

DEVELOPMENT OF A SOLVENT EXTRACTION-
GAS CHROMATOGRAPHIC METHOD FOR
THE IDENTIFICATION AND DETERMINATION
OF POLYCYCLIC AROMATIC HYDROCARBONS
AND SOME RELATED COMPOUNDS IN
METALLURGICAL FACTORIES.

by

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It is hereby declared that this is my own work, both in conception and execution and that the opinions expressed or conclusions reached are not to be regarded as reflecting the views of the above-mentioned persons.

S. BACHE

OCTOBER 1990

Science moves, but slowly slowly, creeping on from point to point.

ALFRED, LORD TENNYSON (1809-1892)

Locksley Hall, line 134.

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SUMMARY

A method for the determination of polycyclic aromatic hydrocarbons (PAH) in carbonaceous materials and on particulate matter produced in the atmosphere during the electrolytic reduction by various methods in the metallurgical industry is presented.

The PAH are extracted into hexane with the aid of ultrasound, which is shown to be more efficient than the conventional Soxhlet thimble technique.

Cyclohexane and hexane are shown to be more selective extractants for PAH than benzene or acetone. Hexane is preferred because it has a lower boiling point than cyclohexane.

Three methods of identification were investigated. These included thin-layer chromatography (TLC), gas chromatography (GC) using retention times and indices and mass spectrometry (GC-MS).

Hexane containing 2 % by volume of N,N'-dimethylformamide was used for the development of a thin-layer chromatogram. This resolved only ten of the twenty PAH investigated adequately.

The non-polar OV-101 capillary column used in the GC-MS work did not resolve ten PAH well enough and the mass spectra did not assist in distinguishing overlapping peaks.

The separation of individual PAH was optimised using a DB-5 wall-coated open tubular (WCOT) capillary column coupled to a flame ionisation detector. A splitless injection technique was used.

Calculated retention indices normalised against four selected PAH, viz. naphthalene, phenanthrene, 1,2-benzophenanthrene and 1,2,6,7-dibenzanthracene were used for the identification of unknown PAH and some related compounds. Problems encountered with this method of identification of some of the more strongly retained PAH are discussed.

The program supplied by "DAPA Scientific (Pty) Ltd." was adapted for quantification of the identified PAH using 1,3,5-triphenylbenzene as internal standard.

Suggestions for the adaption of the above analytical method to different matrices are presented.

OPSOMMING

'n Metode word voorgestel om polisikliese aromatiese koolwaterstowwe (PAK) in koolstofhoudende stowwe en op partikulêre deeltjies wat gedurende elektrolitiese reduksie met verskillende metodes in die atmosfeer vrygestel word, te bepaal.

Die PAK word met hekseen onder ultrasoniese bestraling geëkstraheer. Dit word aangetoon dat hierdie metode meer effektief is as konvensionele Soxhlet vingerhoedbuis ekstraksie.

Dit word verder aangetoon dat siklohekseen en hekseen meer selektief is vir PAK as benseen of asetoon. Hekseen word verkies omdat dit 'n laer kookpunt het as siklohekseen.

Drie identifisiemetodes is ondersoek nl. dunlaagchromatografie, gaschromatografiese retensietye en indekse, en gaschromatografie - massaspektrometrie.

Hekseen bevattende 2 volume % N,N'-dimetielformamied, is gebruik vir die ontwikkeling van 'n dunlaagchromatogram. Dié het 'n bevredigende resolusie slegs vir tien van die twintig PAK wat ondersoek is, opgelewer.

Die niepolêre OV-101 kapillêre kolom wat vir gaschromatografie - massaspektrometrie gebruik is, het nie eens tien van die ondersoekte PAK behoorlik van mekaar geskei nie, en die massaspektra het nie met die onderskeiding van oorvleuelende pieke gehelp nie.

Die skeiding van individuele PAK is geoptimaliseer deur gebruik te maak van 'n DB-5 muur-bedekte oop-tubulêre kapillêre kolom gekoppel aan 'n vlamionisasiedetektor.

Berekende retensieindekse genormaliseer teen vier uitgesoekte PAK nl. naftaleen, fenantreen, 1,2-bensofenantreen en 1,2,6,7-dibensantraseen, is gebruik om onbekende PAK en enkele verwante verbindinge te identifiseer. Probleme wat hierdie metode opgelewer het t.o.v. PAK wat relatief sterk op die kolom teruggehou word, word bespreek.

Die program voorsien deur DAPA Scientific (Eds.) Bpk, is aangepas vir die kwantifisering van die geïdentifiseerde PAK deur van 1,3,5-trifenielenseen as interne standaard gebruik te maak.

Aanbevelings word gemaak oor hoe die analitiese metode hierbo gewysig kan word om voorsiening te maak vir verskillende matrysmateriale.

GLOSSARY

BSM	:	Benzene-Soluble Matter.
CTPV	:	Coal-Tar Pitch Volatiles
DAPA	:	Data Acquisition, Plotting and Analysis
DMF	:	Dimethylformamide
DMSO	:	Dimethylsulphoxide
ECD	:	Electron Capture Detector
EPA	:	Environmental Protection Agency
ESP	:	Electrostatic Precipitator
FID	:	Flame Ionization Detector
GC	:	Gas Chromatograph(y)
HETP	:	Height Equivalent to a Theoretical Plate
HPLC	:	High Performance Liquid Chromatograph(y)
IUPAC	:	International Union of Pure and Applied Chemistry
MS	:	mass spectrometer/mass spectra
NIOSH	:	National Institute of Occupational Safety and Hygiene
PAC	:	Polycyclic Aromatic Compounds
PAH	:	Polycyclic Aromatic Hydrocarbons
psi	:	Pounds per square inch
IS	:	Internal Standard
MDL	:	Minimum Detectable Level
MSD	:	Mass-selective Detector
RI	:	Retention Index

(x)

SFC	:	Supercritical Fluid Chromatograph(y)
TLC	:	Thin-layer chromatograph(y)
TLV	:	Threshold Limit Value
UV	:	Ultraviolet
WCOT	:	Wall-Coated Open Tubular

CHAPTER 1

INTRODUCTION

1.1 GENERAL

Polycyclic aromatic hydrocarbons (PAH) may be defined as a group of organic compounds whose structure consists of three or more unsaturated benzene rings fused together in a linear, angular or cluster arrangement.¹⁾ A large number of polycyclic aromatic compounds (PAC) containing heteroatoms and/or saturated ring systems fused to a PAH molecule are also known.¹⁾

PAH are produced in significant quantities during the incomplete combustion of various organic materials such as coal, wood, tobacco, meat and animal fats.²⁾

Some PAH are known carcinogens. They become airborne by adsorption on particulate matter. The higher death rate from lung cancer in urban areas compared to rural areas is believed to be partly due to this.³⁾

1.1.1 Motivation for this work

Increased industrial activity throughout the world has resulted in an increase in the level of PAH in the environment in the past 100

years.³⁾ 3,4-Benzopyrene has received special attention in this regard because of its carcinogenic properties³⁾(see section 1.3.3). The carcinogenic effect of some liberated PAH on the health of exposed workers during various industrial processes has caused concern.¹⁾

An investigation was therefore started, and an attempt was made to extract, isolate and determine PAH associated with particulate matter taken in work place atmospheres. The metallurgical industry was selected for this dissertation, and is highlighted in this regard.

1.1.2 The metallurgical industry

In the metallurgical industry, the raw materials that are used include either petroleum coke or pitch coke with tar or pitch as the binder.⁴⁾ Graphite electrodes are then obtained by baking the mixture in furnaces above 1000°C. A second step usually entails a temperature of around 2700°C to produce the graphitized electrode mass. It is during the first step that the bulk of the PAH are volatilized.⁴⁾ Other important industrial processes⁵⁾ which release PAH include gasification of coke, the production of steel notably where molten iron or steel is poured into molds lined with tar-containing preparations, and in the electrolytic production of aluminium where molten fluxes are in contact with carbonaceous pot linings and electrodes.

In a Söderberg potroom where primary aluminium is produced, anode briquettes, about 5 to 6cm long, are added daily to replace those oxidized during the electrolytic reduction process.^{4,6} A coherent carbon mass results. Due to the high temperature of the process, the heat, gas and dust that are generated are removed from the working atmosphere by a ventilation system.⁴

Recent surveys in the United States and Scandinavia have indicated that the concentration of PAH in a Söderberg potroom atmosphere are about twice as high as those in coke furnace air.⁷ The discharge of PAH from the urine taken from workers in the vicinity of a coke furnace was found to be 100 times higher than that taken from workers in a Söderberg potroom.⁷ This lead to the conclusion that the PAH in a Söderberg potroom were adsorbed onto particles of alumina and therefore less bioavailable.⁷

The amounts of PAH excreted by cigarette smokers were found to be far higher than those excreted by non-smoking workers in a Söderberg potroom even though the latter were exposed to a much higher PAH concentration.⁸ The tobacco PAH were believed to be more bioavailable and therefore even though the concentration of PAH which workers were exposed to in a Söderberg potroom were higher, smokers were considered to be at a higher risk of acquiring lung, pancreas or bladder cancer.^{7,8}

Concentrations in work atmosphere are usually expressed in $\mu\text{g m}^{-3}$ and are compared to threshold limit values (TLVs). TLVs refer to airborne concentrations of any substance, inorganic or organic which workers may be exposed to.⁹

1.1.3 Threshold Limit Values

In 1967, the American Conference of Governmental Industrial Hygienists (ACGIH) adopted a TLV of 0.2 mg m^{-3} of coal tar pitch volatiles (see page 19) in air defined as the benzene-soluble fraction of the particles collected on a glass fibre filter.*'

3,4-Benzopyrene is a component of particulate dust and is extracted by both benzene and cyclohexane.*' This compound has been used as a measure of the potential carcinogenic activity present in particular workplaces.*'

Cyclohexane was prescribed by "The United States National Institute for Occupational Safety and Health" (NIOSH) in 1977 as a medium for the extraction since it was far less toxic than benzene.*' At the same time it was proposed to decrease the TLV to 0.10 mg m^{-3} cyclohexane-soluble matter because this was the lowest concentration which could be determined with reasonable accuracy by the method.*' However, this TLV has never gained acceptance.*'

In Sweden, a TLV of $10 \mu\text{g m}^{-3}$ was introduced for 3,4-benzopyrene in 1978 and then lowered in 1982 to $5 \mu\text{g m}^{-3}$.*' The average 3,4-benzopyrene content of benzene-soluble matter (BSM) found over a 15 year period was 1.3% in aluminium electrolysis potrooms.*' Therefore, if 3,4-benzopyrene is assumed to be 1.5% of the CTPV, the American TLV for a CTPV would correspond to a 3,4-benzopyrene concentration of $3 \mu\text{g m}^{-3}$.*' This has lead to the adoption of both BSM and 3,4-benzopyrene TLVs as representative of the total PAH content.*'

In South Africa, the American TLV of 0.2mg m^{-3} BSM is used. The inadequacies of this have been illustrated by MacEachen et. al.⁹ This necessitated the development of a specific extraction, isolation and quantification method for PAH released in occupational areas in the metallurgical industry which is presented in this dissertation.

1.1.4 Chromatographic methods

Lee et. al.¹⁰ illustrated the reproducibility of a gas chromatographic (GC) method of determining PAH with a flame ionisation detector (FID). Results agreed well with high performance liquid chromatography (HPLC) (reverse phase columns - chapter 1.5.1.3) using fluorescence and ultraviolet (UV) detectors.

Bjorseth¹¹ and Bjorseth et. al.¹² took advantage of the high precision and sensitivity of the GC-FID technique for determining PAH sampled from metallurgical factories.

A more extensive review of gas chromatography is given in chapter 1.5.1.2.

For this dissertation a GC fitted with a FID was used, which at the time was compatible with available financial support given by the sponsor. It is a simpler, more direct method for determination of PAH than HPLC, UV/visible spectroscopy and other methods (see 1.5.1.3). The sensitivity and separation efficiency of a capillary GC-FID technique is demonstrated in this dissertation by means of standards and actual samples.

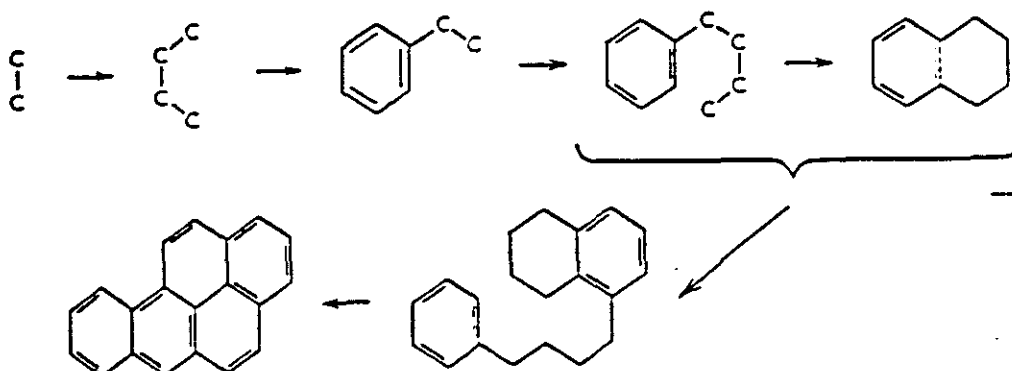
1.2 FORMATION AND OCCURRENCE

1.2.1. Pyrosynthesis of polycyclic aromatic hydrocarbons

The formation of PAH by pyrolysis has been reviewed by Lee et. al.¹³⁾ and may be summarized as follows.

The most commonly accepted mode of formation is that by pyrosynthesis. This is initiated by the formation of radicals by pyrolysis which recombine yielding larger relatively stable PAH.^{1, 13)}

Badger et. al.¹⁴⁾ suggested that 3,4-benzopyrene could be synthesised by a stepwise mechanism with acetylene as a starting material and 1,3-butadiene and styrene as intermediates:



This mechanism was supported by Lang et. al.¹³ who found that more highly condensed ring structures were formed from aromatic compounds of lower molecular mass on heating at the appropriate temperature.

Inefficient burning of fossil fuels produces carbonaceous aerosols which have been used as a measure of PAH concentration. Lee et. al.,¹³ reviewed the occurrence of PAH in the air, water and in sediments. Their review on this topic may be summarized as follows:

- a) In unpolluted air, measured 3,4-benzopyrene concentrations ranged from 0.1 to 0.5ng m⁻³. In polluted air, 74ng m⁻³ or more have been detected. PAH tend to accumulate on particulate matter and smaller particles appear to be more efficient as adsorbents of PAH than larger particles.
- b) Since PAH are essentially non-polar they would not be expected to dissolve in water to any appreciable extent. However, they are known to adsorb readily on particulate matter and are consequently expected to occur in water associated with suspended matter.
- c) Factors such as solar radiation, dissolved oxygen, ambient temperature affect the persistence of PAH in both air and water.
- d) PAH occurring in sediments are generally more complex than those normally found in air and water.

1.3 PHYSICAL AND CHEMICAL PROPERTIES

1.3.1 Nomenclature

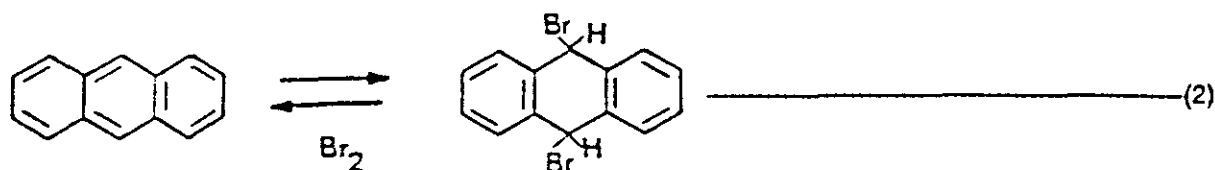
For well over a century, individual PAH have been known by trivial names, and these are still used extensively in the literature.

