl 1-Pentane 9)Benzene 10)2-Methyl-Hexane 11) 2,2,4-trimethyl-pentane 12)n-Heptane 13)2,5 Dimethyl hexane 14)2,4 Dimethyl hexane 15)Methyl cyclohexane 16)Ethyl cyclopentane 17)2,2,4 trimethyl pentane 18)4,4 Dimethyl cylopropane 19)2-Methyl heptane 20)Toluene 21)2,3 Dimethyl hexane 22)1,2,3 trimethyl-cyclopentane 23)2,3,4-trimethyl-hexane 24)Ethyl benzene 25)m&p-xylene 26)o-xylene 27)Propyl benzene 28)1,3 Ethyl methyl benzene 29)1,4 Ethyl methyl benzene 30)1,3,5 Trimethyl-benzene 31)1,2,4 Trimethyl-benzene 32)1,2,3 Trimethyl-benzene, 33)1-ethyl-2,5-dimethyl benzene 34)1-ethyl-2,4-dimethyl benzene 35)1-ethyl-3,4-dimethyl benzene 36) 1,2,4,5-Tetramethyl-benzene 37) 1,2,3,5- Tetramethyl-benzene 38)Naphthalene 39)1-Methyl naphthalene 40)2-Methyl naphthalene

Figure 5.20 Chromatogram from petrol

benzene, m- and p-xylene, o-xylene) found in the chromatogram were measured.

To obtain samples, a 40 cm metal tube was placed in the car exhaust, and the outlet of the tube connected to a Carbotrap. The pump was adjusted to a flow rate of 70ml/min. so that volume of each sample was 15-20ml as sampling time was 15-20 seconds.

Two types of cars were tested;

1. Toyota Carina without catalyst, with unleaded petrol from Sainsbury

2. Toyota Corolla, petrol injection with catalyst, with unleaded petrol from Sainsbury

**Figure 5.21 Sampling with a small pump from car exhaust**

### 5.11.1 Results and discussion

#### 5.11.1.1 Identification of pollutant

62 hydrocarbons can be identified in car exhaust (Table 5.11). The concentrations of some hydrocarbons are low, e.g. methane, ethylene 1,2,4,5-tetramethyl benzene, methyl naphthalene and some are high, e.g. toluene, benzene, xylene, ethyl benzene, 1,2,4 trimethyl benzene, butane etc. Fig. 5.22 shows a chromatogram from a sample of car exhaust.

#### 5.11.1.2 Statistical results

Data relating selected hydrocarbons compounds were recorded, and are included in Table 5.12. The ratios between toluene and individual hydrocarbons in the car exhausts are between 1.50 and 1.30. These indicate the situation in the exhaust gases of a particular vehicle.

The ratio of toluene to benzene shows a consistent pattern over the different modes of engine operation and is close to that calculated from the Cleveland Road measurement.

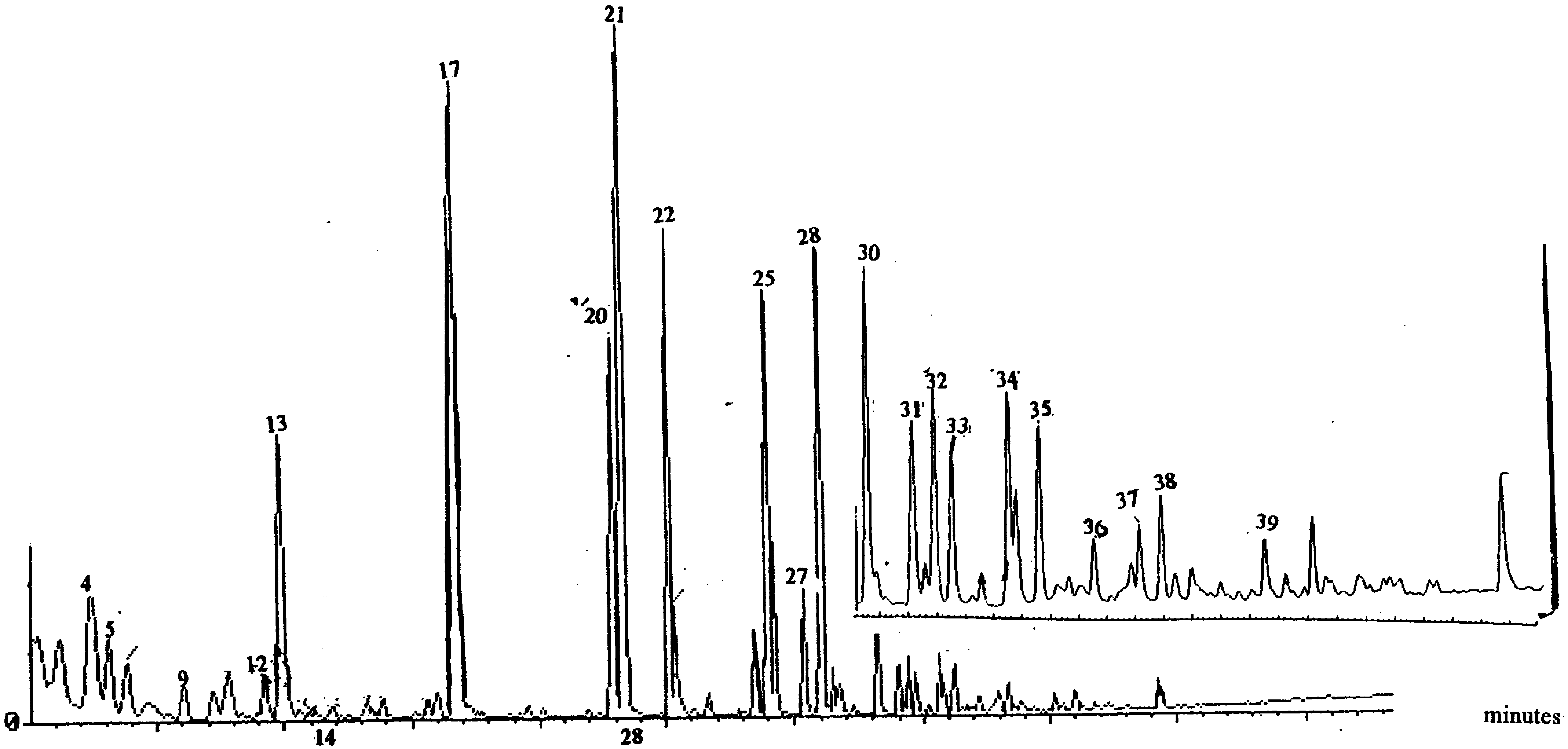
The correlation of toluene and benzene for direct measurement of engine emissions is better than the correlation for aromatic hydrocarbons in ambient air conditions at the Cleveland Road site. The correlation of the two compounds is given by the linear equation:

$$Y=67.23 + 1.09X$$

It is evident from Table 5.12 that emissions of individual pollutants are greatest during a cold start of the engine, the concentrations of benzene, toluene, m- and p-xylene, o-xylene and ethyl-benzene being 2.15, 2.61, 2.47, 2.60, 3.35 times higher respectively than the concentration resulting from a hot start. In a cold start with catalyst,

Table 5.11 Hydrocarbons identified in car exhausts

| No. | Hydrocarbons | No. | Hydrocarbons |
|---|---|---|---|
| 1 | Methane | 34 | trans-2-Octane |
| 2 | Ethylene | 35 | Dimethyl heptane |
| 3 | Propylene | 36 | Cis-2-octane |
| 4 | Propane | 37 | Ethyl cyclo hexane |
| 5 | Cyclopropane | 38 | Ethyl benzene |
| 6 | Isobutane | 39 | m- and p-xylene |
| 7 | n-butane | 40 | o-xylene |
| 8 | 3-Methyl-1-butane | 41 | 2-Methyloctane |
| 9 | 2-Methyl-1-butane | 42 | n-nonane |
| 10 | n-pentane | 43 | Iso-propyl-benzene |
| 11 | Cyclo pentane | 44 | Propyl benzene |
| 12 | 2-Methyl pentane | 45 | 1,3 Ethylmethyl benzene |
| 13 | 3-Methyl pentane | 46 | 1,4 Ethylmethyl benzene |
| 14 | 2-Methyl-1-pentane | 47 | 1,3,5 Trimethyl-benzene |
| 15 | 2-Ethyl-1-butane | 48 | 1,2,3 Trimethyl-benzene |
| 16 | Hexane | 49 | n-decane |
| 17 | Methyl cyclopentane | 50 | 1,2,4 Trimethyl-benzene |
| 18 | 2,4-Dimethyl-pentane | 51 | Indane |
| 19 | Benzene | 52 | 1,3 Methyl propyl benzene |
| 20 | Cyclohexane | 53 | 1-ethyl-2,5-dimethyl benzene |
| 21 | 5-Methyl-1-Hexane | 54 | 1-ethyl-2,4-dimethyl benzene |
| 22 | 2,3 Dimethyl pentane | 55 | 1-ethyl-3,4-dimethyl benzene |
| 23 | 2,2,4-trimethyl-pentane | 56 | 1,2,4,5-Tetramethyl-benzene |
| 24 | n-heptane | 57 | 1,2,3,5-Tetramethyl-benzene |
| 25 | 2,3,4 Trimethyl-pentane | 58 | 2,2,3,3-Tetramethyl-benzene |
| 26 | Toluene | 59 | 2,9 Dimethyl decane |
| 27 | 2,3,3-Trimethyl-pentane | 60 | Naphthalene |
| 28 | 2,3-Dimethyl hexane | 61 | 2-Methyl naphthalene |
| 29 | 3,4-Dimethyl hexane | 62 | 1-Methyl naphthalene |
| 30 | 2,3,5 trimethyl hexane | | |
| 31 | 1-Octane | | |
| 32 | n-Octane | | |
| 33 | trans-2-Octane | | |



1)Methane 2) Propane, 3)Cyclopropane 4)Isobutane 5)Butane 6)3-Methyl pentane 7)n-pentane 8)Cyclo pentane 9)3-Methyl pentane 10)2 Methyl-1-pentane 11)Hexane 12)2-Methyl 1-Pentane 13) Benzene 14) 2,3 Dimethyl pentane 15) Methyl cyclohexane 16) 2,3,4 trimethyl pentane 17) Toluene 18)2,3,5 trimethyl hexane 19) n-Octane 20)Ethyl benzene 21)m&p-xylene 22)o-xylene 23)n-none 24)Propyl benzene 25)1,3 Ethyl methyl benzene 26)1,4 Ethyl methyl benzene 27)1,3,5 Trimethyl-benzene 28)1,2,4 Trimethyl-benzene 29) n-decane 30)1,2,3 Trimethyl-benzene 31) Indane 32)1,3 Methyl propyl benzene 33) 1-ethyl-2,5-dimethyl benzene 34) 1-ethyl-2,4-dimethyl benzene 35) 1-ethyl-3,4-dimethyl benzene 36) 1,2,4,5-Tetramethyl-benzene 37) 1,2,3,5-Tetramethyl-benzene 38)2,9 Dimethyl decane 39) Naphthalene 40)2-Methyl naphthalene

**Figure 5.22 Chromatogram of pollution from car exhaust**

Table 5.12 Concentration of individual hydrocarbons in car exhaust

| Condition of car | Sta. Cal | Concentration µg/l | | | | |
|---|---|---|---|---|---|---|
| | | Benzene | Toluene | Ethyl benzene | m- and p-xylene | o-xylene |
| Cold start (without catalyst) | Mean. | 168.35 | 246.69 | 65.64 | 146.25 | 81.80 |
| | SD | 19.6 | 20.69 | 15.01 | 14.00 | 15.64 |
| | Min. | 154.37 | 210.16 | 50.23 | 120.43 | 68.23 |
| | Max. | 190.21 | 299.37 | 81.34 | 163.45 | 95.23 |
| Hot start (without catalyst) 2000 rpm | Mean | 78.14 | 94.34 | 26.55 | 56.17 | 24.39 |
| | SD | 12.00 | 11.86 | 4.16 | 4.73 | 3.59 |
| | Min. | 62.29 | 80.69 | 31.66 | 63.44 | 20.28 |
| | Max. | 105.48 | 121.37 | 54.35 | 80.35 | 29.55 |
| Cold start (with catalyst) | Mean. | 143.25 | 205.06 | 59.40 | 130.79 | 64.15 |
| | SD | 13.21 | 18.14 | 10.93 | 10.10 | 5.31 |
| | Min. | 122.64 | 174.39 | 40.39 | 112.26 | 54.39 |
| | Max. | 160.34 | 224.37 | 73.21 | 140.27 | 70.14 |
| Hot start (with catalyst) 800 rpm | Mean | 15.94 | 20.58 | 2.80 | 9.11 | 4.06 |
| | SD | 4.31 | 5.97 | 0.84 | 2.18 | 0.82 |
| | Min. | 9.88 | 10.39 | 1.60 | 5.13 | 2.87 |
| | Max. | 22.45 | 30.17 | 4.17 | 12.11 | 5.17 |
| Hot start (with catalyst) 2000 rpm | Mean | 10.13 | 12.00 | 1.99 | 5.08 | 2.80 |
| | SD | 2.89 | 2.68 | 0.97 | 1.89 | 1.17 |
| | Min | 6.44 | 8.21 | 0.71 | 1.66 | 1.23 |
| | Max. | 13.80 | 15.94 | 3.89 | 8.14 | 4.94 |

concentrations of benzene, toluene, m- and p-xylene, o-xylene and ethyl-benzene are 14.14, 17.08, 25.74, 32.23, 21.21 times higher respectively than the concentration resulting from a hot start with catalyst. The results indicate that the effect of the catalyst on individual hydrocarbons increases in the order benzene < toluene <ethylbenzene < m- and p-xylene< o-xylene. This is indicative of the reduced efficiency of the combustion process at low temperature.