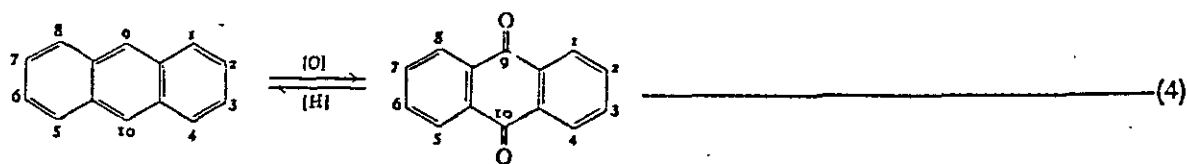
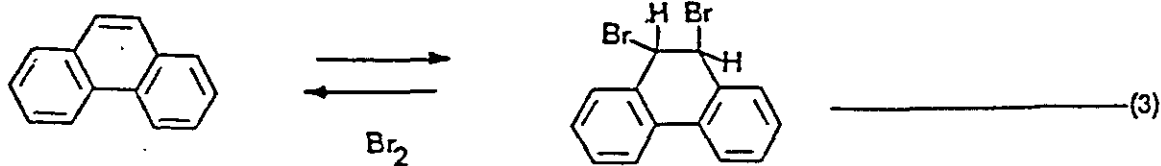
However, in the present dissertation, the nomenclature recommended by IUPAC¹⁶⁾ will be used throughout. A list of synonyms is given in Appendix 1.

1.3.2 Reactions

The chemical properties of PAH have been reviewed by Lee *et. al.*¹³⁾ Some of the pertinent reactions are outlined in the following paragraph. Theoretical background is given by Fleming.¹⁷⁾

Like most aromatic compounds, PAH tend to undergo substitution rather than addition reactions. There are two series of addition reactions that are of special interest in the environmental chemistry of PAH. These additions occur at the 9,10-position of anthracene(2) and phenanthrene(3) presumably involving a Diels-Alder type adduct as intermediate. The middle or meso positions of anthracene(2) acquire the numbers 9 and 10 because it is converted into anthraquinone(4).



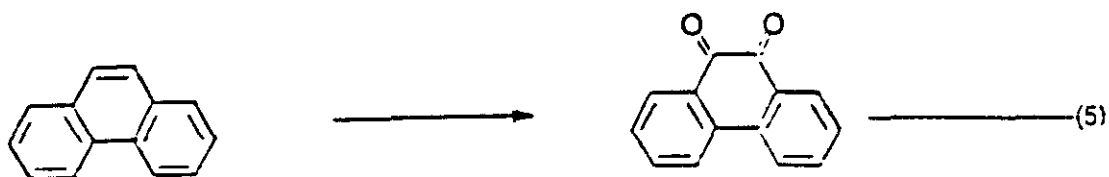


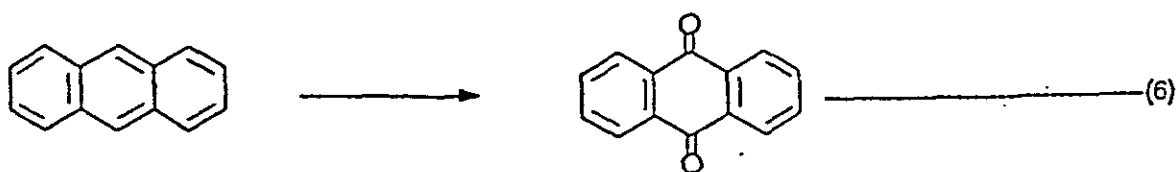
The reason for the fact that the 9,10-positions of these two PAH are susceptible to electrophilic attack can be explained by the greater stability of isolated benzene rings.¹⁷⁾

The positions where electrophilic attack can occur in these as in other PAH is determined by the position of the highest electron density.¹⁷⁾ For example for 1,2- and 3,4-benzopyrene this is at the 4,5-positions whilst for 1,2-benzanthracene it is the 5,6-position¹⁸⁾.

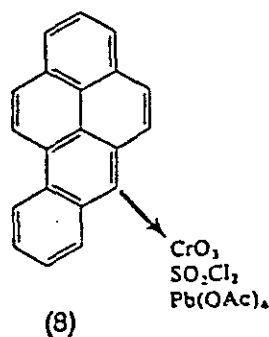
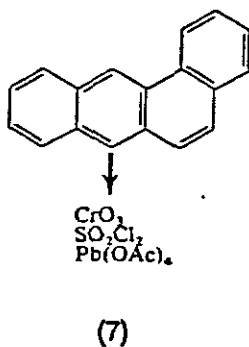
These positions of highest electron density are also implicated in the carcinogenicity of PAH (see section 1.3.3).

In contrast to the Diels-Alder reaction, many of the PAH react with oxidizing agents such as lead tetraacetate, chromic acid and sulphuryl chloride which react only at one site at a time.¹⁷⁾ Phenanthrene and anthracene react with chromic acid to give products (5) and (6).



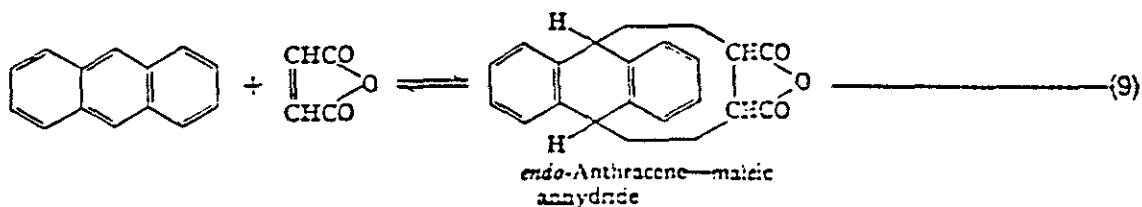


1,2-benzanthracene (7) and 3,4-benzopyrene (8) undergo similar reactions at the positions indicated:



These reagents do not react at the positions of highest electron density.¹⁷⁾ This may be explained in terms of the highest occupied molecular orbital (HOMO).¹⁷⁾

Maleic anhydride is a reagent often used to compare the reactivities of PAH which is related to their carcinogenicity.¹³⁾ Phenanthrene and 3,4-benzopyrene are inert to maleic anhydride under normal conditions but anthracene reacts readily:¹³⁾



Differences in reactivity of linear and angular PAH are maintained with an increasing number of rings. Furthermore along the group of linear PAH to the seven-ring heptacene there is an increasing tendency to undergo addition and redox reactions. Angular PAH, typified by the 9,10-bond of phenanthrene show resistance to these reactions.

Inscoc^{1*} irradiated various linear and angular PAH with UV light in air. The compounds based upon the anthracene structure, such as anthracene, 1,2-benzanthracene, 2,3-benzanthracene, 1,2;6,7-dibenzanthracene and 1,2;3,4-dibenzanthracene were more stable than the angular phenanthrene, 1,2-benzophenanthrene and 9,10-benzophenanthrene. The clustered PAH compounds pyrene, 1,2-benzopyrene, 3,4-benzopyrene and hexabenzobenzene were also more stable than the angular PAH.

These results indicated that the angular PAH would be lost at a faster rate than the linear and condensed PAH during sampling.

1.3.2.1 Influence of sampling

The effect of using an airpump fitted with glass fibre filters to capture particulate dust containing adsorbed PAH as a sampling method has been studied by many workers. Leinster and Evans^{1*} have reviewed this work which may be summarized as follows:

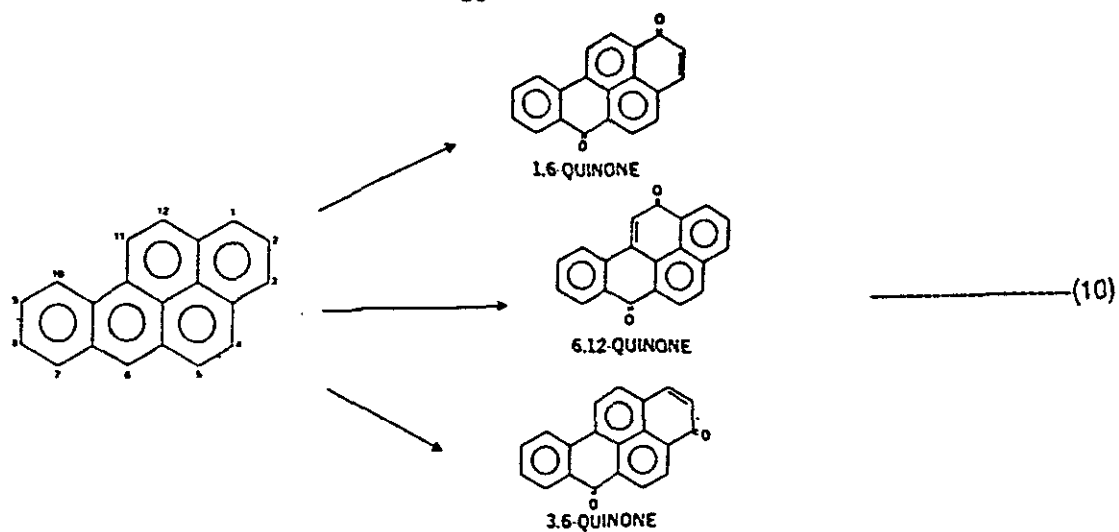
Two choices of sampling are possible: (1) Long periods at low throughput rates. (2) Short periods using high volume sampling pumps. A

number of workers have utilized these sampling methods. Tomingos,²⁰ Van Vaeck et. al.²¹ and Katz and Chan²² found that samples collected over an extended period contained lower concentrations of PAH on a single filter than those collected on a series of filters sampled over the same total time at the same flow rate. This lack of agreement was ascribed to volatilisation or sublimation of compounds such as phenanthrene, anthracene, fluoranthene and pyrene.

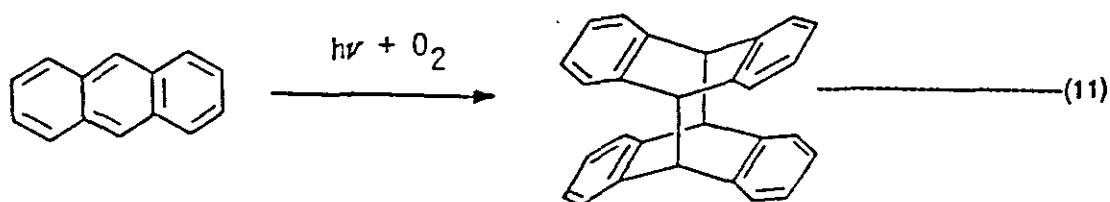
Peters and Seifert²³ recorded a loss of 10% of ¹⁴C-labelled 3,4-benzopyrene from a glass fibre filter over a period of 24 hours using a high volume sampling pump at 90m³hr⁻¹ at ambient temperature. Lao and Thomas²⁴ on the other hand showed that particulate matter stabilised adsorbed PAH during high volume sampling to the extent that high molecular mass compounds such as 3,4-benzopyrene were not lost in appreciable amounts at ambient temperature. Commins and Lawther²⁵ showed that losses of 3,4-benzopyrene started at 100°C and were complete between 170 and 200°C. These results were confirmed by De Weist and Rondia.²⁶

1.3.2.1.1 Ozone

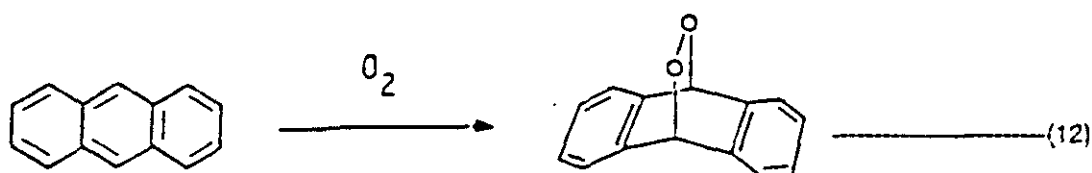
Thomas et. al.²⁷ found that ozone reacted with 3,4-benzopyrene more readily than oxygen. Peters and Seifert²³ found that less than 50ppb ozone oxidized 3,4-benzopyrene to the corresponding quinone at temperatures below 20°C. (10)



Oxidation of anthracene under UV light gave the photodimer:



Oxidation in the dark produces the photooxide:



Lane and Katz²⁸ showed that 3,4- and 2,3-benzofluoranthene were fairly resistant to low ozone concentrations in the dark, while 3,4-benzopyrene reacted rapidly and the rate was little influenced by UV

light. These findings were supported by Barton et. al.,²⁰ who observed that as much as 50% of 3,4-benzopyrene were lost during sampling, and that the concentration of ozone was a critical factor.

1.3.2.1.2 Sulphur dioxide

Butler and Crossley²⁰ found that the reaction of SO₂ with PAH depended on the SO₂ concentration and was not affected by UV light. These points were supported by Jager and Rabovic²¹ and Hughes and co-workers.²²

PAH sampled from a stack were found by Brorstrom and Lindskog²³ to be altered by SO₂ and SO, to give an under-estimation of their concentration. Karcher and associates²⁴ showed the products to include thiophene derivatives of 3,4-benzopyrene.

1.3.2.1.3 Nitrogen dioxide

Pitts²⁵ studied the nitration of gaseous PAH. His earlier laboratory work revealed that nitration of 3,4-benzopyrene and pyrene on glass fibre filters exposed to ambient levels of NO₂ and gaseous HNO₃ was slow, and concluded that the nitration products were unlikely to occur in significant concentrations in urban air as a consequence of a simple nitration substitution. He thence suggested that the presence of 2-nitrofluoranthene and 1-nitropyrene in significant concentrations in the polluted air might be explained by a mechanism involving preliminary addition of OH radicals at the positions of high electron density.

Further work by Pitts³⁵, revealed that N_2O_5 reacted with fluoranthene in the dark to produce 2-nitrofluoranthene.

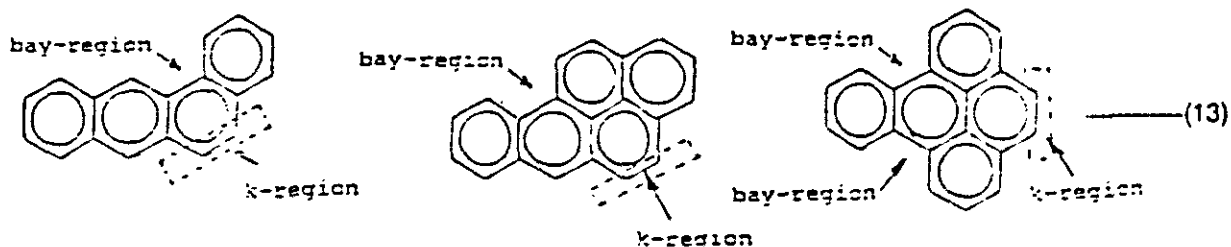
1.3.3 Biological activity

In the early part of the present century, it was realised that individuals in specific occupations who were exposed to coal-tar products tended to show an abnormally high incidence of skin cancer.^{1, 3, 20}

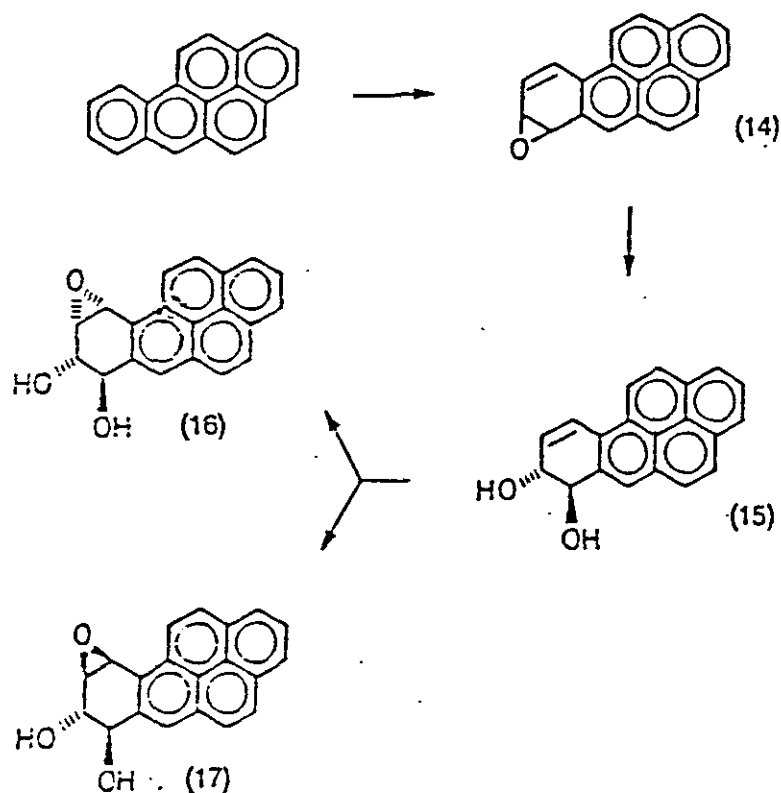
There are three main features used for predicting the carcinogenic character of a compound. These are: (i) shape; (ii) size; and (iii) steric effects associated with molecular overcrowding.¹³

Selkirk and Macleod³⁶, have demonstrated that 3,4-benzopyrene and 1,2-benzopyrene differed with respect to the binding to cultured cells.