The concentration of individual hydrocarbons at cold start with a catalyst is only 10-15 percent lower than without catalyst (cold start). This is because catalysts operate at about 300°C. Analysis indicates that the first sample from a cold start under catalysed conditions has a pollution level comparable to that from an engine without a catalyst. Samples obtained after a few minutes of engine- running have a greatly reduced overall pollution level.

## 5.12 General discussion and conclusion

The work described in this chapter is in two parts:

1. A study of the use of the Carbotrap as part of a methodology for the analysis of volatile organic compounds in ambient air. This study was a development of the successful use of Carbotrap for the analysis of PAHs described in Chapter 4.

2. A study of the use of the Carbotrap methodology in the measurement of air quality at the Brunel University site in Uxbridge and in the analysis of VOCs from vehicle emissions.

The following results show that the Carbotrap is fit for purpose for VOCs analysis:

The data in Figure 5.5 indicate that the Carbotrap can tolerate temperatures up to 400°C. The experiment described in section 5.5.5 shows that the Carbotrap does not form permanent compounds with volatile organic compounds and for this reason the accuracy of release of organic molecules from the Carbotrap is 99± 2%.

The length of sampling time and flow rate of the sampling pump for use of the Carbotrap were optimized in the development of the analytical method. An increase of flow rate to greater than 100 ml/minute causes breakthrough to occur in the Carbotrap because of insufficient contact time to trap compounds. The results from Table 5.2 and Figure 5.4 show that increasing the length of sampling time to more than 45 minutes results in observed low values for concentrations of pollutants, because the humidity in the air obstructs the pores of the Carbotrap. The optimum sampling time was found to be 45 minutes.

The qualitative list of 62 hydrocarbons that were detected by the Carbotrap methodology in car exhausts (Table 5.11 ) shows that a wide range of compounds are trapped by this sampler.

Six volatile organic compounds were analysed using the Carbotrap collection system which proved to be very useful in obtaining samples of hydrocarbons in ambient air because it collects a wide range of hydrocarbons in low traffic areas. Using a Carbotrap tube over a period of one year has shown that adsorbed material may be desorbed several times and the packing has a good thermal stability.

In the Carbotrap methodology used in this study 27 hydrocarbons were identified but in a central London study demonstrated below in which a Tenax samplers was used only 14 hydrocarbons were identified. This indicates that the Carbotrap is a more sensitive absorbent than Tenax for VOCs.

The Carbotrap adsorbent method developed in this study was used for the collection of a large body of information on the concentration of aromatic hydrocarbons at Uxbridge. Comparing this study with another study by Clark (11) et al. in 1982 in central London, shows concentrations of benzene and toluene 4-5 times lower at Uxbridge. This is because the density of traffic in central London at the site of sampling (3500 vehicles an hour) was 6-7 times higher than in Cleveland Road (Uxbridge, Middlesex). In addition, more cars now have catalyst converters than in 1982. A comparison of the composition of fuel for 1982 compared with 1996, however, indicates that the amount of aromatic hydrocarbons in unleaded petrol now is more than that in regular fuel in 1982.

The results from measurement of the concentration of five individual hydrocarbons in the different locations with this method developed in this work, show an overall consistent correlation of these pollutants with each other (Figure 5.19). A diurnal variation study demonstrated, that the pollutant levels depend on traffic flow and meteorological conditions. The concentrations have a negative correlation with wind speed (Figure 5.16 and 5.17).

The ratio of toluene to benzene in the car parks is 1.07, i.e. lower than at the roads. This phenomenon may depend on the photochemical reaction of toluene in exhaust gases as they draft from the road to the car park or it may be related to the higher evaporation rate of benzene compared to toluene.

The correlation factor $C_7/C_6$, $C_7$/ethyl benzene, and $C_7$ /Xylene showed very good consistency through this study and this suggests that all of the pollution is emitted from similar sources.

The variations in the concentrations of individual air pollutants studied were found to be closely related to traffic flow, a fact which confirms that vehicle exhaust emissions are the main source of these pollutants.

From the two engines with and without exhaust catalyst system studied, the mean $C_7/C_6$ ratios were 1.20 and 1.50 respectively. This indicates that the effect of the catalyst is greater on toluene than on benzene. It is clear that, this must affect the commonly reported ratio of toluene to benzene, as an indicator of traffic pollution, which must result from a wide range of emissions by different vehicles plus evaporative losses.

Catalytic converters operate well under hot start condition and decrease hydrocarbons emissions between 10 to 30 times depending on the compounds. In a cold start only, 10 percent lower emission values are achieved compared to a cold start without catalyst. The effectiveness of catalytic converters increased according to benzene <toluene< ethyl benzene <m&p-xylene< o-xylene.

From the health hazard perspective, pollution concentrations found in Cleveland Road do not represent any immediate threat to human health although for seven separate days the concentration of benzene was more than the Standard Limit for benzene (5 ppb). Emissions of monocyclic aromatic hydrocarbons from internal combustion engines are greater than from diesel engines because aromatic hydrocarbon levels in diesel fuel are low and the number of diesel engine vehicles in use is much lower than petrol engines. Emission of aromatic hydrocarbons from exhaust is related to the amounts of these compounds in fuel. In general, the higher aromatic content in petrol causes higher emission of aromatics such as benzene, toluene and xylene to the ambient air. The composition of UK fuels since 1985 is given in Table 5.13. The effect of lead reduction is reflected in the increase of the aromatic content of premium and regular fuels between 1984/85 and 1986 in order to maintain engine performance. The composition of premium fuels in 1990/91 was similar to that in 1987/88. However, unleaded fuels contain a

Table 5.13 The percentage composition of UK fuels 1985-1993

| **Fuel** | | **1984/5** | **1986** | **1987/88** | **1988/89** |
|---|---|---|---|---|---|
| Premium | Saturates | 58.9 | 53.4 | 54.9 | 54.1 |
| | Olefins | 11.2 | 12.3 | 14.1 | 11.8 |
| | Aromatics | 29.9 | 35.9 | 31.0 | 34.1 |
| Regular | Saturates | 72.0 | 60.0 | 61.1 | - |
| | Olefins | 8.9 | 14.5 | 18.1 | - |
| | Aromatics | 19.1 | 25.6 | 20.8 | - |
| Unleaded | Saturates | - | - | - | 57.8 |
| | Olefins | - | - | - | 6.4 |
| | Aromatics | - | - | - | 35.8 |

| | | **1990** | **1990/91** | **1992** | **1993** | **1994** |
|---|---|---|---|---|---|---|
| Premium | Saturates | 53.9 | 56.1 | 55.9 | 54.3 | 55.1 |
| | Olefins | 15.3 | 14.8 | 14 | 13.9 | 14.7 |
| | Aromatics | 30.8 | 29.1 | 30.1 | 32.8 | 30.2 |
| Regular | Saturates | - | - | - | - | - |
| | Olefins | - | - | - | - | - |
| | Aromatics | - | - | - | - | - |
| Unleaded | Saturates | 53.2 | 57.8 | 57.0 | 57.9 | 56.4 |
| | Olefins | 11.2 | 9.5 | 10.3 | 10.7 | 11.5 |
| | Aromatics | 35.6 | 32.7 | 32.7 | 31.4 | 32 .1 |

greater proportion of aromatics than premium fuels. Since the introduction of unleaded petrol in 1988, the consumption of this type of fuel has been steadily increasing and this is one factor which may account for the observed increase in PAH from 1987 to 1992 (7). Results of this study show that the amount of aromatic hydrocarbon in fuel is still high between 29 to 34 percent (described in section 5. 10). Concentration of benzene in UK fuels is about 2.5% although the Shell Company claims that benzene emission from vehicles should drop by 40% from today's level by the year 2000 as a result of further reduction in the benzene content of fuel.

The latest European Community Directive (91/441/EEC) requires that all new light duty motor vehicles be fitted with catalyst converters but in the meantime, half of the petrol sold in the UK is unleaded and only 15 percent of cars have catalytic converters. An increased consumption of aromatic hydrocarbon in fuel and the low percentage of exhaust catalysts fitted causes increased emission of aromatic hydrocarbons in air. The new legislation by Air Quality Standards in the UK recommend 5 ppb for permitted levels of benzene. The result over a four months in this research show that 95% of data was lower than this limit but results from 7 days when wind speeds were lower than 0.8 m/s, indicate values of benzene concentration greater than the recommended safe level. The data from this research can be fited into the world wide data from other research in Table 5.14.

## 5.13 Summary

A method for analysis of volatile organic compound using a Carbotrap as an absorbent has been developed. The method has been used in studies of atmospheric pollution and vehicle emission. The overall concentration of an individual pollutants found at any location low, did not represent any immediate threat to human health, but the concentration of benzene on some days did exceed the standard limit. One should be concerned about the number of days when measured benzene levels are above "safe" values. Any increase in this effect could well lead to an increase health hazard. The ratio of benzene to toluene in a car park is lower than in Cleveland Road because more benzene than toluene evaporates.

Table 5. 14 Comparison of aromatic hydrocarbon concentrations measured at different locations

| **Location** | **Year** | **Benzene** | **Toluene** | **Ethyl benzene** | **m- and p-xylene** | **o-xylene** | **Reference** |
|---|---|---|---|---|---|---|---|
| Johannesburg | 1977 | 3.4 | 10.3 | 1.9 | 4.5 | 1.6 | Louw et al (18) |
| Los Angeles | 1979 | 6.0 | 11.7 | 2.25 | 4.61 | 1.93 | Singh et al (19) |
| London | 1982 | 8.8 | 13.5 | 0.88 | 2.8 | 1.2 | A. I. Clark (11) |
| Helsinki | 1980 | 4.4 | 7.3 | - | 5.4 | 2.1 | E. Hasanen et al (13) |
| Nigata C. and Kurosaki T | 1991 | 1.7 | 2.3 | 0.39 | 0.29,0.70 | 0.29 | Kuniaki Kawata and Yoshimaru Fujieda (10) |
| Turin-Italy | 1993 | 13.88 | 17.32 | | 15.06 | | Giorgio Gilli et al(12) |
| Uxbridge(this work) | 1995 | 2.27 | 3.90 | 0.65 | 1.41 | 0.73 | This work |

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# Chapter Six

## Distribution of Hydrocarbons in Ambient Air Conditions at Tehran

### 6.1 Introduction

Tehran reputedly has the most polluted air in the Middle East. The movement of more than one million cars, the development of hundreds of manufacturing units in the West and South of Tehran, the geographical situation and lack of an underground system has led to Tehran becoming one of the most polluted cities in Asia. Nearly 12 million people live in Tehran and air pollution has an effect upon their health.

Pollution of Tehran air is increasing for the followings reasons;

1. The location of the city: The Alborz mountain range is situated to the north and north east of Tehran and separates the city from northern Iran and the Caspian Sea and limits the amount air movement possible.

2. The weather in Tehran: the weather in Tehran varies over the year with temperature rising to 40°C in summer and down to -10°C in winter. The wind speed is not high because of the mountains to the north and has an average value of less than 1m/s.

3.The movement of millions of cars within a day: most of the vehicular traffic in the city is old and the vehicles do not have exhaust catalyst converters fitted. There is no underground system in Tehran to relieve the situation and only 1% of the buses use electricity.

4.Out-of -town supermarkets: in Tehran out-of-town shopping is not common and basic markets are located in the centre of the city, hence people go there for shopping.

5.Leaded Fuel: about 90% of fuel consumption is of leaded petrol and diesel fuel of which only 10% is unleaded petrol or liquefied gas.

6. Industrial activity: the development of hundreds of large and small factories in the west and south of Tehran have led to an increased pollution level in Tehran. The most important factories are: oil refinery, cement, car manufactures and electrical industry facilities.

In a 1994 study, Rahimi N. and Moattar F. (1), determined lead and atmospheric particulates in the ambient air of Tehran by atomic absorption. The results showed that the concentration of lead was between 2.2 mg/m$^3$ in spring and 4.5 mg/m$^3$ in summer The mean value of lead concentration in the air in different parts of Tehran during the autumn and the winter was compared with the data from investigations made earlier and indicated that the lead concentrations had increased from 0.63 mg/m$^3$ in 1978 to 2.470 mg/m$^3$ in 1988 and 3.662 mg/m$^3$ in 1993.Clinical signs of lead poisoning are fairly well established. Anaemia is a characteristic early toxic effect in people indicated by decrease in haemoglobin levels to a mean level of about 50µg/dl in adults. This can drop to approximately 40µg/dl for some population groups particularly in iron-deficient children (14). Dysfunction of the brain occurs with lead levels of 50-60 µg/dl in children and 60-70µg/dl in adults, while acute or chronic encephalopathy[1] and damage to the kidney

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[1] Any of various diseases that affect the function of the brain.

occurs at level of 60-70 μg/dl in children and approximately 80μg/dl in adults. The current concern for young children is that blood lead levels even as low as 10μg/dl may be causing subtle neurological[2] damage in some susceptible children without children ever exhibiting classical signs of lead encephalopathy. These altered behaviours may be recognized by parents, teachers, and clinicians as attentional disorders, learning disability, or emotional disturbances which may impair progress in school (11).

In a 1981 study, Aghdaie and Abid (10) measured concentrations of PAHs in the ambient air of Tehran. It was found that the concentration of benzo(a)pyrene was 1.27 ng/m$^3$ in summer and 8.29 ng/m$^3$ in winter. But because the number of vehicles has increased subsequently in the period 1981 to 1996, the present concentrations of benzo(a) pyrene could be much higher than these values. Increase of particulates may cause an increase in lung cancer and bronchitis. Benzo(a)pyrene and benzo(a)anthracene are reported by by the International Agency for Research on Cancer to be carcinogens (described in chapter two section 2.2.2).According to the measurements of common pollution by the Institute of Health (section of Minstry of Health) concentrations of CO and $NO_X$ are 2-4 times more than permitted limit. Pollutants are increasing in Tehran annually because of the increasing vehicle numbers.