Such binding is apparently related to the presence of so-called k-regions which are characterized by a high electron density.^{13, 17}



Non-linear PAH readily undergo oxidation of the terminal benzene ring to form an intermediate called an "arene oxide". Hydration occurs to form a transdihydrodiol and oxidation of the adjacent alkenic double bond to form diastereometric diol epoxides.^{13, 37} (16) and (17):



Jerina et. al.³⁸ proposed that the position of the reactive epoxide ring within the molecule is related to its biological activity. The activity is high if the epoxide ring becomes part of a "bay-region" (see chemical structures in (13)). Presumably the carbonium ion intermediate is stabilized by the adjacent aromatic structure prior to formation of structure (18)^{13, 37}.



If the epoxide lies adjacent to a "bay"(19), carcinogenicity is far lower.^{13, 37)}



The bay-region appears to relate observed carcinogenicity to structural features more accurately than the previously popular k-region theory, but some PAH do possess both k- and bay-regions and an overlap does exist between the two theories.¹³⁾

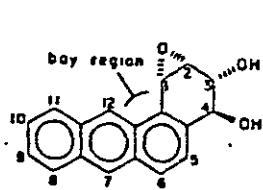
Lee et. al.,¹³⁾ have listed a large number of PAH of various carcinogenic activities. Some are listed in table 1.1.1.

TABLE 1.1.1 CARCINOGENIC ACTIVITY OF SOME PAH

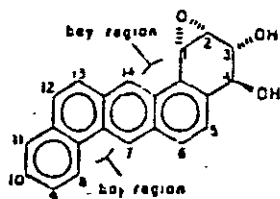
COMPOUND	CARCINOGENIC ACTIVITY (based upon percentage of exposed animals affected)
1,2-benzanthracene	+
1,2-benzophenanthrene	+
2,3-benzofluoranthene	++
3,4-benzofluoranthene	++
3,4-benzopyrene	++
1,2-benzopyrene	0/+
4,5;5,6;9,10-tribenzanthracene	+
2,3-indenopyrene	+
1,2;6,7-dibenzanthracene	+
Hexabenzobenzene	0/+
3,4;8,9-dibenzopyrene	++

Key to table 1.1.1: 0/+: Doubtful
 + : Weakly carcinogenic (<33% affected)
 ++ : Strongly carcinogenic (>33% affected)

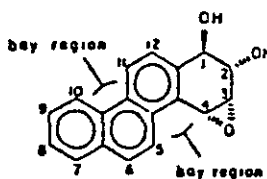
The carcinogenicity of 3,4-benzopyrene is a result of the metabolic formation of the highly reactive intermediate 7,8-dihydrodiol -9,10-oxo-3,4-benzopyrene.³⁹⁾ Other bay-region PAH which form carcinogenic diol-epoxides include 1,2-benzanthracene, 1,2:6,7-di-benzanthracene and 1,2-benzophenanthrene⁴⁰⁾ (20), (21) and (22).



(20)



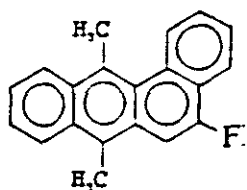
(21)



(22)

The substitution of methyl and fluoride onto a PAH molecule has been shown to decrease the carcinogenicity of some but not all of these compounds.⁴⁰⁾

Substitution of the 4- and 11-position of 7,12-dimethyl-1,2-benzanthracene with a methyl and fluoro group respectively increases the carcinogenicity of the compound. Fluorination at the 5-position on the other hand cancels the carcinogenicity⁴⁰⁾ (23)



..... (23)

The compound 5-methyl-1,2-benzophenanthrene is carcinogenic whereas most other members of the methyl substituted 1,2-benzophenanthrenes are only moderately active.⁴¹⁾ The methyl substitution at the 5-position in 1,2-benzophenanthrene renders the molecule unsymmetric and two non-equivalent angular rings with bay-regions become available for possible activation.⁴¹⁾

Angular benzacridines such as 1,2-benzacridine and 3,4-benzacridine are strongly carcinogenic whereas the linear 2,3-benzacridine is less active.¹³⁾

1.4 REVIEW OF METHODS OF ISOLATING POLYCYCLIC AROMATIC HYDROCARBONS AS A GROUP

1.4.1 Extraction from sample materials

For many of the processes used in the metallurgical industry, pitch is used to bind larger amounts of aggregate petroleum coke and pitch coke.⁴⁾ The majority of extractable compounds in the cokes are of high molecular weight paraffins and waxes while the concentration of PAH is low.⁴²⁾

The benzene-soluble fraction of airborne particulate matter has been widely used as a measure of the PAH content.⁶⁾ Warm benzene was used to extract samples collected on glass fibre filters, and the difference in the weight of the filter represented the benzene soluble fraction.¹⁸⁾

The PAH concentration is not adequately reflected by this method because warm benzene dissolves many other aromatic and aliphatic compounds. This was illustrated by MacEachen et. al.,^{*} who determined BSM of particulate matter sampled in the atmosphere of a pot^{*} relining centre. BSM recovered were 0,47mg m⁻³, but 75% of this were found to be aliphatic compounds. The remainder represented CTPV which correspond more closely to PAH.

Therefore, it follows that more selective solvents and/or prior separations are required for a more accurate measurement of PAH. The present dissertation is devoted to overcome this short-coming.

1.4.1.1 Extraction techniques

The two main extraction techniques^{*} used in this field have been

- (i) soxhlet thimble apparatus; and
- (ii) sonication by ultrasound.

(i) Soxhlet thimble techniques

PAH are soluble in many organic solvents and a variety have been recommended for PAH extraction. Benzene, acetone and cyclohexane have been shown to be nearly 100 percent efficient for extracting 3,4-benzopyrene from filters using the Soxhlet extraction technique.¹³

* A pot is the term given to an electrolytic cell used for the production of steel or aluminium.

Recommended extraction times of between two hours and twenty to thirty hours have been recommended with six to eight hours commonly used as a compromise.

Colmsjo and Stenberg⁴³ used a cyclohexane:acetone (2:1) mixture to Soxhlet extract particulates collected from a car's exhaust.

Lee et. al.,¹⁰ Soxhlet extracted PAH from a wet sample of silt clay sediment using acetone:hexane (59:41). The lower boiling point of this solvent mixture made evaporation easier thus it was selected over other solvent systems such as benzene:methanol (1:1) and cyclohexane:hexane (1:1) which gave similar yields of PAH.

Katz and Chan²² Soxhlet extracted particulate matter using methylene chloride in the dark for ten hours.

Hagenmaier et. al.,⁴⁴ determined six PAH in sewage after extracting for four hours in an acetone:hexane (1:1) mixture.

Mangani et. al.,⁴⁵ spiked two coal-ash samples with known amounts of PAH at concentrations differing by a factor of ten. The PAH were extracted in a stainless steel tube pressurized under nitrogen. The recoveries by a Soxhlet method using methylene chloride and then toluene gave a 100 percent yield for the two-ring PAH. Anthracene was poorly recovered, thought by these workers to be due to light and heat exposure.

The poorer recoveries for the low concentration spiked samples was put

down to PAH adsorption as a single layer on the active sites on the ash surface. A multilayer was believed to form when larger amounts of PAH were applied resulting in easier extraction giving greater recoveries.

(ii) Ultrasonic extraction

This method has become popular because a small volume of solvent is used at room temperature to extract the PAH.¹³ Chalot et. al.,¹⁴ found that the extraction of 3,4-benzopyrene and "total PAH" was complete after 30 minutes. Golden and Sawicki¹⁵ refined the procedure by suspending the glass fibre filter sample in cyclohexane and sonicating in the presence of silica powder to adsorb polar extractives. The recovery of PAH was in the range 95 to 98 percent. Extraction efficiency and reproducibility were superior to the soxhlet method.

Lee et. al.¹⁶ carried out ultrasonic extractions of silt clay sediment with hexane-acetone (1:1) which gave recoveries identical to a Soxhlet method. To maintain compatibility with other laboratories analytical results, a Soxhlet thimble technique was preferred by Lee et. al.¹⁶

1.4.2 Separation from extracts

Benzene has been widely used to extract PAH from particulate matter collected on filters such as glass fibre and membranes (see 1.4.1). Such extractions are not selective for PAH.

A separation technique is therefore required to isolate the PAH fraction from the extracts for determination. The main methods used are liquid-liquid partitioning, thin-layer chromatography and column chromatography.¹³⁾

1.4.2.1 Liquid-liquid partition

PAH may be enriched by partitioning the original solution extract with a second immiscible solvent.¹³⁾ If the partition coefficients for PAH differ from these of other material, they will be concentrated in one or the other layer.¹³⁾

The recovery is dependent on:

- (i) the "distribution coefficient" (k)
- (ii) the relative volume of extractant/solvent
- (iii) the number of extractions

For a recovery of about 90 percent, $k > 2.2$ and the partition should be made twice between equal volumes.⁴⁴⁾ The solvents dimethylsulphoxide (DMSO), N,N-dimethylformamide (DMF) and nitromethane were found to have the most favourable partition coefficients for PAH.⁴⁴⁾

Ostman and Colmsjo⁴⁴⁾ found that of these nitromethane was the least efficient, whilst DMSO and DMF gave good recoveries of PAH.

Bjorseth¹¹⁾ partitioned PAH using a DMF/water/cyclohexane system. The PAH were isolated in DMF/water (9:1) and then back-extracted into fresh

cyclohexane. The extract was concentrated using a rotary evaporator and reduced to dryness under nitrogen gas. The average recovery of PAH (except hexabenzobenzene) was between 95 and 122 percent for nine parallel determinations. The poor recovery of hexabenzobenzene was put down to the less favourable distribution coefficient of it between cyclohexane and DMF/water. A similar discrimination was observed for the lower molecular weight and alkylated PAH.

1.4.2.2 Thin-layer chromatography

Dong et. al.¹⁹ used benzene: cyclohexane (1.5:1) to separate PAH from air particulates on silica gel thin-layer plates. The PAH were located on the plates by longwave ultraviolet (UV) light fluorescence and scraped from the plate.

Because physical removal of thin-layer material contaminates the sample, this method has not found general acceptance. However, TLC has found applications for purposes of identification (see chapter 1.5.2).

1.4.2.3 Column chromatography

Two of the most widely used phases are silica gel and alumina.¹³ These two substances have their surfaces covered with strongly bonded hydroxyl groups.¹³ Lee et. al.¹⁰ used 100-200 mesh silica gel activated at 130°C for 18 hours to separate PAH from a sample of silt clay sediment.

Ostman and Colmsjö⁴⁰ activated silica gel at 400°C for a period of 24 hours and then deactivated it by adding 10 percent water. They separated PAH from crankcase oil. The aliphatic fraction was eluted with 10cm³ hexane and the PAH were eluted with 50cm³ benzene which was concentrated and injected into a GC coupled to a FID. The chromatogram revealed a large "hump" of material which was shown by GC-MS to consist of mono and diaromatic compounds, alkenes and alkanes.

Ostman and Colmsjö⁴⁰ recommended reverse phase HPLC for the determination of PAH in samples that gave such chromatograms.

Snook et. al.⁵¹ used a nonmodified silica gel to isolate PAH from cigarette smoke condensate. A similar "hump" was reported similar to that observed by Ostman and Colmsjö.⁴⁰ The two groups of workers applied the size exclusion gel "Sephadex LH-20" to isolate the PAH fraction. The recovery of PAH was not quantitative.

Wilkinson et. al.⁵² compared the recoveries of five PAH at a level of 20ug cm⁻³ on (i) deactivated alumina (3 percent water) and (ii) nonmodified silica gel (silicic acid). Methylene chloride as eluent gave higher recoveries than pentane on both columns, but silica gel gave higher recoveries of PAH in the shortest time.

Sinclair and Frost⁵³ used a column of Florisil (a synthetic magnesium silicate) to retain polar compounds co-extracted with PAH from cigarette smoke condensate. The PAH were eluted with an ether:hexane (5:95) mixture and the recovery of 3,4-benzopyrene was between 90 and 100 percent.

1.4.2.3.1 Size exclusion chromatography

"Bio-beads SX-12" were used by Snook et. al.⁵¹ and Ostman and Colmsjo⁴⁸ to remove extraneous material not retained on a silica gel chromatography column.

Snook et. al.⁵¹ found "Bio-beads SX-12" to be superior to "Sephadex LH-12" in isolating PAH with benzene as eluent especially with regard to the recoveries of ¹⁴C-labelled 3,4-benzopyrene.

1.5 REVIEW OF METHODS FOR THE SEPARATION OF POLYCYCLIC AROMATIC HYDROCARBONS

1.5.1 Resolution

Early separations of PAH were carried out by paper chromatography and later thin-layer chromatography (TLC).¹³ The many disadvantages of TLC include the fact that it is a time-consuming method often attended by oxidation in air by UV light.¹³

1.5.1.1 Chromatographic separation

The process of separation in a chromatographic system is controlled by (i) the nature of the liquid phase, (ii) the phase ratio of the column (β), (iii) the temperature, (iv) the column efficiency, (v) the mobile phase flow rate and (vi) the width of the starting band.⁵⁴

TLC is a powerful identification technique. It is best suited to the separation of compounds of different polarity.⁷³⁾ The stationary phase is coated as a thin film usually onto glass. The stationary phases most commonly used include silica gel, alumina and charcoal.^{13, 73)}

Silica gel is preferred because 1) it is relatively inert, 2) it undergoes little irreversible adsorption or decomposition, 3) it can be prepared in a pure form and 4) its pore size can be controlled giving reproducible results.^{13, 73)}

The best separations of PAH are obtained using mixtures of water with DMF, acetic acid or formic acid.⁷⁴⁾ Decreasing the percentage water favours separation of smaller hydrocarbons. Separation of larger hydrocarbons is obtained using larger proportions of water.³⁰⁾

Column efficiency may be quantitatively described by the height equivalent to a theoretical plate (HETP).^{54, 55)} The HETP is that length of column necessary for the attainment of solute equilibrium between the mobile and stationary phases.⁵⁴⁾ Furthermore, HETP calculation allows comparisons between columns of different lengths.⁵⁵⁾ It is the preferred measure of column efficiency.⁵⁵⁾

The extent to which a component band spreads on passing through a capillary column can be expressed in terms of physical constants and the velocity of the mobile phase by the Van Deemter⁵⁴⁾ equation 1.5.1.

$$\text{HETP} = \frac{B}{u} + Cu \dots\dots\dots \text{equation 1.5.1}$$

u

B = a constant which accounts for the effect of molecular diffusion of the solute in the direction of the column axis.^{54,55} C = a constant which is proportional to the resistance of the column stationary phase to mass transfer of solute through it.^{54,55}

The magnitude of B may be increased by changing from a low molecular weight carrier gas such as hydrogen or helium to those heavier like nitrogen.⁵⁴ This is because the lighter elements diffuse through the column more readily.