Some new regulations have been established in Tehran for keeping the air clean and the Mayor of Tehran and the authorities have persuaded people to use new cars and have banned diesel engine movement in central Tehran from 7.00 a.m. to 10.00 p.m. daily. The Methrow Company of Tehran along with the Mayor of Tehran has begun to construct an underground railway system in the city. The Mayor claims that the first track will be open at the end of 1996, but air pollution in Tehran is still high and this work will be insufficient to end the hazard to people's health.

### 6.2 Objective

Because of the importance of air quality to the health condition of the citizens of Tehran and the potential effects caused by hydrocarbons in the ambient air found there, the

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[2] Effect on nervous system

objectives of this work are:

(1) to identify the hydrocarbons present in the air

(2) to evaluate the distribution of hydrocarbons in ambient air in Tehran

(3) to obtain quantitative measurement of principal hydrocarbons present in the air.

(4) to assess the current health hazards arising from the presence of contaminates in the air.

To fulfil the objective, a program of work was established on October 1994 and August 1995 as a short term study on concentrations of hydrocarbons in Tehran. The analytical methods used are described in section 5.3 in chapter 5.

This study has benefited from the use a method developed during research which has been proved to be both sensitive and specific in the range of concentrations of hydrocarbons found in street air. The method provides detailed statistical data which show the correlations that exist between these compounds at different geographical locations. The sampling points were at kerbs at a height of 1.5-2 m above ground level. Sampling sites are shown in Figure 6.1 and density of traffic in each site is shown in Table 6.1.

Samples were taken separately at the north and south of Tehran during work hours from 7.00-19.00 hour. The work hours in Tehran are between 0800 to 1600 hour but the market is opens until 1900 hours.

A few Carbotrap tubes were selected as blank samples and about 20 samples were collected.

## 6.3. Results and Discussion

### 6.3.1 Identification of hydrocarbons

Fifty four hydrocarbons were identified in the Tehran air as shown in Table 6.2 and concentrations of five aromatic hydrocarbons: benzene, toluene, ethyl benzene, m- and

Table 6.1 Sampling sites in Tehran

| Location | Site | Number of vehicles per hour (approximately) |
|---|---|---|
| South of Tehran | 1.Pirozi Street | 2000 |
| | 2. Ammam Hussain Square | 3500 |
| | 3.Shosh Square | 3500 |
| | 4.Enqalab Street | 2500 |
| | 5. Bazzar | 2500 |
| North of Tehran | 1.Tajrish Square | 3500 |
| | 2.Niaveran Street | 250 |
| | 3.Resalat Street | 2700 |
| | 4. Lavizan | 1800 |

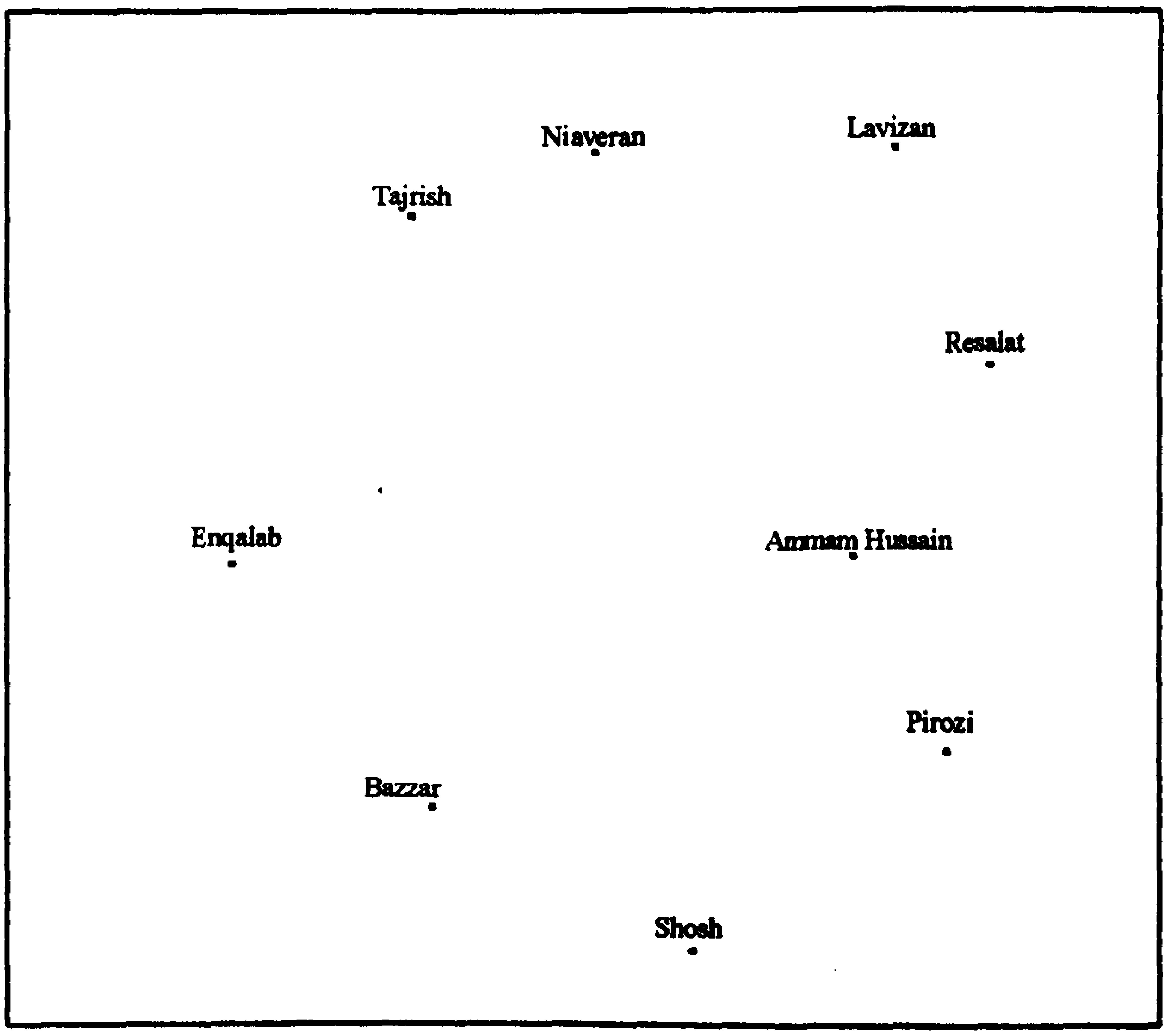


Figure 6.1 Localization of airborne sampling in Tehran 1 Kilometer ——

p-xylene and o-xylene occur as large peaks on the chromatograms which were determined using GC/MS and GC. Figures 6.2 and 6.3 are chromatograms of two samples Tehran in high traffic.

The majority of substances identified were aliphatic and aromatic hydrocarbons. The origins of most pollutants were car engine exhausts but some of compounds do arise from secondary pollution for example (1-3 Ethyl oxiranyl)Ethanone and propanal.

### 6.3.2 Diurnal variation

The diurnal variations in the concentration of five aromatic hydrocarbons (benzene, toluene, ethyl benzene, m- and p-xylene, o-xylene) were measured on 10.09.95. The concentration data for the pollutants plotted against time are shown in Fig.6.4 at the times 0730 ,0915, 1015, 1200, 1630, 1900. The air temperature was between 25-30°C with a wind speed lower than 0.5 m/s. Distributions for these compounds in all the samples are in Figs. 6.5 (a,b,c,d,e).

The data clearly indicate, an increase in the concentration of the five hydrocarbons through the morning and afternoon periods.

### 6.3.3 Statistical results

Data obtained at several street locations have been analysed statistically to show correlation between individual hydrocarbons.

The results of the statistical analyses of the data for all samples are shown in Table 6.3 and 6.4 and indicate that toluene concentrations are greater than those of all other compounds. Concentrations of toluene are between 39-380 $\mu g/m^3$. The lowest concentration of pollutants was at Niavaran Street in the north of Tehran with an average traffic flow of about 300 vehicles hour where concentrations of benzene and toluene were 16 and 39 $\mu g/m^3$, respectively.

The greatest pollution was at Resalat Square with concentrations of benzene and toluene of 290 and 380 $\mu g/m^3$, respectively. Resalat Square is a high density traffic area where six streets cross, and the number of vehicles is more than 2700 per hour. Shosh Square has the most pollution south of Tehran with traffic more than 2000 vehicles/hour.

Although the highly polluted Resalat Square is in the north east of Tehran, most pollution is in the south of Tehran where the average for benzene and toluene are 155.5, 236.5 $\mu g/m^3$, respectively. It is evident from Table 6.3 that emissions of individual pollutants in the south of Tehran are greater than in the north of Tehran. The concentrations of benzene, toluene, m- and p-xylene, o-xylene and ethyl benzene from south of Tehran being, 1.57, 1.60, 1.28, 1.41, 1.60 times higher respectively than the concentrations found in the north of Tehran. With reference to the geographical situation, the north of Tehran is at a higher level than the south of Tehran and there is a southerly gradient. There is a central market that causes high traffic congestion in the south of Tehran.

### 6.3.4 Correlation between individual hydrocarbons

The mean ratio and variation of mean ratio between toluene and other compounds in the Tehran air are shown in Table 6.5 and as indicated by the standard deviation values, those between benzene and toluene are lower than those between toluene and other compounds.

The best correlation is for toluene and benzene with a standard deviation ($\delta_n$) of 0.57 which indicates little variation and a correlation as good as 93% .

This can be confirmed by reference to Fig. 6.6 (a), where benzene data is plotted against toluene in a regression mode and linearity is expressed by the equation:

$$Y=56.82 + 1.13X$$

The equation of linearity used and the correlation between toluene and other compounds are as follows:

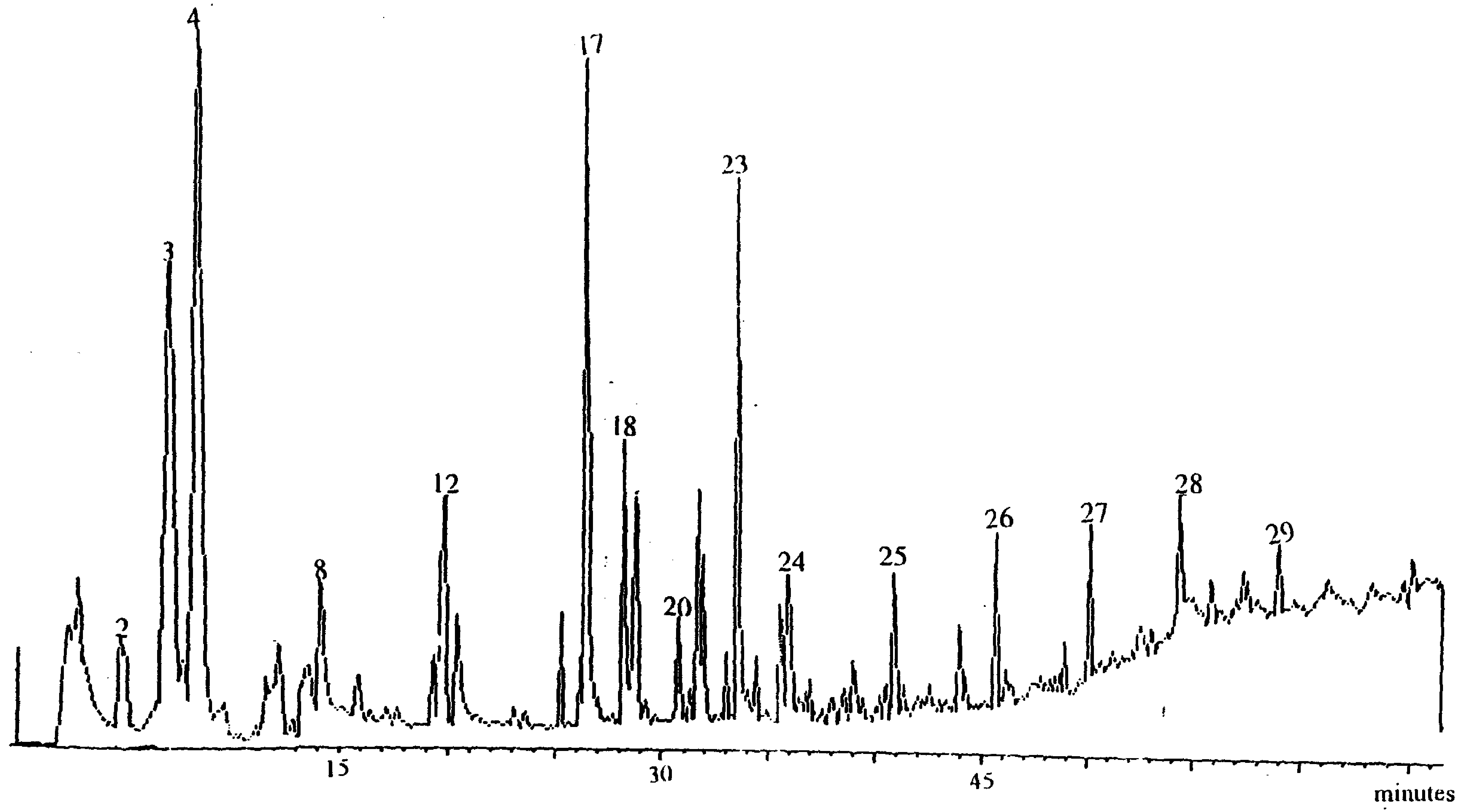
| | | |
|---|---|---|
| Toluene and ethyl benzene | $Y= 30.95 + 2.93X$ | 77% |
| Toluene and m- and p-xylene | $Y=-13.79 + 1.94X$ | 87% |
| Toluene and o-xylene | $Y=2.38 + 3.45X$ | 87% |

Correlation between toluene and xylene and toluene and ethyl benzene is lower than for toluene and benzene. As can be seen in Fig. 6.4. This is because the toluene and xylene concentrations are closer to each other in the morning than in the afternoon. Table 6.5

shows the ratios between benzene and m- and p-xylene and also between benzene and o-xylene in the afternoon are 2.91 and 3.81, respectively which are more than the ratios in the morning at 1.40 and 2.91 respectively. The temperature of the air during sampling was between 15°C in the morning to 30°C in the afternoon.