The magnitude of the C -term can be decreased by using a column with a thin film of stationary phase.⁵⁴ Too thin a film however creates peak tailing due to adsorption of solute on the capillary walls.⁵⁴

Optimization of HETP is largely by experiment.

1.5.1.2 Gas chromatography

In GC, the sample is instantaneously vapourized at the injector port and the analyte is transported through the length of the column by a carrier gas at an elevated temperature. Selection of the stationary phase, type of carrier gas, its flow rate and temperature are important aspects to be considered in the optimization of analyte resolution.

1.5.1.2.1 Packed columns

The first GC columns used for resolving components in a mixture were

packed; i.e. consisting of a length of coiled tubing such as glass or stainless steel containing solid particles coated with a stationary phase.

The Environmental Protection Agency (EPA) in Method 610 specifies that a packed 2m x 2mm i.d. column containing 3% OV-17 on chromosorb WHP (80/100 mesh) may be used for resolving the carcinogenic PAH.⁵⁶

Augood and Seim⁵⁷ used 3% OV-7 on chromosorb G-HP to determine PAH. Generally resolution was poor.

Columns packed with liquid crystals have been used to improve the resolution of PAH.⁵⁸ Liquid crystals are organic compounds that, with increasing temperature, pass from a solid to a nematic state and finally to a normal liquid phase.⁵⁹ Because of this property, they have a narrow operating temperature and samples are chromatographed isothermally rather than by temperature programming.⁵⁸

Good resolutions of PAH have been reported on liquid crystals.^{13, 54} The liquid crystals used to resolve PAH have been based upon N,N'-bis (p-X- benzylidene) X-X'-bi-p-toluidene (BXBT) where -X- represents methoxy (BMBT) butoxy (BBBT), hexyloxy (BHxBT) or phenyl (BPhBT).⁵⁴ BHxBT and BPhBT are thermally more stable, and suitable for determination of five-ring PAH which require temperatures of up to 265°C.

Suzuki and Imai⁶⁰ used a 1:1 mixture of BHxBT and BPhBT for determining 3-5 ring PAH in urban air particulates. Resolution of thirteen

PAH was good with the exception of 2,3-benzofluoranthene and 1,2-benzopyrene which co-eluted. However the separation of 9,10-benzophenanthrene from 1,2-benzophenanthrene which is difficult on capillary GC columns was successfully achieved on this column.

1.5.1.2.2 Capillary columns

Samples containing a large number of different PAH and PAC require capillary columns because of their greater efficiency, and ability to withstand the high temperatures required to elute six and seven ring PAH.¹³⁾

Wall coated open tubular (WCOT) columns are often used because of their high efficiencies and good resolution.¹³⁾ Separation occurs in a thin film of stationary phase coated on the inside of the capillary. Capacity is small, but this allows for a high permeability, though a disadvantage is the requirement for a relatively small sample. For most applications a split valve is used to decrease the quantity of sample that reaches the column.

Lee and Wright¹⁴⁾ reviewed the suitability of GC capillary columns for resolving PAH.

At constant column dimensions and carrier gas velocity, the capacity of a column increases with film thickness. However, efficiency decreases with an increase in film thickness. As a result resistance to mass transfer increases (B-term in equation 1.5.1).

If hydrogen is used as a carrier gas, very short capillary columns with fast flow rates can be used which reduce analysis times while maintaining good resolution.

Liberti et. al.,⁶² showed in 1964 that glass capillaries could resolve PAH which remained unresolved in packed columns. Leaching of the glass capillaries with certain Lewis acids has greatly improved efficiency of column's and detection limit for PAH.

The most widely used stationary phases for PAH analyses are SE-52 and SE-54¹³. The "DB" series manufactured by "J & W Scientific" replaces the SE-54 phase in their catalogue. The compounds usually difficult to separate by GC include the benzofluoranthenes and 1,2-/9,10-benzophenanthrene. An OV-61 phase gives a slightly improved resolution of the benzofluoranthenes and chemically bonded phenylmethyl silicone gives partial resolution of 1,2-/9,10-benzophenanthrene.⁶¹

Bjorseth¹¹ used OV-1 and OV-101 coated capillaries to determine PAH in cyclohexane extracts of particulate matter taken from the air in an aluminium reduction plant. A 50 metre long capillary column of 0.38 millimetre inner diameter (50m x 0.38mm i.d.) coated with an OV-1 stationary phase was used by Bjorseth et. al.¹² to resolve PAH extracted from samples obtained in an aluminium reduction plant. Both authors used hydrogen as the carrier gas as it gave good resolution on the long columns in the shortest time.

Alfheim et. al.⁶³ used a DB-5 coated 30m x 0.25mm i.d. capillary

column to resolve PAH extracted from particulate matter collected in a non-ferrous metal reduction plant.

1.5.1.2.2.1 Injection technique

To produce a narrow starting band on the capillary column, a very small amount of the sample should be injected.⁶⁴ To achieve this, the split injection technique can be used for concentrated samples. In this way, a small fraction reaches the column, say one hundredth of the sample injected, at a split ratio of 100:1. If a dilute sample is injected, the splitless injection technique can be used. The entire sample is introduced as a broad band, which is "focused" to a narrow band using the heated carrier gas.⁶⁵ The splitter is reopened after a predetermined time for chromatography to take place.

Splitless injection is based upon the "solvent effect" as a mechanism condensing large vapour clouds down to infinitely shortened bands.⁶⁶ Its effect is controlled by altering the column temperature, volatility, the amount of solvent and the rate of injection.⁶⁷

Grob⁶⁴ recommends splitless injection for determining PAH in environmental samples. There are some drawbacks such as the adsorption of compounds on active or cold surfaces and the effect of residence time on heat sensitive compounds prior to opening the splitter opening.¹³

This effect can be minimized by using a slow injection technique.⁶⁸ Unfortunately the high molecular mass PAH (such as hexabenzobenzene) tend not to reach the column because the lower molecular mass PAH

evaporate in the needle rather than the injector and a larger amount of the latter reaches the column. A denser solvent is recommended.⁶⁷

On-column injection therefore has to be used to extend the range of PAH which can be determined to molecular masses higher than hexabenzobenzene.⁶⁶

1.5.1.2.2.2 Detection

Response, linearity, sensitivity and reliability have made the FID almost universally employed.⁵⁴

PAH that enter from the column are cracked producing stripped protons and terminal groups.⁵⁴ The reaction is in proportion to the amount of the compound. It is quantitative and equivalent to the number of carbon atoms being burned rather than the mass of the compound.⁵⁴ This is called the effective carbon number and is the number that accounts for the response of the compound.⁵⁴

Response factors differ from instrument to instrument and therefore literature values cannot be used. They need to be determined prior to quantification.⁵⁴

The electron capture detector (ECD) is more specific and sensitive than the FID for PAH, but is more susceptible to column bleed and especially oxygen contamination of the carrier gas.⁵⁴ Molecular sieves are therefore mandatory if the ECD is used.⁵⁴

Structural features of some PAH, such as the positioning of methyl groups show an enhancement in the ECD's response. The FID and ECD can be used together for identifying PAH as shown by Bjorseth and Eklund.⁶⁶ These workers could differentiate between 1,2-benzanthracene and 2,3-benzanthracene (response ratio = 0.874).

Spectroscopic detectors are also used for identifying PAH. These include UV and fluorescence detectors.¹³ Because of higher sensitivity, the latter is more applicable to PAH analysis, but both detectors suffer from poor response if oxygen is present in the carrier gas.^{13, 54}

Bagheri and Creaser⁶⁷ demonstrated that a fluorescence detector coupled to a GC (GC-FS) offered benefits over GC-FID for certain PAH. They applied this technique to the determination of naphthalene, 1-methylnaphthalene, 2-methylnaphthalene and fluorene in light hydrocarbon fractions. Co-extracted aliphatic hydrocarbons were not detected in the sample by GC-FS, while the chromatogram was very complex when GC-FID was used.

1.5.1.3 Other techniques

Techniques such as HPLC, HPLC-GC, HPLC-MS, GC-MS and supercritical fluid chromatography (SFC) have found use in determining PAH.¹³ About 15% of the known compounds lend themselves to analysis by GC owing to insufficient volatility or thermal stability.⁷⁰ HPLC does not have this limitation and therefore competes well with GC.⁷⁰ Lack of resolution on some HPLC columns can be improved by using selective detectors. Furthermore, gradient elution techniques can improve the

resolution.¹³⁾ Use of polar mobile phases on less polar pellicular columns (reverse phase), such as chemically bonded octadecylsilane (C18) resolves PAH well.¹³⁾ However, modern HPLC instrumentation for PAH is expensive because UV and fluorescence detectors are usually required.⁷¹⁾

Barker et. al.⁷²⁾ used SFC to resolve 1,2-benzophenanthrene, 1,2-benzanthracene, benzopyrenes and alkylated PAH. A large number of theoretical plates resulted when compared to the same column in HPLC. Resolution was comparable to that obtained by capillary GC.

1.5.2 Detection and identification

1.5.2.1 Thin-layer chromatography

Sawicki and Johnson^{73,74)} located and identified PAH on TLC plates by fluorescence. Lederer and Lederer⁷⁴⁾ used a hexane-DMF mobile phase to separate PAH on silica gel plates. Location of PAH was facilitated by their fluorescence under UV light. Average R_f values, for a number of PAH (calculated as the fraction of distance moved by the component to that moved by the mobile phase) were reported.

Bender and Sawicki⁷⁷⁾ reported some sensitivity limits for PAH using a fine mist of concentrated sulphuric acid sprayed onto the plate. Subsequent heating of the plate at 100°C revealed the PAH as dark "spots". Similarly, Kucharezyk et. al.⁷⁸⁾ used a mixture of 0.2cm³ of 37% formaldehyde in 10cm³ of 97% sulphuric acid (conc.) as a spray

to locate PAH on TLC plates. Various coloured spots indicative of PAH resulted after the plate was heated in an oven at 100°C.

The physical removal of PAH from the plates leads to contamination.⁷⁹⁾ Laser mass spectrometry has been applied for identification of overlapping compounds.⁷⁹⁾

1.5.2.2 Retention data in gas chromatography

Retention data are strongly dependent on two factors for identification: a) the peak due to the unknown must be in a definite position relative to other peaks, b) peak position and shape must be reproducible.^{13,54)}

In a GC column, retention is related to the distribution of a solute between the mobile and stationary phases.⁵⁴⁾ The time that elapses from injection of the sample to the recording of the peak maximum of the component band or peak is defined as the absolute retention time. Subtraction of the retention time for an unretained peak gives the adjusted retention time.⁵⁴⁾

The product of adjusted retention time of the sample component and the volumetric flow rate of the carrier gas is the adjusted retention volume.⁸⁰⁾

The number relating the adjusted retention volume of an unknown to the adjusted retention volume of normal alkanes which bracket the unknown with respect to retention time is the retention index.⁸⁰⁾

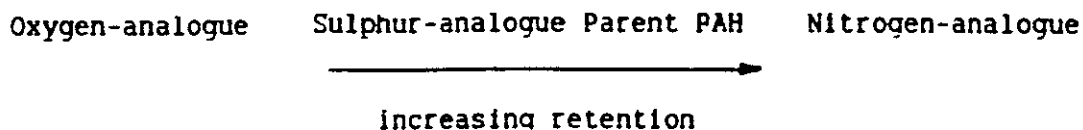
A plot of the logarithm of the adjusted retention volume or time against $100Z$ where Z = number of carbon atoms in the alkane, yields a straight line of slope "b". For a given column, the value of b is characteristic.⁸⁰

At a given temperature, b is dependent only on the variation of ΔG° the standard free energy of solution of the alkanes in the stationary phase.⁸⁰ Therefore, if published retention indices are to be used, the column that was used to produce these retention indices must have a similar value of b.⁸⁰

1.5.2.2.1 Retention of polycyclic aromatic hydrocarbons

The retention order of PAH in GC is mainly governed by their boiling points. Boiling points of PAH are related to structure.

The retention of PAC, differing only by the presence or absence of heteroatoms has been established to be:¹³



PAH structurally less condensed (smaller number of bay-regions) and of similar molecular mass and ring number than more condensed compounds are usually associated with a longer retention. Thus the three isomers with molecular weight 252 are eluted in the following order:

1,2-benzopyrene < 3,4-benzopyrene < 4,5;9,10-dibenzanthracene.

Hydro derivatives of PAH are generally eluted before the parent compound, whilst the alkylated PAH are eluted later.

Retention studies of 209 PAH and related compounds were carried out by Lee et. al.¹¹ Changes in flow rate, different temperature programming rates, stationary phase film thickness, column length were all found to have adverse effects on retention reproducibility when n-alkanes were used as reference compounds. When appropriate PAH compounds were used as reference, these adverse effects were minimized. A retention index system for programmed temperature runs was developed, using a nominal retention index of 200.00 for naphthalene, 300.00 for phenanthrene, 400.00 for 1,2-benzophenanthrene and 500.00 for 2,3-naphthophenanthrene. The average 95% confidence limits for four measurements on the 209 compounds were ± 0.25 index units.

1.5.2.3 Other methods

Due to the simple mass spectra obtained, a mass spectrometer has gained wide acceptance for PAH identification.¹³

Lee et. al.,¹³ have summarized the following. The mass range of a mass spectrometer usually extends from 600 to 1200 atomic mass units (amu) with typical resolutions of 0.1 to 1.0 amu. Some of the dedicated instruments attain 0.001 amu. Prior separation of a complex mixture is provided by capillary columns giving narrow scan times making a computer mandatory for such systems. A quadropole MS is well suited, providing four mass spectra per second.

Electron-impact mass spectra of PAH are simple and mainly consist of an intense molecular ion (M^+) and small ions due to the loss of one to

four hydrogen atoms, termed $(M-1)^+$, $(M-2)^+$, $(M-3)^+$ and $(M-4)^+$ respectively.¹³⁾ The $(M+1)^+$ ion is always present: which is due to the ^{13}C isotope being in relatively high abundance.¹³⁾

Chemical ionization mass spectrometry using methane as the reagent gas gives different mass spectra of PAH than that of electron impact.¹⁴⁾ Because of the proton affinities of PAH, the $(M+1)^+$ ion is most abundant.¹³⁾ The second most abundant ion is $(M+29)^+$ due to addition of an ethyl group.¹³⁾

For complex mixtures, compounds other than PAH tend to interfere by overlapping. One way of approaching this problem is to use single-ion monitoring (SIM). In this method the mass spectrometer is focused on a m/e value characteristic of the compound under investigation. Used in this way the mass spectrometer acts as a mass-selective detector (MSD).¹⁵⁾

Lee et. al.¹⁶⁾ used this technique to identify PAH extracted from a lake sediment. A DB-5 capillary column (30m x 0.25mm i.d.) was used to resolve their mixture. The column was interfaced with an electron-impact ion source for maximum sensitivity. Once obtained, the mass spectra were reconstructed by only including the more abundant ion peak for each compound. This they found was a highly sensitive and specific quantitation method.

Another means of detection is by UV absorption and fluorescence.¹³⁾ For example the PAH 3,4-benzopyrene, and 2,3-benzofluoranthene have

almost indistinguishable UV absorption spectra, but the fluorescence spectra are sufficiently different that they can be distinguished. Both of these detection techniques have been used extensively in HPLC (see chapter 1.5.1.3).

The four-, five- and six-ring PAH show fluorescence as broad bands between 360 to 480 nm. To resolve the bands the sample is frozen in an n-alkane solvent at below 100K. The fluorescence spectrum of the frozen sample known as the Shpol'skii spectrum, is a specific method and it can be used for fingerprinting PAH.¹³⁾

Nuclear Magnetic Resonance Spectroscopy (NMR) and Infrared spectroscopy (IR) are generally not sensitive enough for analyte detection in GC.¹³⁾

1.5.3 Quantification

The ionizability of PAH in an FID is presumably affected by their structure. Equivalent concentrations of different PAH would therefore produce peaks of different areas. Coefficients relating the peak areas to solute concentrations, so-called response factors need to be calculated in order to determine concentration in the original sample.^{13, 34)}

The internal standard (IS), a pure compound not known to be present in the sample is added to both standard and sample. Response factors, calculated from the response of the IS relative to pure PAH compounds in

the standard, are used in quantifying PAH in a sample. Use of the IS has the additional advantage of eliminating the need to measure the aliquot accurately and corrects instrument variation automatically.

1.5.3.1 Requirements of an internal standard

Requirements for an IS are as follows:⁵⁴⁾

- (i) It must not co-elute with any sample component.
- (ii) It must elute as closely as possible to the desired components, and preferably before the last of the desired components such that analysis time is not increased.
- (iii) It must be structurally similar to the sample components.
- (iv) It must be non-volatile, and stable such that it can be stored for long periods of time.

Usually only one IS is required, but some workers have found a need for two or more in PAH analysis by GC. Bjorseth¹¹⁾ and Alfheim and Lindskog¹²⁾ used 3,6-dimethylphenanthrene, B,B'-binaphthalene and/or m,m'-tetraphenyl prior to Soxhlet extraction of PAH from particulate matter. The compounds p,p'-binaphthyl and m-quarterphenyl were added by Bjorseth et. al.¹²⁾ as IS.

Suzuki and Imai¹⁰⁾ used 1,3,5-triphenylbenzene as IS to determine PAH

in airborne particulate matter. These workers pointed out that the compound exists in coal tar but not in pitch.

1.5.3.2 Integration of aquired data

For many years, conventional potentiometric recorders have been the standard recording device for GC. The signal taken from the electrometer amplifier of the FID gives a permanent record as a peak on moving chart paper.

In 1977 Bjorseth¹¹ used an electronic integrating device together with a simple computer program which compared the areas of the PAH to the IS giving the amount of each compound in the sample. In 1978 Bjorseth et. al.¹² used a similar device to determine peak areas. A comparison was then made with the IS to quantify PAH.

In 1987, Sheppard and Bronswijk of "DAPA Scientific Software", Kalamunda, Western Australia, released version 4.52 of "Data Acquisition Plotting and Analysis (DAPA)".¹³ This computer software is a package which acquires an analog signal from the detector and converts it to a digital form for storage on floppy disks for future reference. A complete list of all operations and data required to produce the final answers desired can be entered through a keyboard and stored in the microprocessors read-write memory. Such a list is called a "Method". Included in the "Method" are peak identification data, response factors, etc. One of four standard calculation procedures are possible. i.e. area %, normalization %, internal standard and external standard. Hard

copies of original or modified data can be obtained by printing the chromatogram and/or an integration and internal standard report.

1.5.3.3 Minimum detectable level

The detection limit is here defined as the concentration of the analyte that produces an output signal twice the root mean square of the background noise; i.e. a signal-to-noise ratio of 2. The "minimum detectable level" (MDL) is characteristic of a detector, and is not related to column parameters or sample size. For a FID, units for the MDL are in grams of carbon per second (gsec^{-1}). Such data were not available for PAH and were therefore determined in this dissertation.

1.6 DETERMINATION IN METALLURGICAL FACTORIES

In metallurgical factories, metal oxides are reduced in a reduction cell or pot (see 1.4.1). Carbonaceous anodes are manufactured from a porous aggregate coke material bound by pitch (see 1.1.2).

Application of heat (about 1000°C) and high current densities release particulate matter into the working environment. Depending upon the type of anodic starting material (ie graphitized or ungraphitized - see 1.1.2) the amount of residual PAH on particulate matter will differ.

Some workers have quantified PAH associated with particulate matter in the abovementioned process plants. Bjorseth *et. al.*¹² determined particulate matter PAH by GC-FID in samples taken by a stationary

sampling pump. This is a fixed air suction pump which draws a large constant volume of air through a preweighed filter (usually glass fibre) to capture particulate matter over a period of time. A time weighted average is obtained.

Ten samples were taken this way in a plant where an ungraphitized anode was used. An average of about 380 ug of total PAH ranging from fluorene to 3,4:8,9-dibenzopyrene were found. Those PAH having a molecular mass greater than pyrene were present in greater amounts. Their GC-FID technique could not detect PAH similarly sampled in a plant where graphite electrodes were installed. An HPLC technique was necessary. About 6 ug of total PAH were recovered. Of the PAH found, fluoranthene was the compound of lowest molecular mass that could be detected.

Anderson et. al.²⁴ determined low levels of PAH by HPLC at a coke oven and in an aluminium plant. They quantified PAH in samples collected by using a personal sampling pump attached to a worker. This sampling method is similar to that of stationary sampling. A personal sampler collects a sample which is more directly related to a worker's occupational exposure. However, it collects less material than a stationary sampling pump and the amount of material can differ considerably (see 3.1). Samples collected by a personal pump do not contain enough PAH for a GC-FID method¹².

The work presented by Bjorseth et. al.¹² and Anderson et. al.²⁴, both included the sampling of gaseous and particulate PAH. In both cases, the more volatile lower molecular mass PAH (less carcinogenic)

were found in greater amounts in gaseous form than on particulate matter.

For this investigation, the carcinogenic content of workroom air was considered a prerequisite and therefore emphasis was placed on collecting particulate matter by stationary sampling and subjected to the method presented in this dissertation.

Postscript

Both the book by T. Vo-Dinh²⁵, on the chemical analysis of PAC, and the updated software "DAPA Scientific Software version DAPA SD" were not available in time for inclusion in the present dissertation.

CHAPTER 2

ISOLATION OF POLYCYCLIC AROMATIC HYDROCARBONS AS A GROUP

2.1 EXTRACTION FROM PITCH

2.1.1 Introduction

Pitch was selected because it could be considered to be representative of samples likely to be encountered. It is used in many industrial processes (see 1.1.2) and is the main source of PAH in the working environment. The effect of different solvents using Soxhlet and ultrasonic extraction on pitch samples was studied.

2.1.2 Experimental

2.1.2.1 Equipment

The ultrasonic bath was obtained from "Ultrasonic Engineering (Pty)Ltd.." (catalogue no CV100/170). Samples were kept in glass test-tubes (8cm x 1cm).

Two sets of Soxhlet glass apparatus were available. Cellulose thimbles ("Whatman", single thickness of 45mm x 123mm) contained samples for

extraction. The solvents used to effect Soxhlet extraction (see 2.1.2.2) were contained in round bottomed flasks. Isomantles were used to heat the solvents.

A "Heidolph OB-2000" rotary evaporator was used to concentrate Soxhlet extracts under reduced pressure.

2cm³ Clear glass vials complete with plastic caps and teflon-lined silicone rubber septa ("Varian", catalogue no 66-000104-00) were used to store concentrates from both ultrasonic and Soxhlet extractions.

All glassware was washed with hot water to remove detergent residues and rinsed with deionised water and acetone and finally dried in an oven at 110°C.

A "Varian" 3600 series GC fitted with a 1077 split/splitless injector and a FID was used. High temperature septa (silicone with teflon face) were used in the injector. Hamilton glass syringes (#701, 10ul) were used for injecting samples.

A 30m x 0.25mm i.d. WCOT DB-5(0.1 um thickness) capillary column was used. Graphite ferrules were used to install the column into the injector and detector parts of the GC. The ends of the columns which came into contact with the ferrules were cut off to prevent adsorption of PAH onto residual graphite.

The computer used to acquire and save chromatograms was an IBM compatible PC/XT ("Spring Circle Computer Inc.", Taiwan, R.O.C.) fitted with

a 640k R.A.M. and a 8MHz turbo board. A monochrome screen was used, but the computer had a colour graphics adaptor (CGA) card. It could house up to two 5¹/₄-inch double sided floppy diskette drives with approximately 320kB of storage for each drive.

The disk operating system MS-DOS, version 3.30 was used to "boot" the computer. DAPA software (see 1.5.3.2) was used to acquire chromatograms. The DAPA 14-bit low resolution printed circuit board was used.

Once saved and integrated, a print-out of a chromatogram and integration and internal standard reports were obtained on an "Epson LX-800" printer.

2.1.2.2 Reagents

Solvents used were purchased from "Merck", Darmstadt, West Germany through "Merck", Durban, Natal, and from Saarchem (Pty) Ltd., Muldersdrift, South Africa through Polychem Supplies, Durban, Natal. The "Merck" reagents were of the "for residue analysis" grades and were used as received. The "Saarchem" solvents were redistilled before use. Anhydrous sodium sulphate obtained from Saarchem (Pty) Ltd., was used to remove moisture from solvent extracts.

The PAH standards were purchased from "Sigma Chemical Company", St. Louis, USA and "TCI Organic Chemicals", Tokyo, Japan through "Capital Enterprises", New Germany, Natal. All were of 98% or better purity and

were used as received. Ten were selected, viz. fluorene, phenanthrene, anthracene, fluoranthene, pyrene, 1,2-benzofluorene, 1,2-benzophenanthrene, 2,3-benzanthracene, 3,4-benzopyrene and 1,2-benzopyrene.

The internal standard 1,2,5-triphenylbenzene (92% pure) was purchased from "Aldrich Chemicals", West Germany through "Capital Enterprises," New Germany, Natal. It was recrystallised from cyclohexane before use.

Gases used for the GC and for concentrating extracts were purchased from "Afrox", Durban, Natal and were of "instrument grade" quality.

2.1.2.3 Procedure

2.1.2.3.1 Soxhlet extraction

0.5g of ground pitch was weighed into each of two Soxhlet cellulose thimbles. The thimbles were each placed into a Soxhlet extractor. About 300cm³ of cyclohexane was placed into one of the distillation flasks and 300cm³ of benzene into the other. The isomantles were switched on and the pitch samples extracted for 16 hours.

After extraction, a rotary evaporator was used to concentrate the extract under reduced pressure to about 10cm³. The concentrate was filtered through anhydrous sodium sulphate into glass vials and evaporated to dryness under a stream of nitrogen gas. The residues were taken up in 1cm³ of fresh cyclohexane and benzene respectively.

2.1.2.3.2 Ultrasonic extraction

About 0.05g of ground pitch was weighed into two test-tubes. About 10cm³ of benzene and cyclohexane was added to each. The test-tubes were placed into an ultrasonic bath and the power was switched on for 30 minutes.

The extracts were then filtered through anhydrous sodium sulphate into glass vials and treated further as under Soxhlet extraction.

This procedure was repeated using acetone, benzene and hexane as solvents taking up the dried residues in 1cm³ of acetone, benzene and hexane as appropriate. After concentration under nitrogen gas, 60ug of the internal standard 1,3,5-triphenylbenzene (see 1.5.3.1) was added to each extract.

2.1.2.3.3 Injection into gas chromatograph

A 2ul of the benzene and cyclohexane extracts obtained from soxhlet and ultrasonic methods were injected in the GC.

A 10ul volume of the ultrasonic extracts obtained using acetone, benzene and hexane and containing the internal standard, were injected.

The following GC-FID conditions were used:

- a) Column: 30m x 0.25mm i.d. WCOT with 0.1 micron of DB-5.
- b) Carrier gas: Helium (instrument grade).
- c) Injection: 5 microlitre - splitless for 60 seconds.
- d) Injector temperature: 320°C.
- e) Detector temperature: 250°C.
- f) Detector make-up gas: Helium (instrument grade).
- g) Detector attenuation and range: 1×10^4 respectively.
- h) Temperature program:
 - (i) 70°C at injection. Ramped immediately to 100°C at 20°C/minute.
 - ii) Held at 100°C for 30 seconds.
 - iii) Ramped to 200°C at 20°C/minute.
 - (iv) Held at 200°C for 30 seconds.
 - (v) Ramped to 300°C at 3°C/minute.
 - (vi) Held at 300°C for 15 minutes.

2.1.3 Results

After Soxhlet extraction, benzene had dissolved 70% of the pitch whereas cyclohexane dissolved 30%. This suggested either selectivity of the latter or incomplete recovery during the extraction.

Evidence for the former was obtained for peak area units per microgram given in table 2.1.1.

TABLE 2.1.1 PEAK AREA UNITS PER MICROGRAM OF TEN PAH
EXTRACTED BY SOXHLET THIMBLE USING BENZENE AND
CYCLOHEXANE

PAH	Peak area units per microgram	
	Benzene	Cyclohexane
Fluorene	16.08	9.84
Phenanthrene	40.60	30.67
Anthracene	9.02	6.60
Fluoranthene	18.46	16.94
Pyrene	23.05	20.63
1,2-benzofluorene	3.51	2.58
1,2-benzophenanthrene	5.70	4.14
2,3-benzanthracene	5.82	4.67
1,2-benzopyrene	2.22	3.06
3,4-benzopyrene	3.84	3.94

The data in table 2.1.1 indicates benzene to be more efficient for lower molecular mass and cyclohexane possibly more difficult for higher molecular mass PAH.

Results obtained from ultrasound extracts are shown in table 2.1.2.

TABLE 2.1.2 PEAK AREA UNITS PER MICROGRAM OF TEN PAH
EXTRACTED BY ULTRASOUND USING BENZENE AND
CYCLOHEXANE

PAH	Peak area units per microgram	
	Benzene	Cyclohexane
Fluorene	23.74	16.20
Phenanthrene	77.13	63.97
Anthracene	17.65	15.79
Fluoranthene	48.13	42.08
Pyrene	59.71	50.33
1,2-benzofluorene	9.68	7.14
1,2-benzophenanthrene	18.98	11.05
2,3-benzanthracene	25.53	13.36
1,2-benzopyrene	14.76	2.96
3,4-benzopyrene	20.25	4.20

Comparison of tables 2.1.1 and 2.1.2 show ultrasound assisted extraction to be significantly more efficient than Soxhlet extraction with benzene more efficient than cyclohexane for the higher molecular mass PAH.

Figures 2.1.1, 2.1.2 and 2.1.3 show the gas chromatograms obtained for the ultrasonic extracts of pitch using benzene, acetone and hexane as extractants respectively.