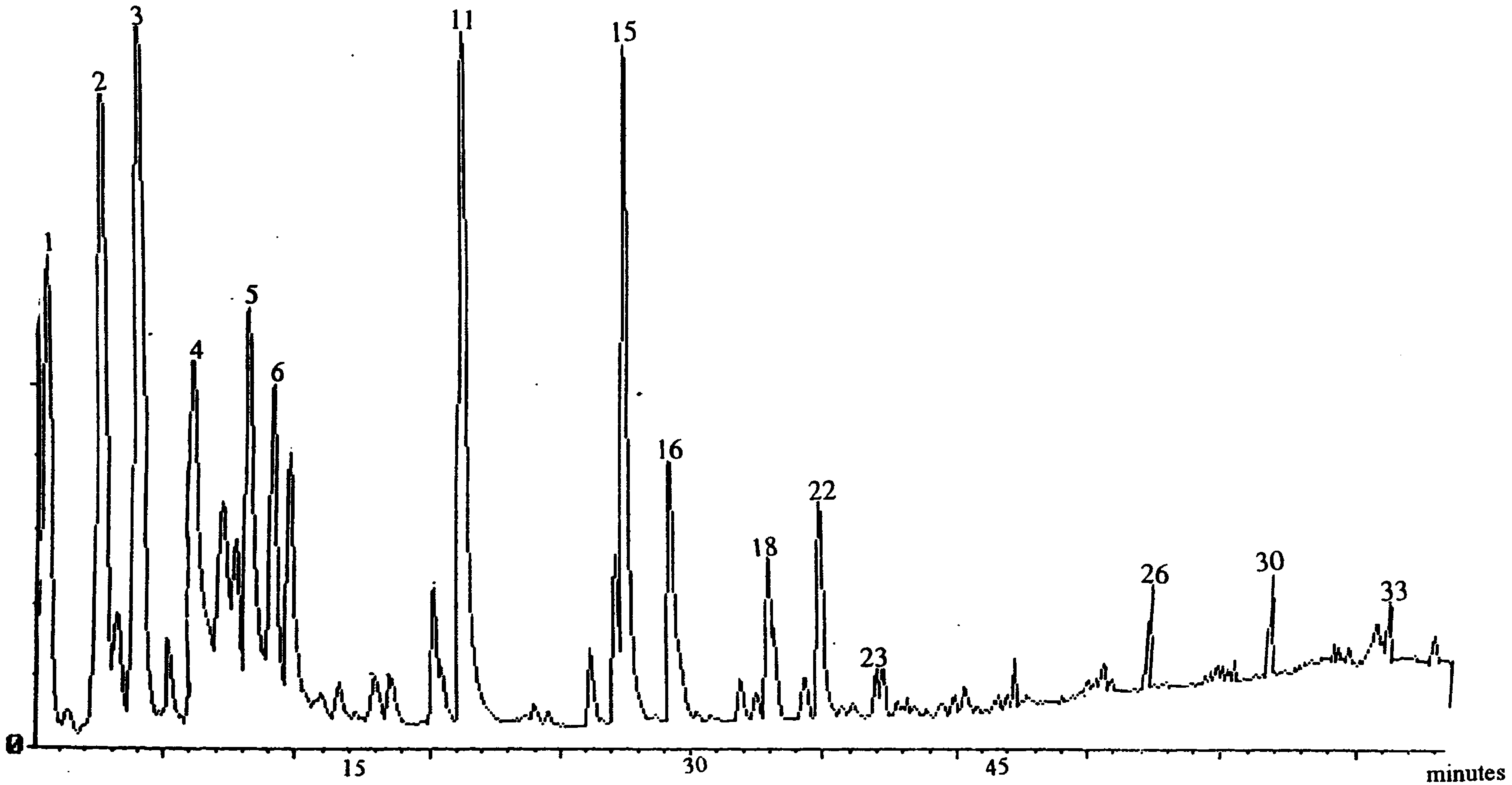
Table 6.2 Hydrocarbons were recognised at Tehran samples

| No. | Hydrocarbons | No. | Hydrocarbons |
|---|---|---|---|
| 1 | Propane | 30 | o-xylene |
| 2 | Isobutane | 31 | n-none |
| 3 | Butane | 32 | Propyl benzene |
| 4 | Iso pentane | 33 | 1,3 Ethylmethyl benzene |
| 5 | 2-Methyl-butane | 34 | 1,4 Ethylmethyl benzene |
| 6 | 2-Methyl pentane | 35 | 1,3,5 Trimethyl-benzene |
| 7 | 3-Methyl pentane | 36 | 1,2 Ethylmethyl benzene |
| 8 | Ethanol | 37 | 1,2,4 Trimethyl-benzene |
| 9 | Hexane | 38 | Undecane |
| 10 | 2,3-Dimethyl butane | 39 | 1,2,3 Trimethyl-benzene |
| 11 | 5-Methyl-1-Hexane | 40 | Indane |
| 12 | 2-Methyl-1-pentane | 41 | 1,3 Methyl propyl benzene |
| 13 | Benzene | 42 | 1-ethyl-2,5-dimethyl benzene |
| 14 | 2,3 Dimethyl pentane | 43 | 1-ethyl-2,4-dimethyl benzene |
| 15 | Methyl cyclopentane | 44 | 1-ethyl-3,4-dimethyl benzene |
| 16 | Ethyl cyclopentane | 45 | 1,2,4,5-Tetramethyl-benzene |
| 17 | 2,2,3 Trimethyl-butane | 46 | 1,2,3,5-Tetramethyl-benzene |
| 18 | (1-3 Ethyl oxiranyl) Ethanone | 47 | 2,2,3,3-Tetramethyl-benzene |
| 19 | Toluene | 48 | 2,9 Dimethyl decane |
| 20 | 2,4-Dimethyl hexane | 49 | Naphthalene |
| 21 | 3,4-Dimethyl hexane | 50 | 2-Methyl naphthalene |
| 22 | 2,3,5 trimethyl hexane | 51 | 1-Methyl naphthalene |
| 23 | n-Octane | 52 | 2-Ethyl-1-Decanol |
| 24 | 3,5-Dimethyl heptane | 53 | Tridecanol |
| 25 | 3-Ethyl-heptane | 54 | Tetradecane |
| 26 | 2 Butanone | | |
| 27 | Propanal | | |
| 28 | Ethyl benzene | | |
| 29 | m- and p-xylene | | |



(1) Propane (2)Isobutane (3)n-butane (4)Iso pentane (5)3-Methyl pentane (6)2-Methyl-1-pentane (7) 5-Methyl-1-Hexane (8) Benzene (9) 2,3 Dimethyl pentane (10) Methyl cyclopentane (11)Ethyl cyclopentane (12)Toluene (13) 2,5-Dimethyl hexane (14) 3,5-Dimethyl heptane (15) 3-Ethyl-heptane (16) Ethyl benzene (17)m&p-xylene (18)o-xylene (19)n-none (20)Propyl benzene (21)1,3 Ethylmethyl benzene (22)1,3,5 Trimethyl-benzene (23)1,2,4 Trimethyl-benzene (24)1,2,3 Trimethyl-benzene (25)Indane (26)1-ethyl-2,5-dimethyl benzene (27)1-ethyl-2,4-dimethyl benzene (27)1,2,4,5-Tetramethyl-benzene, (28)1,2,3,5-Tetramethyl-benzene (29)2,9 Dimethyl decane

**Fig. 6.2 Chromatogram of sample Number three of Tehran (morning)**



(1)Propane, (2)Isobutane, (3)Butane, (4) 3-Methyl pentane (4) Hexane (5) 2-Methyl 1-Pentane, (6)Benzene, (7) 2,3 Dimethyl pentane, (8) Methyl cyclohexane, (9) Ethyl cyclopentane (10) (1-3 Ethyl oxiranyl) Ethanone (11)Toluene (12)2,3,5 trimethyl hexane (13) n-Octane, (14)Ethyl benzene (15)m&p-xylene, (16)o-xylene, (17)n-none, (18)Propyl benzene, (19)1,3 Ethylmethyl benzene, (20)1,4 Ethylmethyl benzene, (21)1,3,5 Trimethyl-benzene, (22)1,2,4 Trimethyl-benzene (23) n-decane, (24)1,2,3 Trimethyl-benzene, (25) Indane, (26)1,3 Methyl propyl benzene, (27) 1-ethyl-2,5-dimethyl benzene, (28) 1-ethyl-2,4-dimethyl benzene, (29) 1-ethyl-3,4-dimethyl benzene, (30)1,2,4,5-Tetramethyl-benzene (31)1,2,3,5-Tetramethyl-benzene, (32)2,9 Dimethyl decane (33) Naphthalene (34)2-Methyl naphthalene

**Fig. 6.3 Chromatogram of sample Number Seven of Tehran (afternoon)**

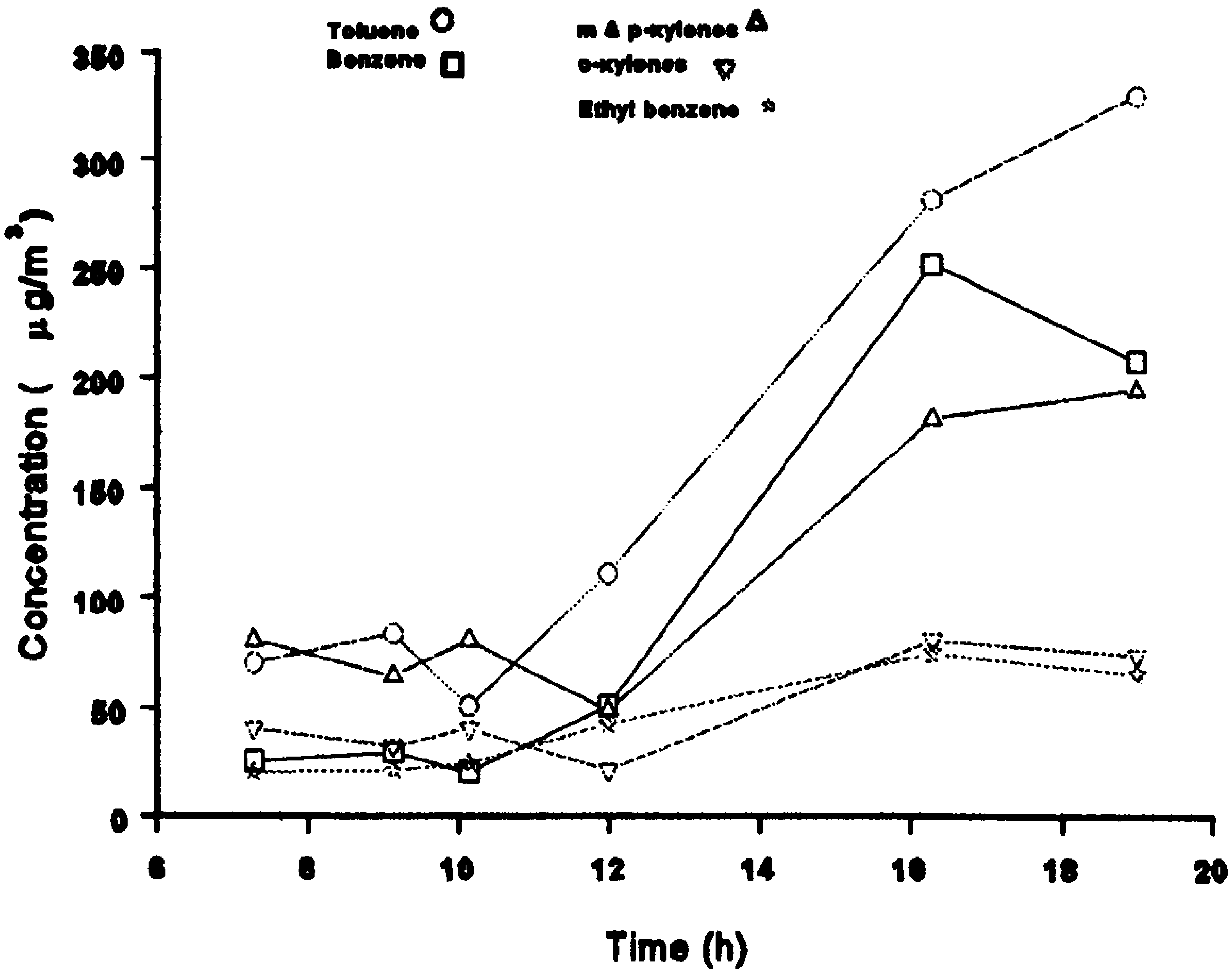


Fig. 6.4 Dirunal variation of five hydrocarbons on Pirozi street in Tehran on the 10.09.1995

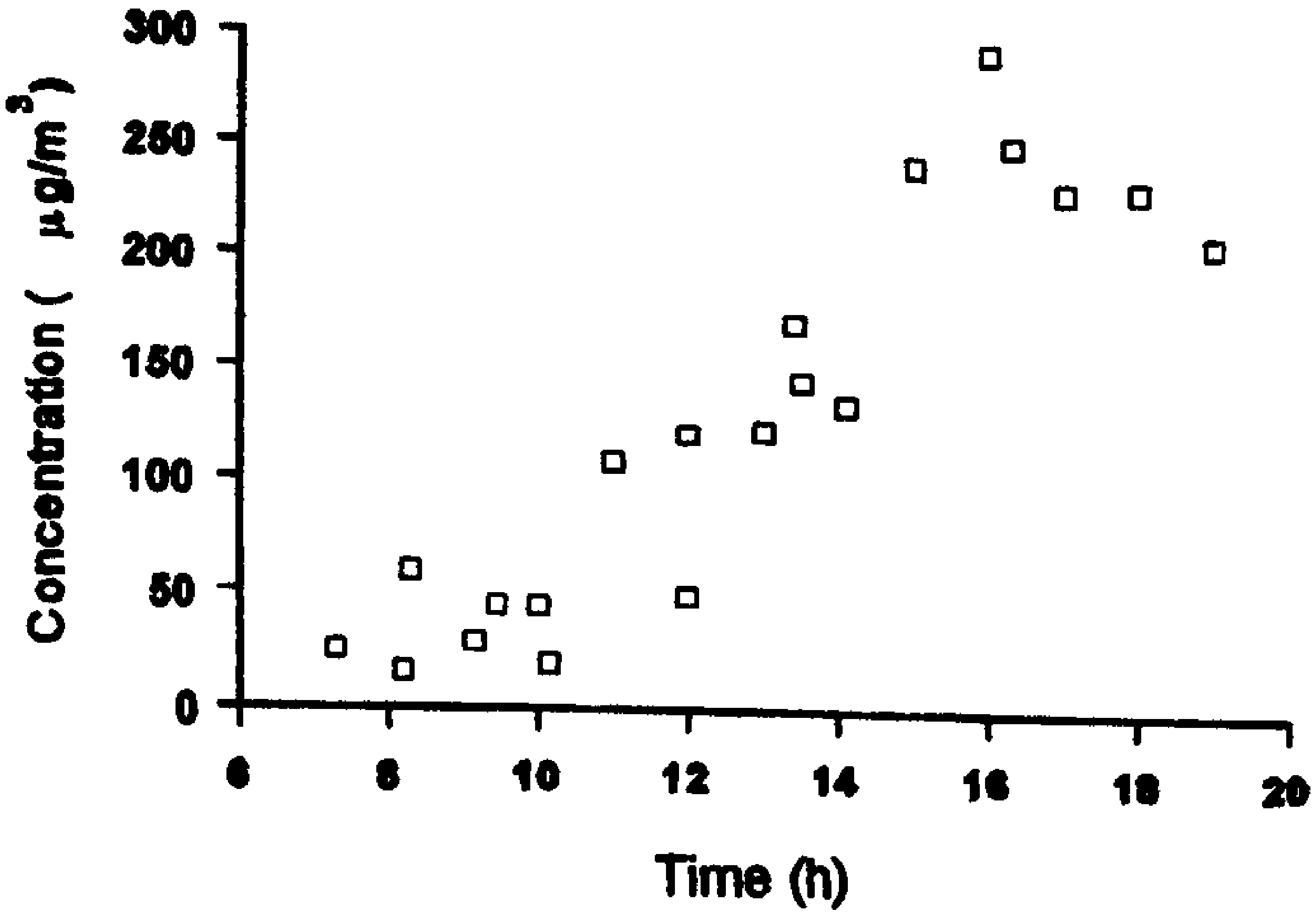


Fig. 6.5(a) Hourly distribution of benzene in ambient air of Tehran in September 1995 and October 1994

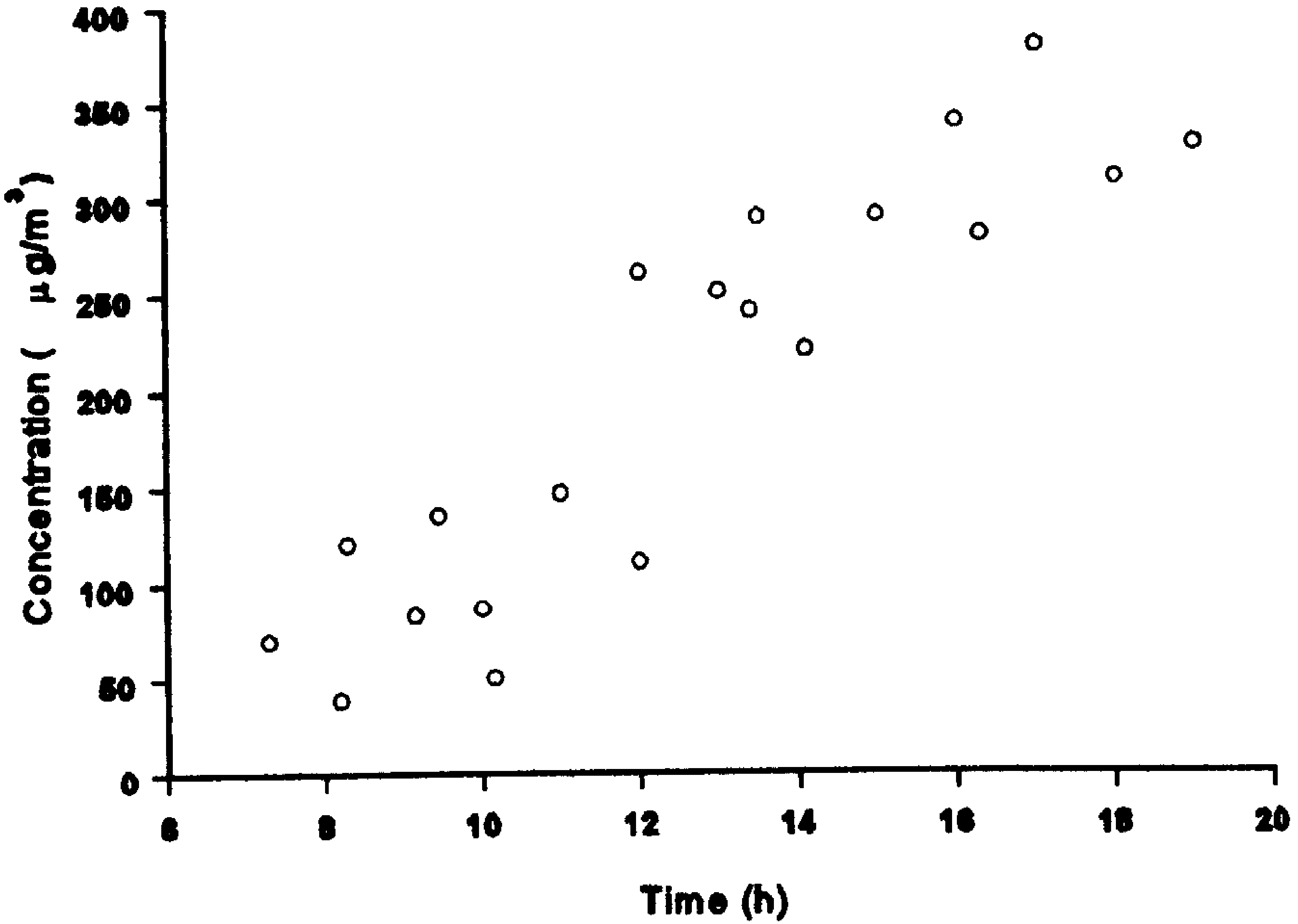


Fig. 6.5(b) Hourly distribution of toluene in ambient air of Tehran in September 1995 and October 1994

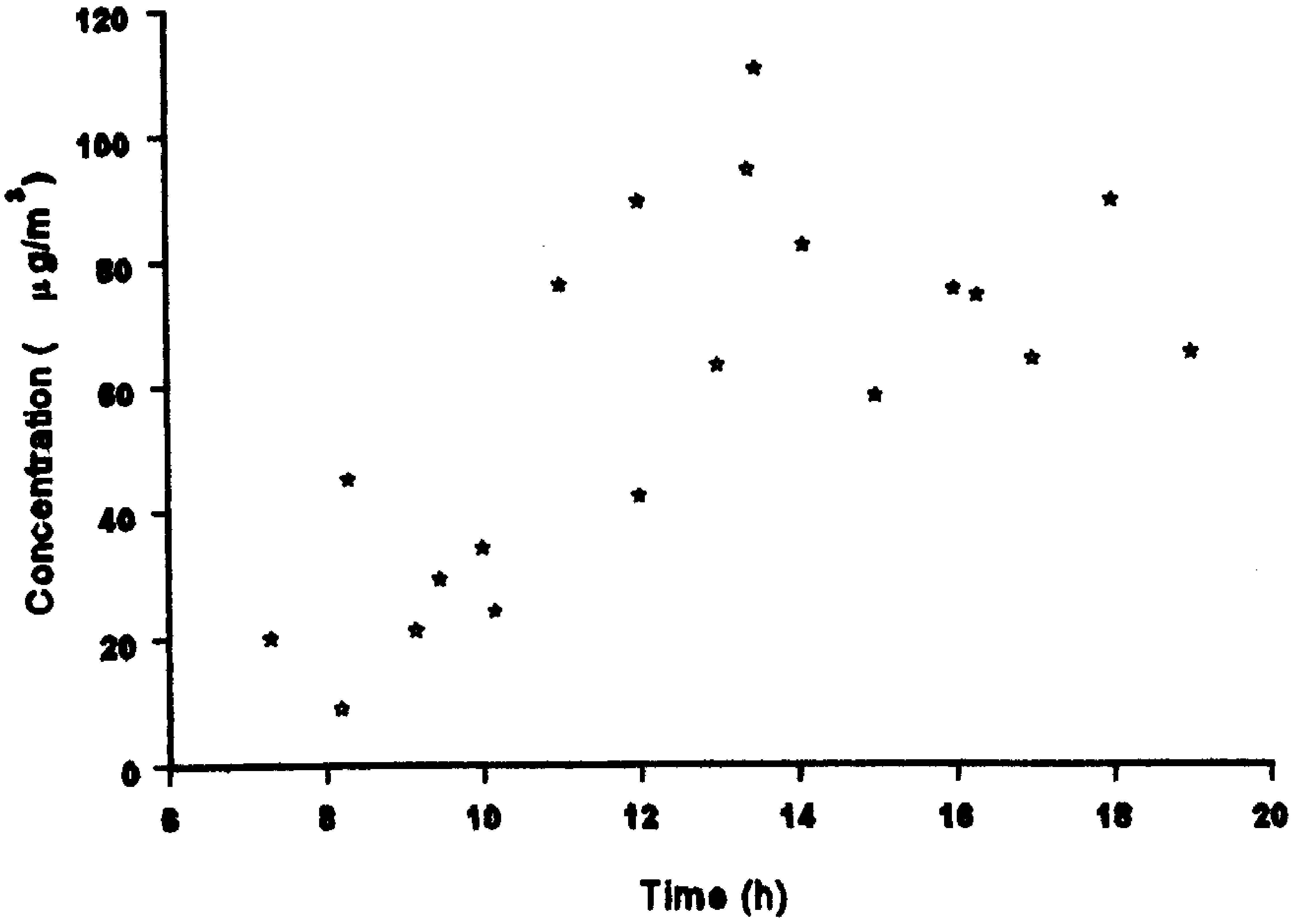


Fig. 6.5(c) Hourly distribution of ethyl benzene in ambient air of Tehran in September 1995 and October 1994

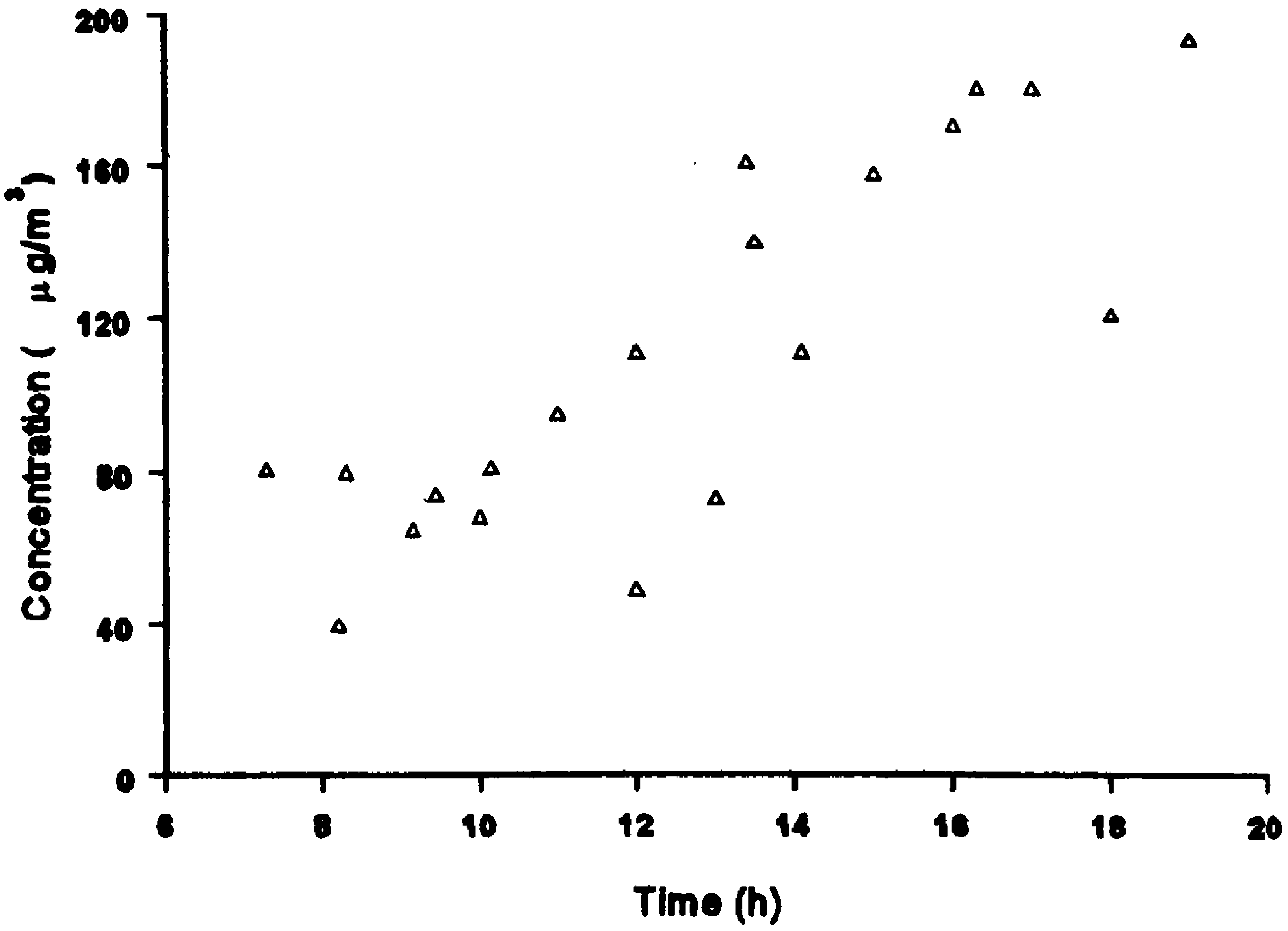


Fig.6.5(d) Hourly distribution of m&p-xylene in ambient air of Tehran in September 1995 and October 1994