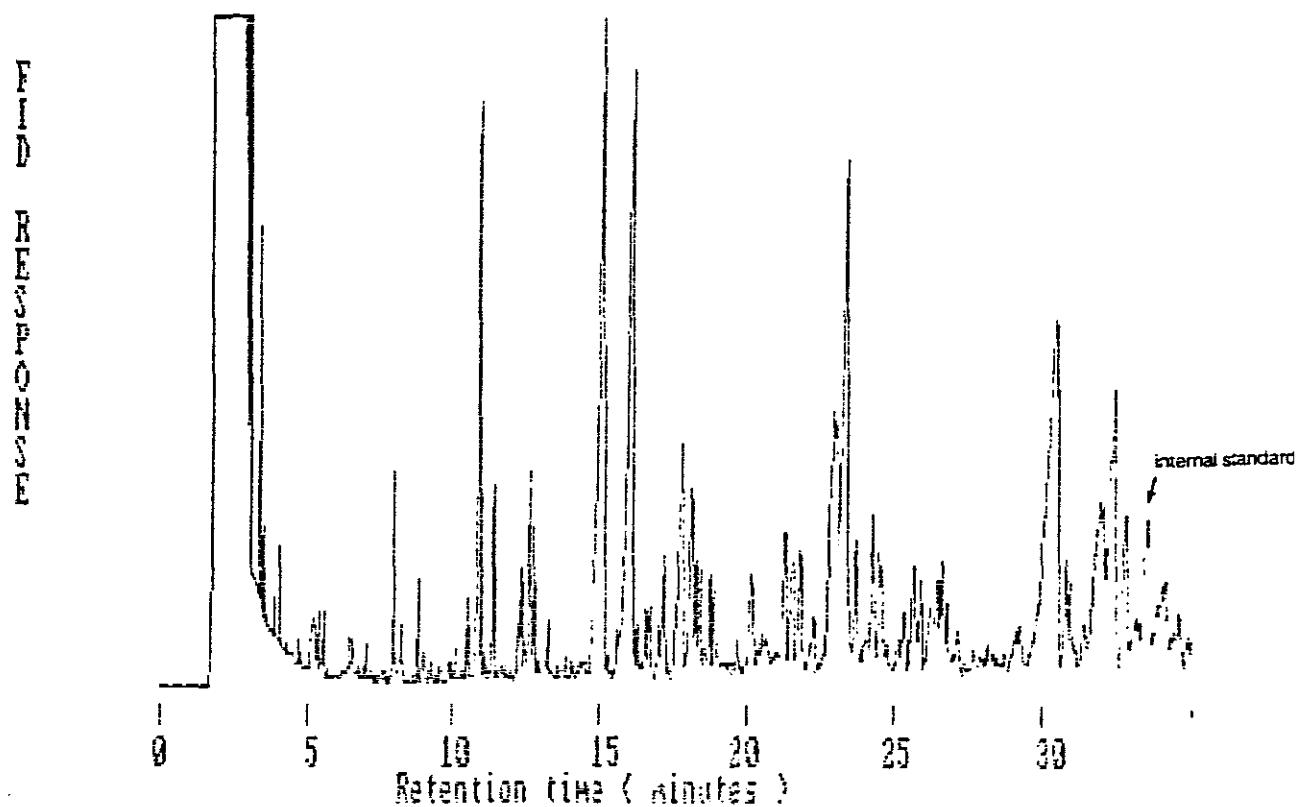


FIGURE 2.1.1 GAS CHROMATOGRAM OBTAINED AFTER ULTRASONIC
EXTRACTION OF PITCH WITH BENZENE

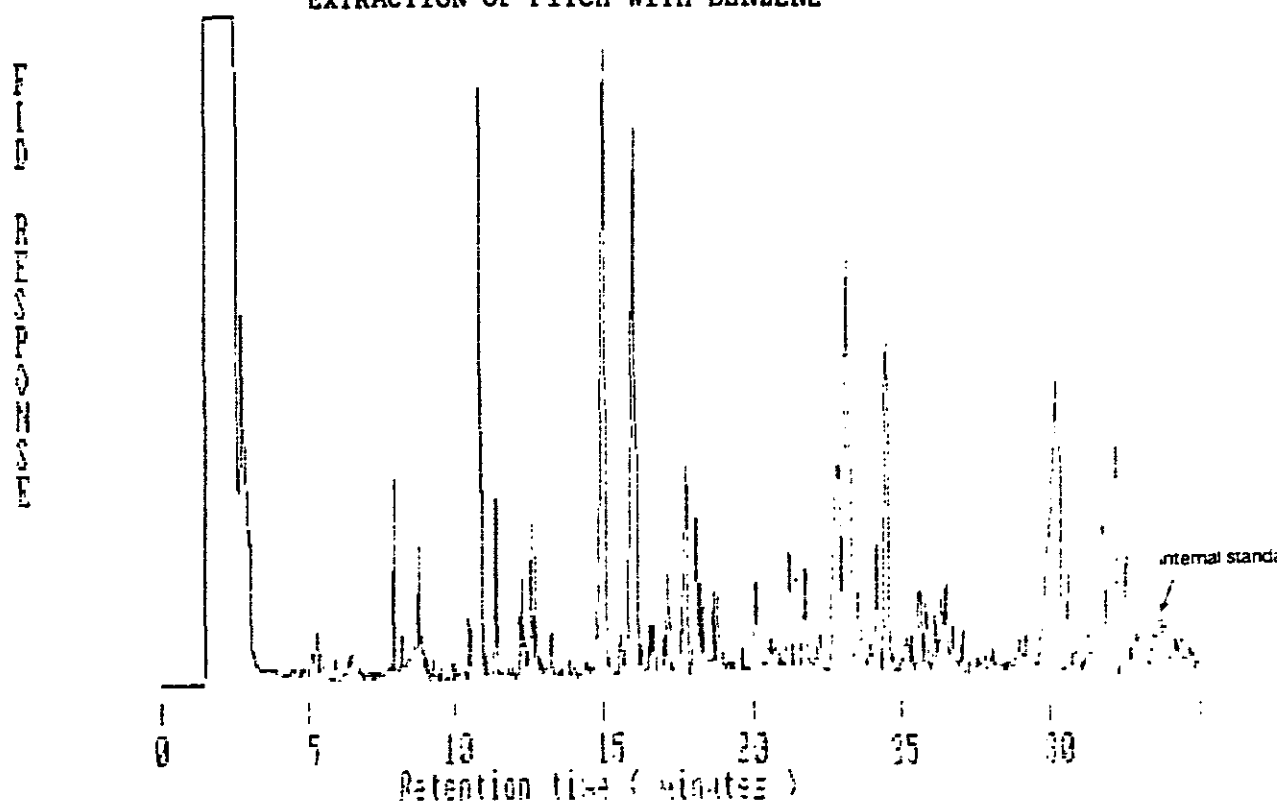
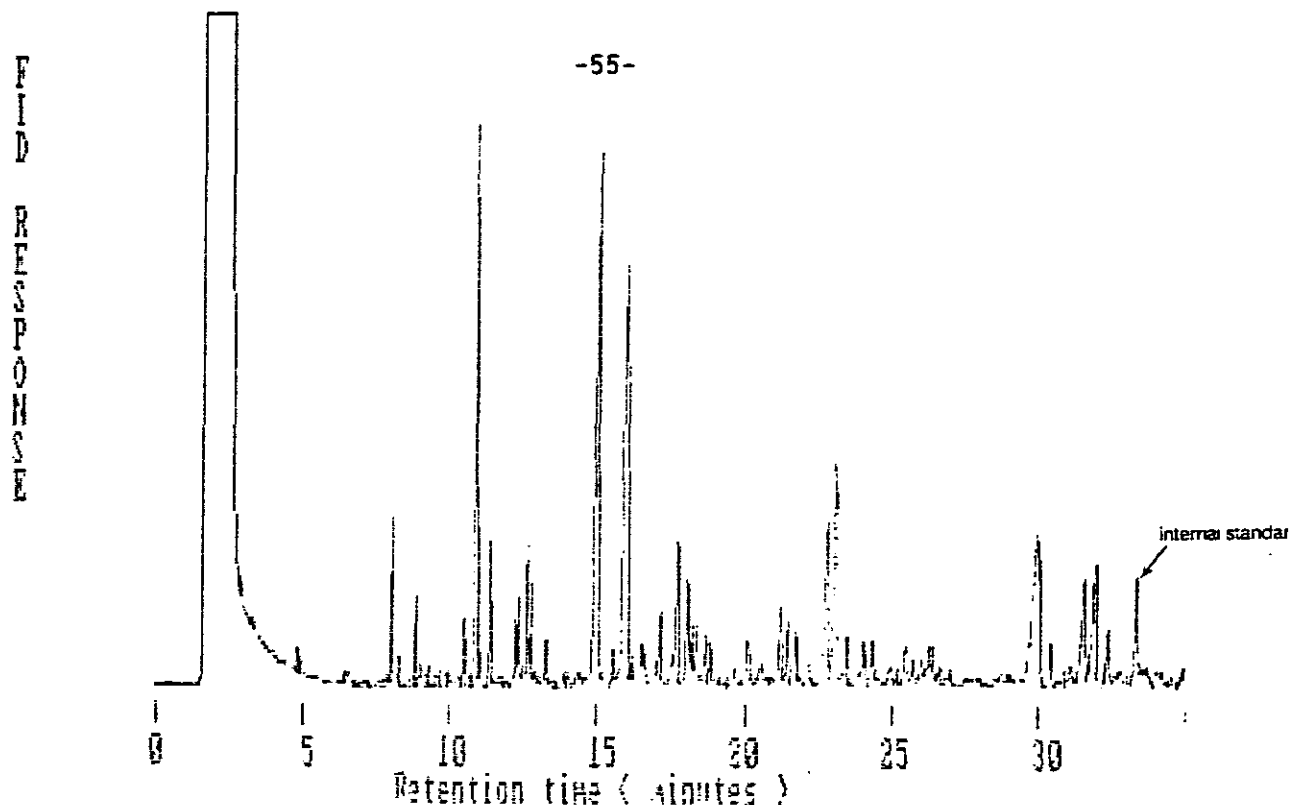


FIGURE 2.1.2 GAS CHROMATOGRAM OBTAINED AFTER ULTRASONIC
EXTRACTION OF PITCH WITH ACETONE



**FIGURE 2.1.3 GAS CHROMATOGRAM OBTAINED AFTER ULTRASONIC
EXTRACTION OF PITCH WITH HEXANE**

The figures show clearly the decrease in background noise relative to undoubted PAH peaks in the sequence benzene > acetone > hexane.

2.1.4 Discussions and conclusions

Ultrasound extractions appeared to give more quantitative recoveries of PAH than soxhlet thimble extraction. Ultrasound permitted faster sample throughput, required no heating and less handling.

Hexane evidently extracted PAH as efficiently as the other two solvents while co-extracting far less matrix.

Furthermore, hexane was more easily removed by evaporation. Cyclohexane was not investigated further because it tended to form emulsions.

2.2 SEPARATION FROM EXTRACTS

2.2.1 Introduction

The selection of hexane as the solvent for extracting pitch as described in chapter 2.1 showed it to be specific for PAH, and no isolation step was needed.

Snook et. al.,⁵¹ extracted PAH from a coal-tar pitch sample and found that the chromatogram was relatively simple. It consisted of very low levels of alkylated PAH and an isolation of the compounds from interfering matter was not required.

When these workers applied their method to samples of crude oil and asphalt the chromatograms indicated the presence of substantial proportions of alkylated and heterocyclic PAH, and this necessitated an isolation step.

Both petroleum coke and pitch coke as used in the metallurgical industry, are produced from crude oil.

It was therefore expected that similar interfering compounds might be present, and that a method was required to isolate the PAH fraction from the coke extracts.

Liquid-liquid partitioning and column chromatography were investigated as possible candidates. As regards the former, the method described by Bjorseth¹¹ seemed most appropriate. Because of the high cost of high purity DMF, the semi-micro method adaption of Stenberg et. al.¹² was investigated.

Column chromatography on silica gel has been used by a number of workers^{11, 12, 13, 14} to isolate the PAH fraction from many types of samples. Snook et. al.¹⁵ applied a column chromatographic separation technique with silica gel to elute PAH from a pitch extract. The PAH were eluted using a 1:3 mixture of benzene:petroleum ether (BPE).

As mentioned before (1.4.2.3), Ostman and Colmsjo¹⁶ obtained good recoveries of PAH from crankcase oil using hexane on 10% deactivated silica gel.

Therefore silica gel was chosen as the stationary phase and hexane and BPE as the mobile phases. The elaborate equipment described by Ostman and Colmsjo¹⁶ for preparing a homogeneously deactivated silica gel was not available. Therefore unhomogeneously undeactivated silica gel was used instead.

2.2.2 Experimental

2.2.2.1 Equipment

Two 250cm³ glass separating funnel fitted with teflon stopcocks were used for each extraction method as described by Bjorseth¹¹. A rotary evaporator (Heidolph. OB-2000) was used to concentrate the extract under reduced pressure.

Three 7.5cm³ capacity glass vials fitted with teflon-lined screw-on lids were used for semi-micro liquid-liquid extraction. The extracts were concentrated under nitrogen gas (Afrox, instrument grade).

The chromatographic columns used were from "Supelco", and consisted of glass, 300mm by 10.5mm o.d. (catalogue no 6-4756) loaded with silica gel. Sample extracts were stored in 2cm³ clear glass vials.

The GC-FID and computer with software used, have been described in 2.1.2.1.

2.2.2.2 Reagents

Reagents have been described previously except DMF which was of "for residue analysis" grade. (Merck, Darmstadt, West Germany) and used for liquid partition.

Silica gel (63 to 200 microns in diameter) was obtained from Saarchem

(Pty)Ltd.. Muldersdrift, South Africa through Polychem Supplies, Durban, Natal, catalogue no 57084.

Petroleum ether (30-60°C) was obtained from Saarchem (Pty) Ltd., and redistilled before use.

Additional PAH standards naphthalene, dibenzopyrrole, 2-methylphenanthrene, 1-methylphenanthrene, 9,10-benzophenanthrene, 1,2-benzophenanthrene, 4,5;9,10-benzophenanthrene, 3,4-benzofluoranthene, hexabenzobenzene and 3,4;8,9-dibenzophyrene were purchased from "Sigma Chemical Company", St. Louis, USA and "TCI Organic Chemicals", Tokyo, Japan, through "Capital Enterprises", New Germany, Natal. All were of at least 98% purity and were used as received.

Procedure

A) A stock solution containing nineteen PAH standards (table 2.2.1) was made up in hexane. Because of differing solubilities, different concentrations had to be used for individual PAH. Benzene could not be substituted for hexane because it was miscible with DMF.

A known volume of PAH stock solution was made up to 50cm³ with cyclohexane. The PAH were partitioned twice fresh aliquots of into 50cm³ of 9:1 DMF:water in a separating funnel by shaking for one minute each time.

The PAH were then back-extracted into a mixture of 50cm³ cyclohexane and 75cm³ water. 25cm³ cyclohexane was used to extract for a second time. The combined extracts were concentrated to a few cm³ using a rotary evaporator. A known volume of cyclohexane was added to the residue and a volume was injected into the GC. The GC conditions in 2.1.2.3.3 were used. The recovery of each PAH was calculated from the corresponding peak area, and that obtained on aliquots of the unextracted stock solution.

Bjorseth¹¹ showed that the precision of the method, which was tested with standard mixtures and actual samples, corresponded to a relative standard deviation of 4.8% for fifteen compounds over a wide range of initial masses of PAH. Therefore no further study with different initial masses of PAH was done.

- B. Five aliquots were taken from the stock solution, and diluted separately to a known volume with hexane.

A 5ul aliquot of each solution was injected into the GC. The area of each chromatographic peak was calculated by the computer.

Each diluted solution was then processed as follows:

A 1cm³ aliquot was transferred to a 7.5cm³ glass vial with a teflon-lined screw-on cap. About 2cm³ hexane and 2cm³ of a

9:1 mixture of DMF:water was added. The vial was capped and the PAH extracted into the DMF:water layer by shaking the vial by hand for one minute. The pressure was released during the extraction by slightly opening the cap.

Using a dropping pipette, the upper hexane layer was drawn off into another clean glass vial with a similar screw-on cap. This was extracted with another 1cm³ of the 9:1 DMF:water. The two DMF:water extracts were combined by transferring the second extract into the first one so as to reduce handling error.