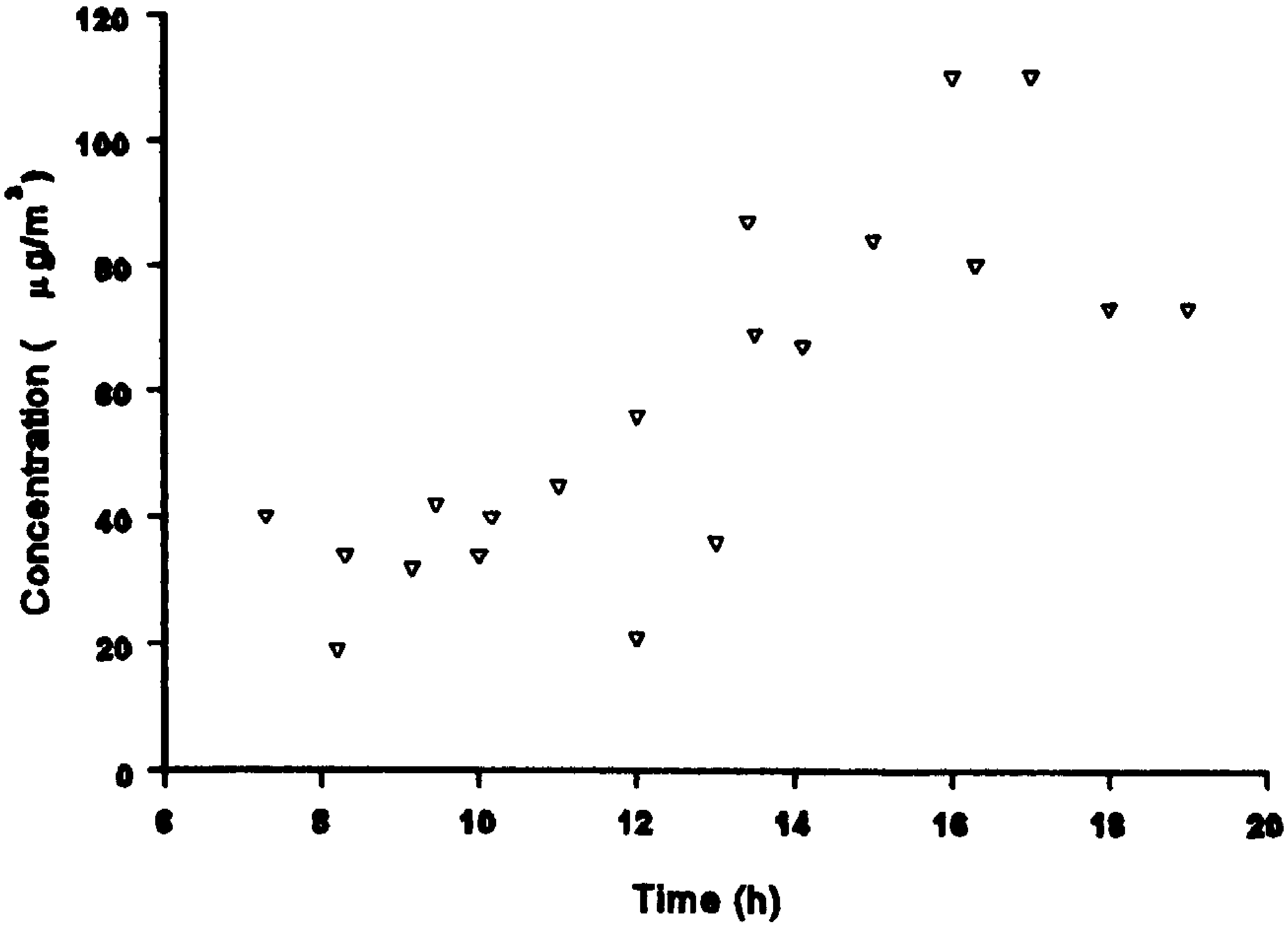


Fig. 6.5(e) Hourly distribution of o-xylene in ambient air of Tehran in September 1995 and October 1994

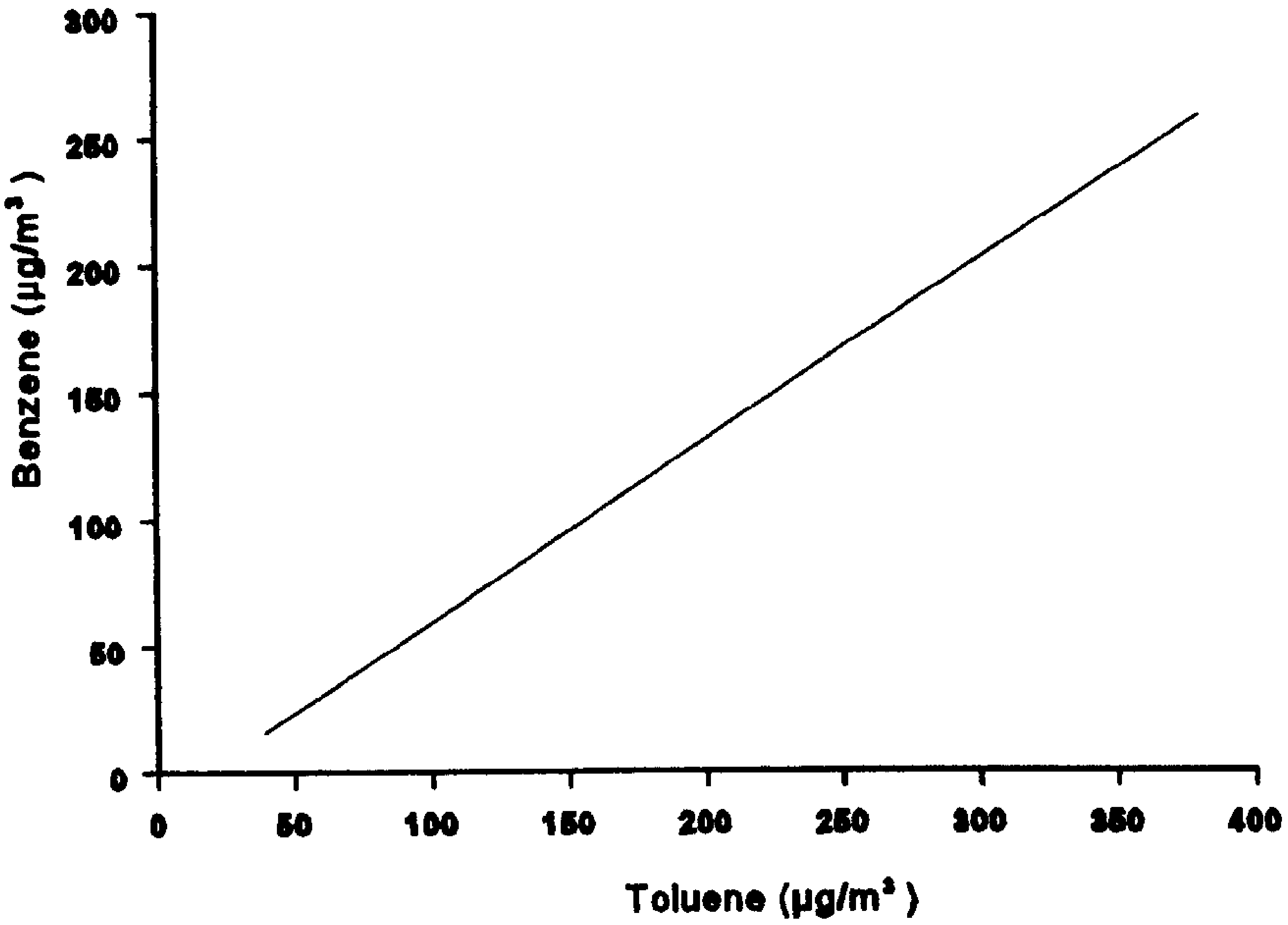


Fig. 6.6(a) Correlation between benzene and toluene in ambient air of Tehran in September 1995 and October 1994

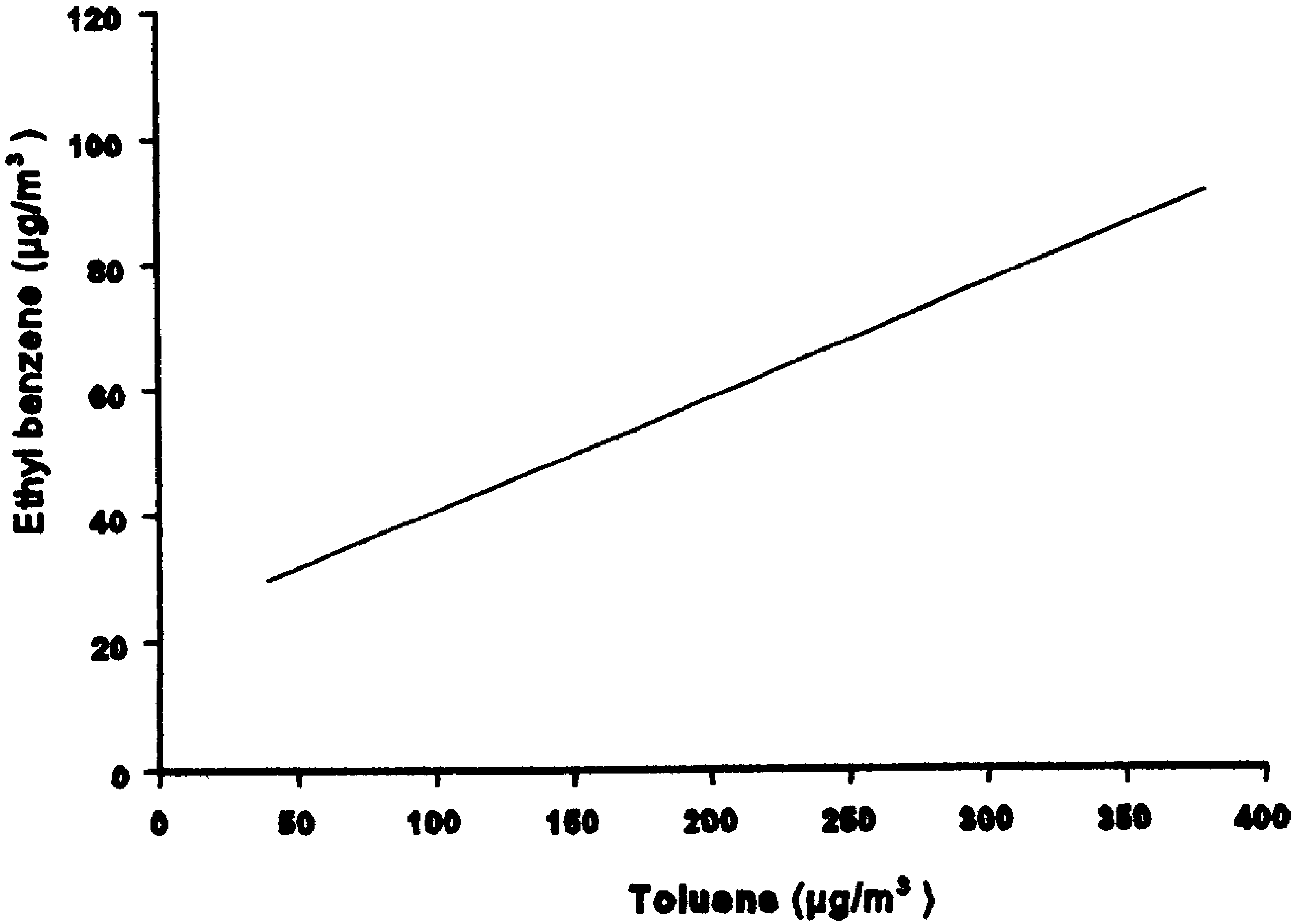


Fig. 6.6(b) Correlation between Ethyl benzene and toluene in ambient air of Tehran in September 1995 and October 1994

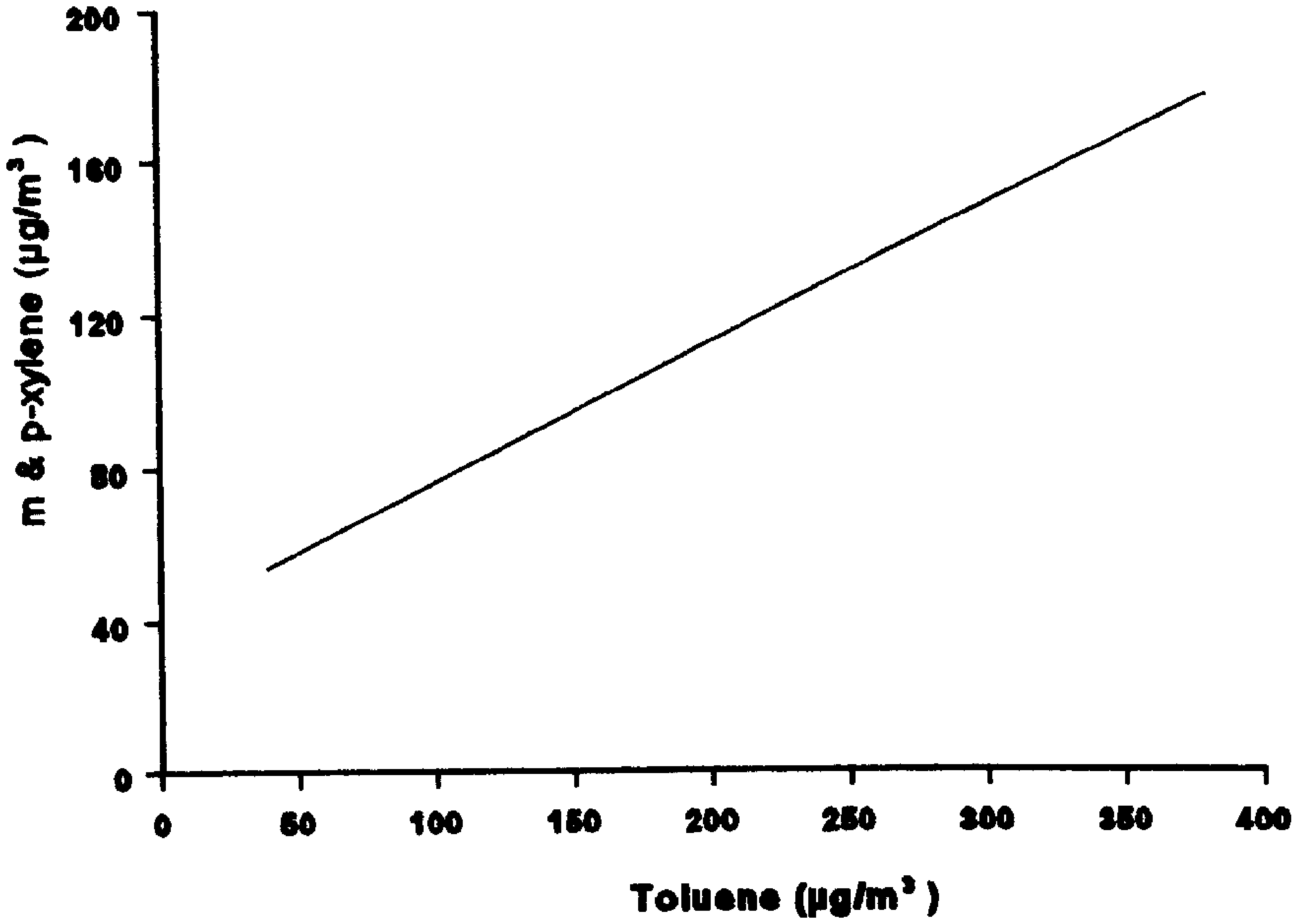


Fig. 6.6(c) Correlation between m&p-xylene and toluene in ambient air at Tehran in September 1995 and October 1994

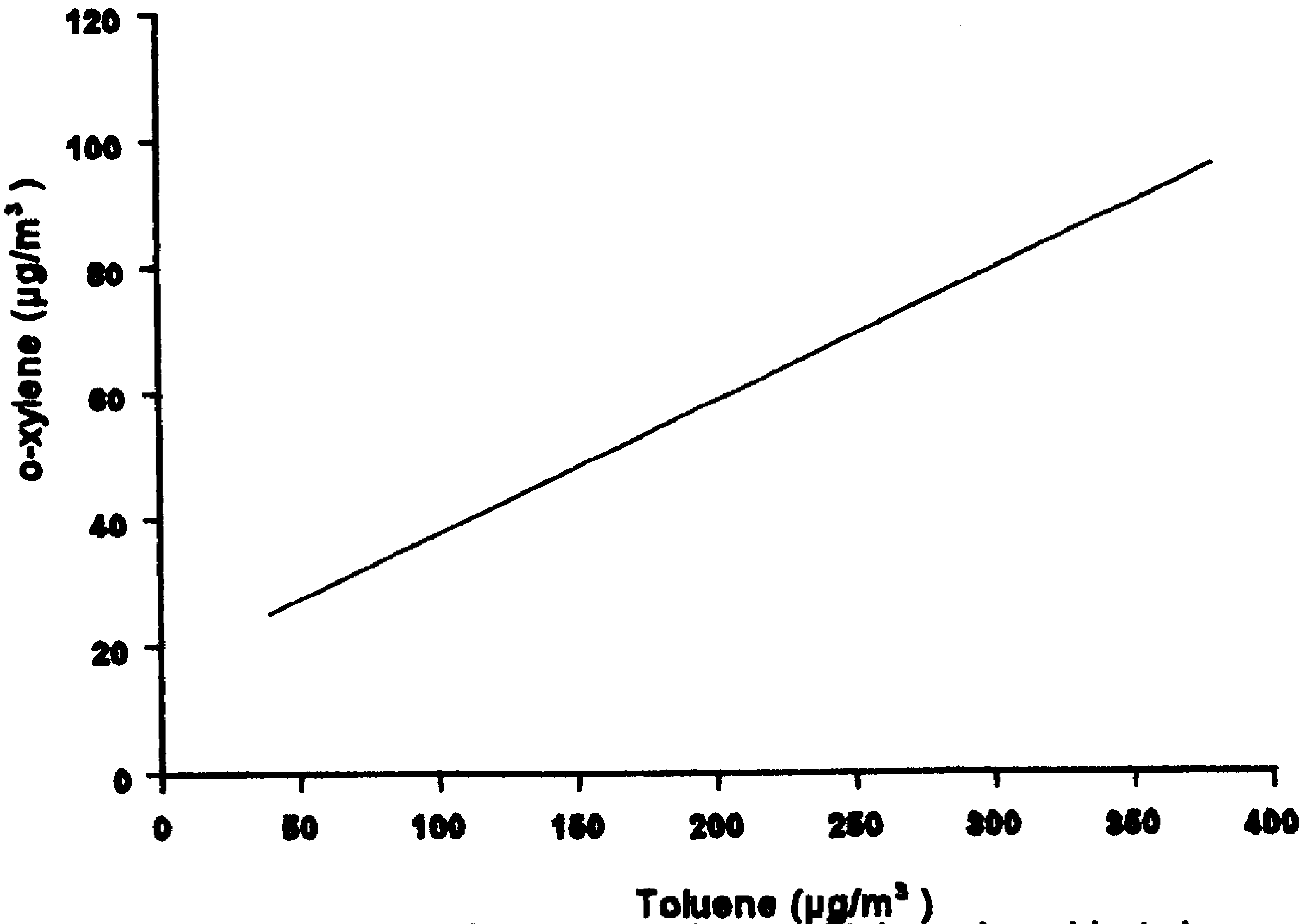


Fig. 6.6(d) Correlation between o-xylene and toluene in ambient air at Tehran in September 1995 and October 1994

Table 6.3 Concentration of aromatic hydrocarbons measured in ambient air condition at Tehran on September 1995 and October 1994

| Site | St. | Concentration μg/m³ | | | | |
|---|---|---|---|---|---|---|
| | | Benzene | Toluene | Ethyl benzene | m- and p-xylene | o-xylene |
| Tehran (total) | Mean | 127.65 | 201.15 | 58.14 | 110.75 | 57.60 |
| | SD | 87.45 | 105.85 | 28.01 | 47.23 | 26.77 |
| | Max | 290 | 380 | 110 | 193 | 110 |
| | Min | 16 | 39 | 8.90 | 39 | 19 |
| South of Tehran | Mean | 155.54 | 236.54 | 62.45 | 122.90 | 66.36 |
| | SD | 94.84 | 109.13 | 28.57 | 42.72 | 26.8 |
| | Max | 290 | 380 | 110 | 180 | 110 |
| | Min | 20 | 50 | 20 | 64 | 32 |
| North of Tehran | Mean | 98.55 | 147.11 | 52.84 | 95.88 | 46.88 |
| | SD | 62.24 | 91.02 | 26.37 | 8.20 | 22.36 |
| | Max | 206 | 328 | 94 | 193 | 87 |
| | Min | 16 | 39 | 8.90 | 39 | 19 |

Table 6.4 Concentration of aromatic hydrocarbons measured in ambient air at Tehran in the morning and afternoon during September 1995 and October 1994

| Site | St. | Concentration μg/m³ | | | | |
|---|---|---|---|---|---|---|
| | | Benzene | Toluene | Ethyl benzene | m- and p-xylene | o-xylene |
| Tehran morning | Mean | 43.75 | 78.62 | 32.23 | 72 | 35.75 |
| | SD | 28.63 | 32.58 | 19.30 | 15.16 | 7.5 |
| | Max | 110 | 135 | 76 | 94 | 45 |
| | Min | 16 | 39 | 8.90 | 39 | 19 |
| Tehran afternoon | Mean | 183.58 | 274.75 | 75.41 | 136.58 | 72.16 |
| | SD | 66.16 | 65.86 | 17.72 | 43.53 | 35.01 |
| | Max | 290 | 380 | 110 | 193 | 110 |
| | Min | 50 | 110 | 42 | 48 | 21 |

Table 6.5 Mean ratio and variation between Toluene and other aromatics in ambient condition of Tehran

| | Compounds | Mean ratio | Standard deviation |
|---|---|---|---|
| Total of samples | Toluene | 1 | 0 |
| | Benzene | 1.90 | 0.57 |
| | Ethyl benzene | 3.55 | 1.08 |
| | m- and p-xylene | 1.77 | 0.62 |
| | o-xylene | 3.46 | 1.24 |
| Samples of the morning | Toluene | 1 | 0 |
| | Benzene | 2.32 | 0.53 |
| | Ethyl benzene | 2.98 | 0.98 |
| | m- and p-xylene | 1.40 | 0.46 |
| | o-xylene | 2.91 | 1.13 |
| Samples of the afternoon | Toluene | 1 | 0 |
| | Benzene | 1.61 | 0.36 |
| | Ethyl benzene | 3.93 | 1.03 |
| | m- and p-xylene | 2.91 | 1.13 |
| | o-xylene | 3.83 | 1.17 |

The reasons of the increasing the ratio of benzene to xylene in the afternoon compared with the morning are as follows;

1. Increased photochemical reaction of xylene in air: The photochemical reaction of xylene with free molecules of oxygen and $NO_X$ in air is more efficient than for benzene. According a study by Atkinson (1990) the rate of photochemical reaction of xylene is 10 to 15 times faster than for benzene (4). It is also 3 to 5 times faster than toluene. In another study by Carter (7) the relative reactivities of benzene, toluene, ethyl benzene,

o-xylene, p-xylene and m-xylene in air are 0.135, 0.88, 0.86, 2.1, 2.1 and 2.6 respectively. Altshuller & Bufalini (1971) and Carter (1995), show that aromatic hydrocarbons can undergo photochemical decomposition in the atmosphere and the reactivity of each species differs increasing order: benzene < toluene <ethyl benzene <xylene <trimethylbenzene (8,9). Relative concentrations of xylene in the atmosphere of Tehran increase at a lower rate during the day than does the benzene concentration.

2. Increases in benzene level in air occur because of effects temperature on carburettors; evaporation of hydrocarbons in the car carburettor increases due to high temperature. The temperature of air in Tehran was between 15-20°C in the morning but increased to 30°C in the afternoon, more hydrocarbons therefore evaporate from carburettor in the afternoon. Evaporation of benzene from carburettor occurs at a greater rate than xylene due to the higher volatility of benzene. Toluene is more volatile than xylene.

3. An increase in benzene levels in the air caused the effect of temperature in the fuel tank; According to study by Vincen E.J.(3) at EPA and Schord (18) temperature influences the concentration of aromatics in the gas phase of the petrol. If the temperature in the petrol tank rises from 5 to 35°C, the concentration of benzene in the gas phase over the petrol increases from 16 to 44mg/l.

The results of the present study show that the concentration of unburned hydrocarbons in ambient air of Tehran is very high. Concern about the connection between leukemia and benzene was explained in chapter two(section 2.1.1.3). Increases in the concentration of volatile organic compounds causes an increasing amount of secondary pollution associated with ozone, peroxyacetyl nitrate (PAN) and aldehydes (described in chapter one section 1.5). Ozone causes eye-irritation. Other oxidants such as PAN are stronger eye-irritants than ozone. Among the aliphatic organics, the aldehydes have been identified as potentially toxic components of the urban air pollution mixture. Some 50%

of total aldehydes may be present as formaldehyde and some 5% as acrolein (15). Secondary pollution is increased in air when inversion occurs in ambient air especially in the autumn. This is where the temperature effect causes pollution to be trapped under a dense layer of air. Indeed, the authorities recommend that the elderly and infirm people remain indoors during this period.

Pollutants affect human health and this is greater for people living in the south of Tehran. Effects of pollution have been related to some occupations such as taxi drivers, shopkeepers also on the health of children, Borgia et al (13) determined mortality rate of taxidrivers by a cohort study. The overall mortality was found to be lower than expected on the basis of regional reference rate but an increase standard mortality ratio was observed in lung cancer (SMR=125).