To this was added 3cm³ of doubly-deionised water and 2cm³ of hexane. The PAH were back-extracted into the hexane by shaking the capped vial for 1 minute.

After the layers had separated, the upper layer of hexane was drawn off by a dropping pipette into another glass vial. A further 1cm³ of hexane was added to the extract and the process was repeated.

The two hexane extracts were combined and the hexane was evaporated to dryness under a steady stream of gaseous nitrogen. The residue was taken up in a 1cm³ aliquot of fresh hexane. A 5ul aliquot of this was injected into the GC, using the GC conditions in 2.1.2.3.3. The recoveries were calculated as under A).

For comparisons the following method using column chromatography was investigated.

About 10g of the silica gel was weighed out into each of two 100cm³ beakers. Two chromatography columns were set-up side by side, one with 10g silica gel slurried in hexane, and the other with 10g silica gel slurried in a 1:3 mixture of BPE.

After settling, about 0.5g of anhydrous sodium sulphate was placed on top of the packing in each column.

A 500cm³ round-bottom flask fitted with a glass funnel containing anhydrous sodium sulphate was placed under the outlet of each column. The supernatant in each column was allowed to drain off until its meniscus touched the top of the packing.

A 1cm³ volume of the PAH stock solution was carefully applied to the top of each column and the compounds were eluted simultaneously with hexane in one column and BPE in the other.

Elution was continued until the last trace of a coloured band representing the PAH had left the column.

This required approximately 350cm³ of hexane, and 100cm³ of BPE. Once collected, the eluent was concentrated under reduced pressure using the rotary evaporator and finally evaporated to dryness under nitrogen gas.

In each case, the residue was taken up in 1cm³ of fresh hexane and a 5ul aliquot was injected into the GC. The recoveries were determined as before.

2.2.3 Results

The speed of the semi-micro liquid-liquid partition method gave it a distinct advantage over the other two methods. Therefore only the results obtained by this method are presented here. The recoveries of PAH as a function of the number of full benzene rings against concentration is given in figure 2.2.1.

Recoveries as a function of loaded mass obtained are shown in table 2.2.1. The minimum percent recoveries expressed in table 2.2.1 were calculated from the MDLs determined and given in chapter 5 and table 5.4.

FIGURE 2.2.1 THE RECOVERY OF POLYCYCLIC AROMATIC HYDROCARBONS BY SEMI-MICRO LIQUID-LIQUID PARTITIONING

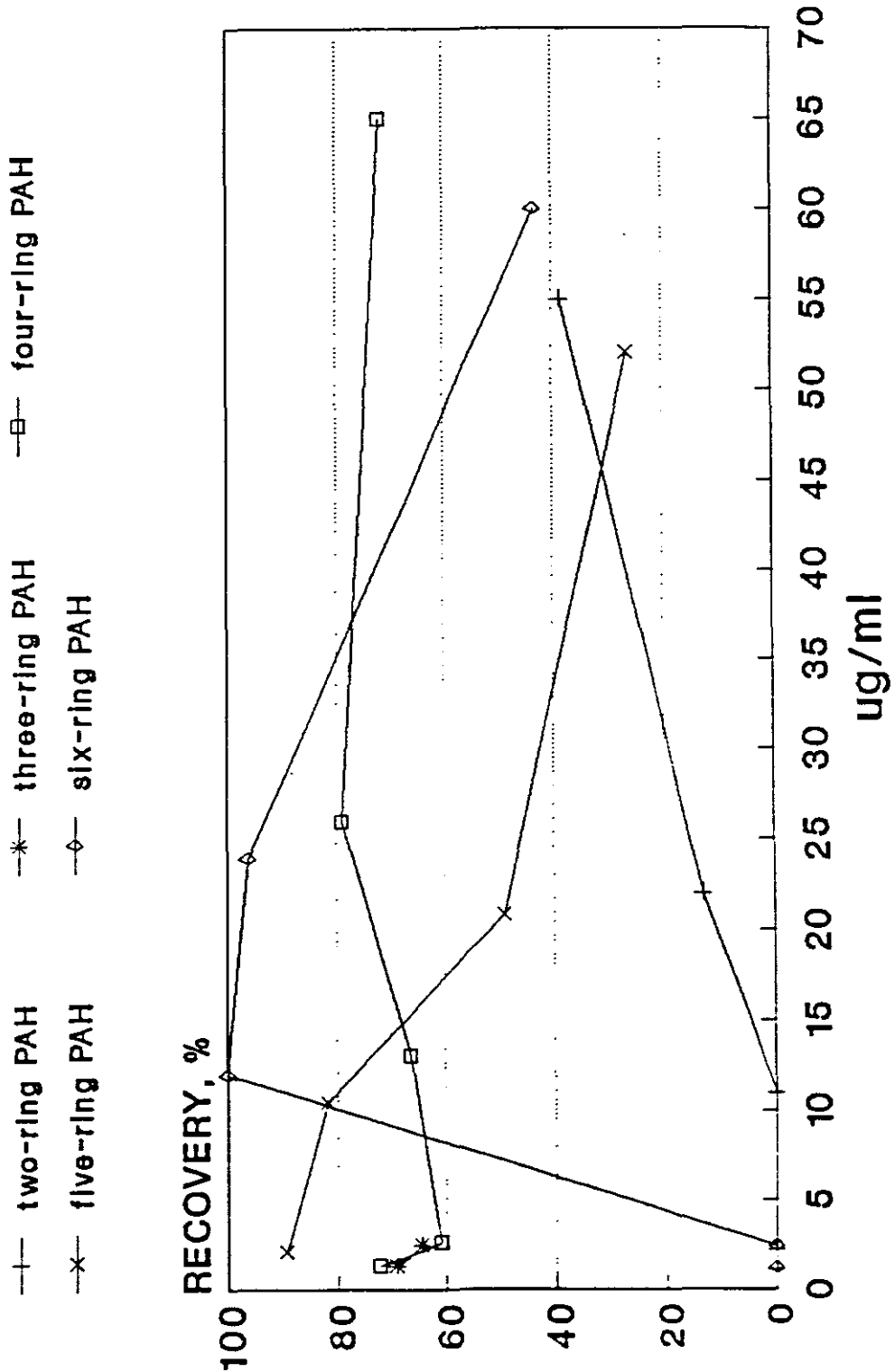


TABLE 2.2.1 THE RECOVERIES OBTAINED FOR THE POLYCYCLIC AROMATIC HYDROCARBONS STUDIED USING BJORSETH'S METHOD (A) COLUMN CHROMATOGRAPHY WITH HEXANE (B) AND 1:3 BENZENE-PETROLEUM ETHER (C) AS ELUENTS AND SEMI-MICRO LIQUID-LIQUID PARTITIONING (D)

PAH	INITIAL MASS (micrograms)	METHOD			
		A	B	C	D
		Percent recovery			
Naphthalene	55.0	21	30	22	39
Fluorene	140.0	41	55	4	62
Phenanthrene	63.5	50	63	86	74
Anthracene	166.5	50	65	11	74
Dibenzopyrrole	89.0	35	<0.01	17	23
2-methylphenanthrene	66.0	47	68	12	67
1-methylphenanthrene	98.0	60	69	11	68
Fluoranthene	117.5	64	81	3	79
Pyrene	65.0	66	82	<0.01	79
1,2-benzofluorene	57.0	69	79	<0.01	90
9,10-benzophenanthrene	55.0	100	100	73	87
1,2-benzophenanthrene	88.5	100	<0.01	<0.01	100
2,3-benzanthracene	60.5	100	7	<0.01	72
3,4-benzofluoranthene	53.0	100	100	<0.01	100
1,2-benzopyrene	255.0	100	100	<0.02	100
3,4-benzopyrene	52.0	100	100	<0.02	90
4,5;9,10-dibenzanthracene	59.0	100	100	<0.02	100
Hexabenzobenzene	60.0	100	37	<0.02	100
3,4;8,9-dibenzopyrene	50.0	100	23	<1.10	100

2.2.4 Discussion

The data in table 2.2.1 show absorption chromatography with benzene-petroleum ether as eluent (C) to be inferior to the three alternative methods investigated. The high recoveries for phenanthrene and 9,10-benzophenanthrene appear to be fortuitous.

The three alternative methods gave closely similar recoveries. The exceptionally low recoveries of dibenzopyrrole, 1,2-benzophenanthrene and 2,3-benzanthracene by absorption chromatography with hexane appear as anomalies. Those for hexabenzobenzene and 3,4;8,9-dibenzopyrene may indicate a decrease in efficiency of hexane as an eluent for the PAH of high molecular mass. An increase in the volume of hexane through the column could have improved recoveries of high molecular mass PAH, but this was not investigated.

Common to methods A, B and D (table 2.2.1) is the relatively low recovery of the lower molecular mass PAH with an essentially systematic increase in recoveries with increasing molecular mass up to 1,2-benzofluorene.

The recoveries obtained for various loading of PAH by semi-micro liquid-liquid extraction (method D in table 2.2.1) appear to be strongly aberrant. Apart from this, the results place the PAH into three groups:

- 1) Three-ring PAH recoveries were essentially independent of load over the entire range of loadings investigated.

- 2) Low to practically zero recovery at low loadings with a tendency to level off at high loadings. Naphthalene, fluorene and dibenzopyrrole exhibited this behaviour.
- 3) High recoveries at low loadings, decreasing at high loadings, usually with low recoveries at lowest loading. Typical of high molecular mass PAH.

2.2.5 Conclusion

On the basis of the above results the method chosen to separate PAH from extracts of petroleum coke and pitch coke was column chromatography on silica gel with hexane as eluent.

Apart from the fortuitous result obtained for dibenzopyrrole, good recoveries were obtained for low molecular mass PAH expected in the above-mentioned cokes.

CHAPTER 3

RESOLUTION OF POLYCYCLIC AROMATIC HYDROCARBONS BY GAS CHROMATOGRAPHY

3.1 Introduction

Kirshen and Almasi⁶⁷ chromatographed sixteen PAH by GC-FID on packed megabore (0.53mm i.d.) and DB-5 coated narrowbore (0.25mm i.d.) and microbore (0.10mm i.d.) fused silica capillary columns. They obtained better resolution on their megabore column than on that recommended by the EPA in method 610 (see 1.5.1.2.1) with helium carrier gas. The narrowbore and microbore columns gave similar resolution to the megabore. On-column injection for the narrowbore and 1:150 split injection was used for the microbore column. Hydrogen was used as carrier gas for the two columns.

Narrowbore and microbore columns coated with 0.1 micron DB-5 were selected for this investigation.

The carrier gases selected for study were nitrogen and helium. Hydrogen was not selected for reasons of safety. Fluoranthene was selected to obtain Van Deemter plots because of its intermediate position in chromatograms and its good response.

The optimum practical gas velocity (OPGV) ensures maximum efficiency per unit time.⁵⁴⁾

The Van Deemter plots were used to obtain OPGV which is defined as the point on the Van Deemter curve where HETP versus the linear carrier gas velocity becomes linear⁵⁴⁾. Experimentally determined OPGV's and corresponding HETP's were used as a basis for comparing the best columns and carrier gas combinations for subsequent work.

The optimum splitless injection time was determined by comparing the peak area of the high molecular mass PAH 3,4-benzopyrene against that of the lower molecular mass phenanthrene. The splitless injection time selected was the one which produced the largest peak area ratio without causing undue overlaps among the peaks eluted ahead of phenanthrene.

Because capillary columns can be easily overloaded, various split ratios were investigated. A minimum injector temperature of 275°C was recommended by Stenberg et. al.⁵⁵⁾ Other workers^{1,11,12)} used 275°C for both the injector and detector. It was therefore thought advisable to study the effect of injector and detector temperatures in conjunction with split ratios.

3.1.1 Experimental

3.1.1.1 Equipment

Two 10cm³ glass volumetric flasks were used which were previously

washed in hot water to remove detergent residues and rinsed with deionised water and acetone and finally dried in an oven at 110°C.

A 10ul "Hamilton" syringe (catalogue no 701) was used to inject aliquots into the GC.

The 2cm³ glass vials described in 2.1.2.1 were used to store PAH solutions.

The GC with FID and computer with DAPA software described in 2.1.2.1 was used.

The capillary columns had 20m x 0.1mm i.d. and 30m x 0.25mm i.d. Both were coated with 0.1um DB-5("J & W Scientific"). Graphite ferrules were used to join the ends of the columns to the injector and detector assembly.

3.1.1.2 Reagents

The PAH standards used were the same as detailed in 2.2.2.2.

3.1.1.3 Procedure

3.1.1.3.1 Determination of the optimum practical gas velocity

About 0.2g of fluoranthene was dissolved in 10ml of toluene in a volumetric flask. Toluene was used because the solubility of

fluoranthene in toluene is high enough for split injections.

GC oven temperature was maintained at 200°C. The injector and detector temperatures were both held at 250°C.

The detector gas flows were 30cm³min⁻¹ for hydrogen and 300cm³min⁻¹ for synthetic air and fed via stainless steel tubing through molecular sieves into the instrument.

The gas chromatograph's attenuation and range were set at 1.0 and 10⁻¹¹ respectively. The computer software attenuation was set at 1.0.

The 30m x 0,25mm i.d. column (narrowbore) was installed with new graphite ferrules placed over the column ends. The ends of the column which came in contact with the ferrules were cut off to prevent contact between eluting gaseous solutes and graphite. Helium was used first as the carrier gas at a head pressure of 275,9kPa (40 p.s.i.). For each run 2ul aliquots of the fluoranthene solution in toluene were injected onto the column by the split technique using a split ratio of 100:1. Helium and nitrogen were used as carrier and make-up gases. The make-up flowrate was maintained constant at 30cm³min⁻¹. The head pressures used were 206,9kPa (30 p.s.i.) and another 2ul aliquot was injected onto the column. It was further reduced to 137,9kPa (20 p.s.i.), 69,0kPa (10 p.s.i.) and 34,5kPa (5 p.s.i.) and each time a 2ul aliquot of the solution was injected.

The series of experiments was repeated with a microbore column of 20m x 0,1mm i.d. using new graphite ferrules.

For each solvent and solute peak, the retention times were measured. Adjusted retention times t^* , where t =time elapsed from injection to the recording of peak maximum and t^1 =time elapsed from injection to a peak obtained for an unretained component, i.e. the solvent in this case.

The widths, $W^{1/2}$, of peaks at half height were measured for each solute.

From the values of t^* and $W^{1/2}$ the number of theoretical plates (N) were calculated using equation 3.1.1.

$$N = 5.54 \left(\frac{t^*}{W^{1/2}} \right)^2 \dots\dots\dots \text{equation 3.1.1}$$

HETP was calculated as the reciprocal of N.

3.1.1.3.2 Development of the temperature program

The ten PAH compounds available at the time, ie fluorene, phenanthrene, anthracene, fluoranthene, pyrene, 2,3-benzofluorene, 1,2-benzophenanthrene, 2,3-benzanthracene, 1,2-benzopyrene and 3,4-benzopyrene were dissolved in toluene to give a concentration of about $100\mu\text{gcm}^{-3}$ for each compound.

With the carrier gas head pressure set at the OPGV for each column and carrier gas, a 2 μ l volume of the standard PAH solution was injected at a split ratio of 100:1.

PAH were found to elute between 200°C and 300°C for both columns, but using the microbore column at a split ratio of 100:1 the carrier gas flow stopped at about 300°C. Column flow was re-established only by increasing the split ratio to almost 1000:1. As a consequence the use of the microbore column had to be abandoned. The narrowbore column was used for the rest of this investigation. A temperature program was developed for this column that would elute the PAH to give the best resolution of the compound in the shortest time.