Concentrations of individual hydrocarbons in different places in Tehran, indicate that pollution is depends on traffic flow. In the hours between 15.00-19.00 traffic is high as can be see in Fig. 6.5(a, b, c, d, e) and pollutant concentrations are found to be higher at this time than in the morning, especially when wind speed is lower than 0.5 m/s. This is also see in the data in Table 6.4 and Fig. 6.4. Most hydrocarbons which were identified in the ambient air of Tehran ( shown Table 6.2) are found in leaded petrol and indicate that unburned hydrocarbons are the basic sources for pollution in Tehran.

The altitude in the north of Tehran is higher than in the south of Tehran. North of Tehran has a gradient down to south. Pollutant transport to the south of Tehran, where traffic also has high density. The concentrations of pollutants in the south of Tehran is higher than in the north.

Fig. 6.6 shows a correlation between toluene and other aromatic hydrocarbons is strong which indicate that all of the compounds are emitted from similar sources and distributed in the same way.

Mean values of the ratio toluene to xylene in the afternoon is greater than in the morning and this is probably due photochemical reaction. The photochemical reactivity of xylene in the atmosphere is greater than toluene and benzene.

Evaporation of the lightest fuels in the carburettor such as benzene and toluene at a temperature of 30°C in the afternoon is more than in the morning (about 24°C).

Finally, the variation of the results between benzene and toluene also benzene and xylene is an agreement with result reportted by Wathine in Oslo (1982) (2).

### 6.4 Discussion and conclusion

Transportation sources produce the major hydrocarbon pollution problems in the ambient air of Tehran. The GC-MS/Thermal Desorption method described in chapter five was used for the qualitative and quantitative analysis of air samples from Tehran. 55 hydrocarbons were identified in the ambient air of Tehran and the average measured concentrations of benzene, toluene, m- and p-xylene, ethyl-benzene and o-xylene were 127.65, 201.15, 110.75, 57.60,58.17 $\mu g/m^3$ respectively. The average concentrations of benzene, toluene, m- and p-xylene, o-xylene and ethyl benzene in south Tehran are 1.57, 1.60, 1.28, 1.41, 1.60 times respectively greater than the concentration in north Tehran. In addition for the whole of Tehran the average result of these aromatic compounds were 4.19, 3.49, 2.32, 1.89, 2.02 times greater in the afternoon than in the morning, is probably due to a combination of the increased evaporation rates and the relative differences in photochemical reaction of the hydrocarbons.

The results of the present study show that the concentrations of volatile organic compounds are high especially benzene. The average concentration of benzene is 40 ppb (127$\mu g/m^3$), 8 times more than the accepted safe levels in the European Community. This compound can have an effect on the haematologic system and on blood-forming tissue and could cause an increase in leukemia in the population of Tehran. Inhalation of volatile organic compounds over a long time can cause the appearance of anaemia and disorder of the nervous system. With increasing concentration certain hydrocarbons eg. benzene, toluene etc there is a related increase in concentration of polycyclic aromatic hydrocarbons (produced in the exhaust system), such as benzo(a)pyrene which are carcinogenic. The area of Tehran where the higher concentration of volatile organic compounds occurs also has the higher population density. Reaction of VOC with $NO_X$ induces smog and aldehyde formation which in turn will produce lung irritation in some individuals. If the present rate of vehicle emission continues in Tehran it is predicted that in the near future there will be a high incidence of illness in that city. The effect of these illnesses will be to affect the productivity of individuals which in turn will adversely affect the economics of the community of Tehran. A fruitful piece of research for the future would be to collect data on health from Tehran and compare it with these predictions.

The statistical correlations between toluene concentration and these of other aromatic hydrocarbons are consistent with the basic sources for pollutants in Tehran, being car exhaust and fuel evaporation from carburettors. Variation in the concentration of individual pollutants studied was found at every traffic location to be very closely related to the traffic flow rates.

Benzene concentrations were found to be increasing at a greater rate than these of other aromatic hydrocarbons in ambient air because it has a lower photochemical decomposition rate. Differing rates between toluene and other aromatic hydrocarbons indicate reactions of benzene < toluene < ethylbenzene < xylene.

Because of high vapour pressures elevated concentrations volatile organic compounds are observed in higher temperatures. In particular benzene concentrations increase greatly after mid-day in Tehran.

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# Chapter Seven: Summary of Research and Conclusions

## 7.1 Introduction

In public health regulation related to air pollution there is a need to understand the measurement and speciation of chemicals of concern to human health. It is clear that no sensible decisions on pollution control to minimize health risks can be taken without detailed knowledge of the nature of the species present and the confidence with which they can be measured. It is too easy in public health regulation to take analytical and speciation data at face value without consideration of the errors involved in their measurement and the precision and accuracy of the methods used. An aim of this thesis has been to link the analytical requirement for accurate pollution measurement in air to known health risks with a view to making use of the information in the highly polluted air situation in Iran. These principles should also be applied to occupational health in Iran. For example Tehran in there are two sources of volatile organic compounds (VOCs) which could affect the health of their employees viz a petroleum refinery and car manufacturing parts other industries in Tehran eg. electrical appliance manufacture, glass manufacture, the workers will also affect the general atmospheric pollution.

All industrial processes contribute to the pollution of our environment. The greatest man-made contributions to atmospheric pollution are processes of combustion in power generation, in industrial plants, in automobile and aircraft engines, and in domestic heating. Such processes are responsible for the generation of a wide range of pollutants; amongst those pollutants which have received considerable attention in recent years, are unburned hydrocarbons and polycyclic aromatic hydrocarbons (PAHs). More recently, interest in this general field has been concentrated on investigations into the identification and measurement of levels of aromatic hydrocarbons.

All hydrocarbons have some effect on human health at different concentrations but some are more significant than others, for example: aromatic hydrocarbons have a strong effect on human health. Benzene, a component in unburned hydrocarbons from vehicle exhaust, is known to be a carcinogen from epidemiological researches. Benzo(a)pyrene and benzo anthracene, also found in vehicle exhaust are known carcinogens, as reported by the International Agency on cancer and links between lung cancer and benzo(a)pyrene have been proved by several groups of workers (1,2,3). An increase in the concentration of volatile organic compounds can also cause an increasing amount of secondary pollution associated with ozone, peroxyacetyl nitrate (PAN) and aldehydes. Secondary pollution causes irritation in eye and lung which are increased in air when inversion (pollution trapped under a dense layer of air) occurs (4).

## 7.2 Objectives

The current methods (EPA Method TO-13 and other methods [5,6,7] ) available for the extraction and analyses of polycyclic aromatic hydrocarbons from particulate samples collected on filters are based on solvent extraction. These take a long time to prepare and can introduce experimental errors. It was found necessary as part of this work to develop a methodology based on Thermal Desorption which would effectively replace solvent extraction. In addition there is no internationally recognized protocol for the measurement of volatile organic compounds using the Carbotrap system. The purpose of the research described in this thesis is to determine the significance of motor vehicle emission sources in air pollution by making use of the improved analytical techniques developed. The work was carried out under the following headings:

1. Development of a method for analyses of polycyclic aromatic hydrocarbons by Thermal Desorption and GC-Mass spectrometry.

2. Characterisation of Polycyclic aromatic hydrocarbons in ambient air conditions at a

site in Uxbridge including quantitative measurement of eight PAHs at local sites using the analytical method developed.

3. Measurement and determination of polycyclic aromatic hydrocarbons (PAH) in vehicle emissions under different engine conditions (e.g. started in the presence or absence of catalytic converters) using the analytical method developed.

4. Development of a method using the Carbotrap system for sampling and characterisation of volatile organic compounds (VOC).

5. Determination and measurement of some volatile organic compounds under ambient air conditions at Brunel University campus using the Carbotrap analytical method developed.

6. Evaluation of qualitative and quantitative analysis of volatile organic compounds using samples from vehicle emissions under different starting catalytic conditions, using the Carbotrap analytical method developed.

7. Determination and measurement of some volatile organic compounds under ambient air conditions in Tehran and relating the results to pollution sources, time of day, geographical location and the potential health hazards arising from the pollution.

## 7.3 Attainment of objects

Airborne particulate samples were obtained by collection on small glass fibre filters. The volatile material from these was thermally desorbed in two stages and refined by transfer to a Gas Chromatography-Mass Spectrometer analytical system. This method provides a rapid means ( 1 hour analytical times) for accurate determination (±4%) of the PAHs in the particulates. The results from this method are less prone to experimental error than the usual procedure of solvent extraction and analysis by high performance liquid chromatography.

The particulate samples were obtained from sites in the region of Uxbridge, Middlesex and measurement was performed on 8 selected PAHs. Some of these PAHs are known to be chemical carcinogens. There are no published concentration limits for these compounds when found in particulates which relate to their ability to produce cancer in humans.

Although the concentration of benzo(a)pyrene, benzo(a)anthracene reported in this thesis would not immediately produce cancer in mice or humans, a possible health hazard could arise because of long term exposure of humans to air polluted with these compounds. Certainly reports have been published by the International Agency for Research on Cancer (IARC) on mortality rates associated with $PM_{10}$ particulates. It has been reported that some of the other PAHs found in samples taken during this thesis work namely chrysene, benzo(e)perylene and benzofluoranthrene will produce cancers in laboratory animals if not in humans. There is, however always the possibility of synergism occurring. This means that individually substances might not be carcinogens but mixed with other chemicals present in particulates, may become active. The research also indicates that the concentrations of PAHs are higher in exhaust emissions from engines which have recently been started from cold which is important since most car journeys average less than 10 miles. The conclusion is that health hazards are greater in regions such as large conurbations where most car journeys are of short distance. Even if a catalytic converter is fitted to an engine it is not efficient at destroying PAHs unless it has a working temperature (300-350°C). The strategy for determining volatile hydrocarbons was based on the use of the Carbotrap absorbent tube. These have the ability to absorb volatile hydrocarbons (VOCs) from air which flows through them. These VOCs can then be thermally desorbed and analysed using GC/MS. The details of these analytical methods had to be established before they could be used for this project. Six low molecular weight aromatic hydrocarbons were selected for investigation, namely benzene, toluene, ethyl benzene and m-, p- and o-xylene. The first of these, benzene, is of extreme importance because of its known association with the onset of the cancer, leukemia. Being the smallest member of this aromatic series benzene is an effective carcinogen by interfering with the replication of DNA during cell division. The exposure limit levels for which benzene is safe have been published and in general the atmosphere of Brunel Campus, has levels that are below these limits. There are, however days on which the concentration of benzene in atmospheric air is still above acceptable levels. Contributions to these VOCs come from engine exhaust and from fuel evaporation from carburetors. As part of the work for this thesis measurements were made of exhaust emission from cars. Similar fuel samples were used under catalytic and non-catalytic conditions when the engine was warm. A very large depletion in the aromatic hydrocarbons was observed if the engine was fitted with a catalytic converter. The fitting of such converters is a requirement for new light duty motor vehicles under the European Community Directive (91/441/EEC)[9]. It was observed that a large proportion of the atmospheric pollution found in private dwellings could be traced to engine emissions.

A study was made of VOC pollution found in Tehran. The reason for carrying out studies of atmospheric pollution at Brunel University was to develop a protocol which could be applied to similar studies in Tehran. There is a major pollution problem in that city which could lead to a potential health problem. The nature of the geographical location and the power of the sun during the day play an important part in the pollution conditions which are observed. Although no samples were taken of particulates in Tehran, black clouds of diesel exhaust were observed. It would not be unreasonable to assume that the composition of these particulats were similar to those observed in the UK. That being the case, the population of south Tehran is exposed to levels of aromatic hydrocarbons which are bad for health, being higher than those acceptable in the UK. In addition the PAHs found in diesel exhaust levels tend to be high because the pollution is trapped under the cool atmosphere.

### 7.4 Deliverables from this work

(1) A new method for PAHs analyses
(2) A new protocol for VOC analysis
(3) A report on pollution levels in Uxbridge
(4) A report on pollution levels in Tehran
(5) A discussion of health aspects

## 7.5 Tehran future studies

1. The present study has resulted in the development of a method analysis of PAHs in particulate phases. Since PAHs are also emitted in the gas phase, the development of a method of analysis of PAHs in gas phase is a topic for further study.

2. Determination of personal exposure to pollutant mixtures using personal monitors especially under inversion conditions in Tehran and the establishment of relationships between exposure assessed on the basis of fixed point measurement and actual personal exposure.

3.Measuring the ratio of indoor to outdoor concentration of pollutants during inversion conditions in the ambient air of Tehran.

4. Much of the data used in assessing the risks to humans of exposure to air pollutants is obtained from experiments with laboratory rodents. Consequently, there is a need for more information on inter-species variation in order to define which animal species will prove the best surrogate for studies of complex pollutant mixtures relevant to human exposure.

5. Determination of the nature of biological and nonbiological particles and their size distribution in ambient air of Tehran to determine percentages of respiratory and thoracic particle.

6. The epidemiology of the health effects of mixtures of air pollutants is poorly developed in Tehran and a more complete picture of the pattern of exposure to all pollutants, gases and particles, is required. Specifically, there could be studies of groups of individuals, identified as being liable to be exposed to traffic-related pollutants, with a view to studying variation of symptoms or lung function on a daily basis during periods inversion. Epidemiological studies should be developed to investigate further the association between exposure to particle and acute effects on health using routinely collected daily data on mortality, hospital admissions and general practitioner

consulations.

The following recommendations should be considered as a means of decreasing pollution in ambient air of Tehran:

1. Expediting the building of an underground train system
2. Changing fuel from leaded petrol to unleaded petrol and/or liquid gas
3. Preventing movement of cars with faulty engines
4. Fitting of catalyst converters in car exhausts
5. Spread of supermarkets to out of town locations
6. Prevent creation of new industries in Tehran

The purpose of this research project which was to obtain experience in the development of methods for the analysis of pollution in ambient air and in the interpretation of the analytical data in terms of public health regulation in Iran has been successfully achieved.

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