The column temperature was set at 70°C at injection to aid the distillation of hexane. The column temperature was ramped at in two stages; viz. 70°C to 100°C and 100°C to 200°C with the switching valve open after 15 seconds. The heating rates investigated were 2, 3, 5, 10 and 20°C min⁻¹. The resolution was calculated using equation 3.1.2.

$$R = 1/2 \left(\frac{t'r_2 - t'r_1}{W^{1/2}_1 + W^{1/2}_2} \right) \quad \text{..... equation 3.1.2}$$

Where R = resolution, t'r₂ and t'r₁ are the adjusted retention times of the second and first eluting peaks and W^{1/2}₁ and W^{1/2}₂ respective widths at half height. Resolutions were compared for phenanthrene/anthracene and 1,2-benzopyrene/3,4-benzopyrene.

3.1.1.3.3 Injection technique

A 2ul aliquot containing the ten PAH compounds was injected onto the narrowbore column using both the split and splitless techniques. Various split ratios were used for the split technique.

The optimum splitless injection time, was determined by injecting a solution of phenanthrene and 3,4-benzopyrene at different injection times and calculating the resolution.

The switching value was subsequently set to 20, 30, 60, 90, 120, 180 and 240 seconds and each time a 2ul volume was injected and the peak areas of the two peaks obtained were compared.

3.1.1.3.4 Split ratio

The injector and detector temperatures were set at 320°C and 250°C respectively. A 2ul volume of the PAH mixture was injected splitless for 60 seconds. For each subsequent injection, the split ratio was altered to give 50:1, 100:1, 200:1 and 350:1 after the splitter switching value had opened.

The peak areas of pyrene were used to normalize the areas of the other peaks because it eluted halfway in the chromatogram. In this way the effect of the split ratio on the response could be monitored.

3.1.1.3.5 Detector and injector temperatures

With the injector temperature set at 275°C, a 2ul splitless injection of the PAH solution was made at detector temperatures of 250°C, 275°C, 300°C and 350°C (maximum).

The detector was then held at 250°C and the injector temperature was set to 275°C, 300°C and 320°C (maximum for septum).

3.1.2 Results and discussion

The Van Deemter plots obtained using nitrogen and helium as carrier gases for the narrowbore and microbore columns are displayed in figures 3.1.1 and 3.1.2 respectively.

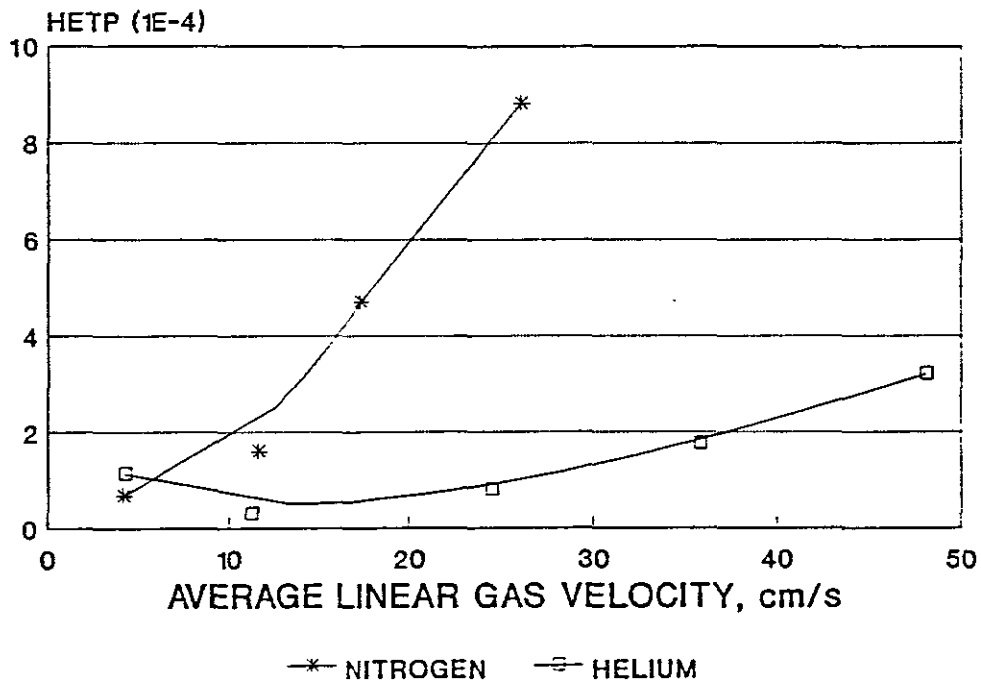


FIGURE 3.1.1 VAN DEEMTER PLOT FOR THE NARROWBORE CAPILLARY COLUMN

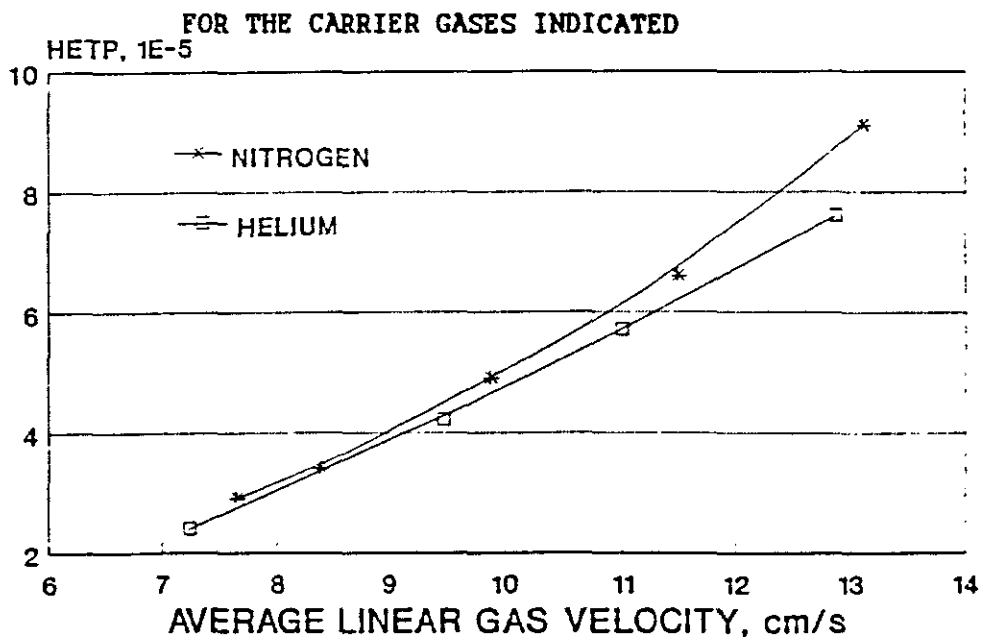


FIGURE 3.1.2 VAN DEEMTER PLOT OBTAINED FOR THE MICROBORE CAPILLARY COLUMN FOR THE CARRIER GASES INDICATED

On the microbore column, (figure 3.1.2) the carrier gas stopped flowing below 8 cm s^{-1} . When the high molecular weight PAH hexabenzobenzene and 3,4;8,9-dibenzopyrene were include for identification purposes, (see 3.2.2.2) this microbore column could not be used because at high temperatures (300°C) the carrier gas flow stopped.

Helium was selected as the carrier gas for further study because the value of HETP (fig. 3.1.1), remained lower than for nitrogen and was less affected by changes in the carrier gas flow rate during a single run. The helium carrier gas head pressure was set at 137,9kPa (20 p.s.i.) to obtain OPGV (38 cm s^{-1}).

The resolution for the pairs phenanthrene-anthracene and 1,2-benzopyrene 3,4-benzopyrene as a function of heating rate is shown in figure 3.1.3.

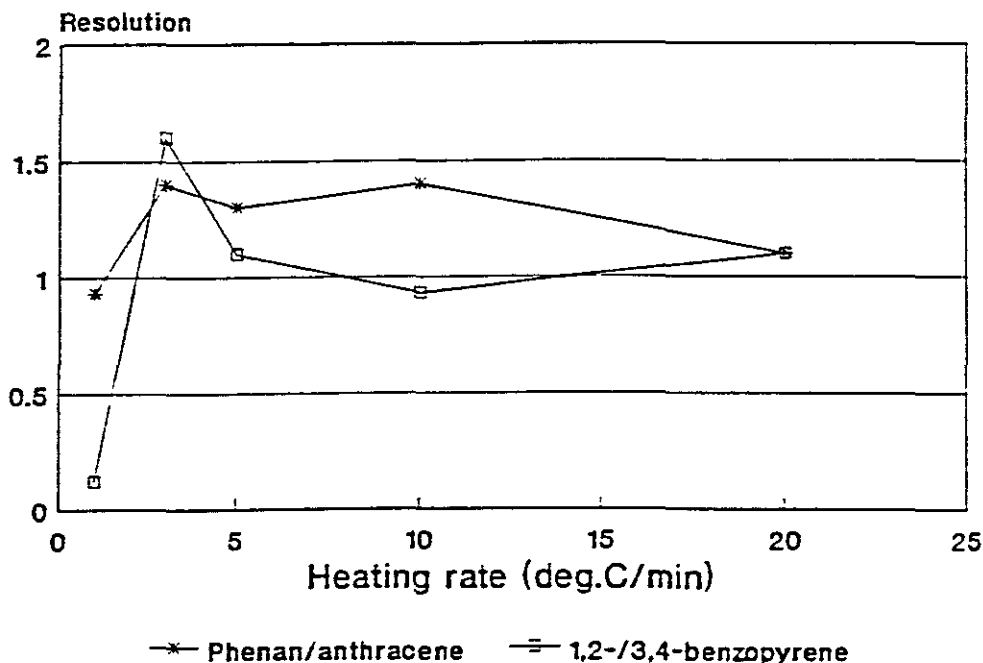


FIGURE 3.1.3 RESOLUTION AS A FUNCTION OF HEATING RATE FOR THE
PAIRS OF COMPOUNDS INDICATED COLUMN = $30\text{ m} \times 0.25\text{ mm}$.
DB-5 COATED CARRIER GAS = HELIUM FLOWRATE = 38 cm s^{-1}

As indicated in figure 3.1.3 the heating rate does affect the resolution. An increase in the heating rate resulted in a steep increase in resolution from near zero to $2^{\circ}\text{C min}^{-1}$ to above 1.5 at $3^{\circ}\text{C min}^{-1}$. At heating rates above $3^{\circ}\text{C min}^{-1}$, the resolution shows a shallow minimum at $10^{\circ}\text{C min}^{-1}$. A similar but less pronounced trend is shown by the phenanthrene and anthracene pair.

The peak area ratio of 3,4-benzopyrene to phenanthrene at the various splitless injection times are illustrated in figure 3.1.4. The splitless injection of 60 seconds duration was considered. It provided the optimal because lower duration gave smaller 3,4-benzopyrene/phenanthrene. Larger durations caused crowding of peaks eluting ahead of phenanthrene.

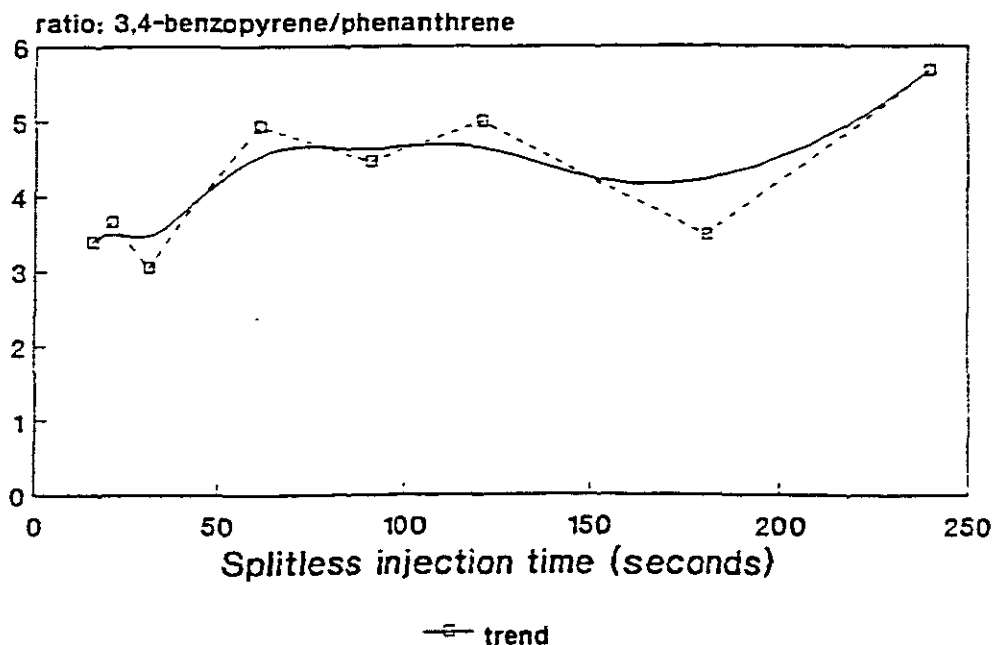


FIGURE 3.1.4 A COMPARISON OF THE 3,4-BENZOPYRENE TO PHENANTHRENE PEAK AREA RATIO FOR DIFFERENT SPLITTER SWITCHING VALUE OPENING TIMES

To obtain maximum response, the injector temperature had to be set to 320°C. The detector temperature was found not to play a significant role and was held arbitrarily 250°C.

The split ratio did not affect the response, but was held at 100:1 to maintain carrier gas flow at the higher column temperatures.

The temperature was held at 300°C for 15 minutes. The column manufacturer (J & W Scientific) warned that increasing the temperature further could have detrimental effects on column life.

3.1.3 Conclusion

The concentration of the PAH in the particulate matter and especially the cokes was expected to be low. The need for splitless injection and high column temperatures excluded the microbore column for use. The microbore column was found not to be compatible with trace analysis.

Optimum conditions for the resolution of PAH were found to be as follows:

Column: 30m x 0.25mm i.d. narrowbore capillary column.

Carrier gas: Helium at a head pressure of 137.9kPa (20 p.s.i.).

The injector and detector temperatures were held at 320°C and 250°C respectively. The injection was splitless for 60 seconds until column flow was stabilised using a split ratio of 100:1.

Heating programme:

- Ramp: (i) 70°C at injection to 100°C at 20°C min⁻¹.
(ii) Hold at 100°C for 30 seconds.
(iii) Ramp 100°C to 200°C at 20°C min⁻¹.
(iv) Hold for 30 seconds at 200°C.
(v) Ramp 100°C to 300°C at 3°C min⁻¹ to elute the PAH.

The fact that helium carrier gas stopped flowing at a temperature approaching 300°C precluded the use of the microbore column. This column was recommended by the manufacturers of the GC for the resolution of PAH, but then hydrogen had to be used as the carrier gas.

To minimize gas leaks through the stainless steel pipe connections from the gas store to the gas chromatograph, the carrier gas cylinder had to be positioned next to the instrument. Because of the risk of explosions, this precluded the use of hydrogen.

CHAPTER 4

IDENTIFICATION OF POLYCYCLIC AROMATIC HYDROCARBONS

4.1 Introduction

The PAH mixtures which result from combustion or high temperature reactions in processes such as coke plants, iron and steel foundries, aluminium smelters, gas works and oil refineries are very complex.⁵⁾

Characterization of a complex mixture of PAH requires a high resolving power and high sensitivity.

The methods available for the identification of PAH have been summarised in chapter 1.5.2. For this work, it was decided to investigate of these, the following:

- (i) A GC/MS method and (ii) a TLC method for identifying PAH in a sample of pitch.
- (iii) Apply the GC-FID retention index method of Lee et. al.²¹⁾

The most powerful identification tool is considered to be GC/MS with a high resolution capillary column.^{13, 34)} Since this was not available in the laboratory where the present work was performed, a sample was submitted to an outside laboratory.

They used a non-polar OV-101 capillary column interfaced with an electron-impact ion source and a mass spectrometer as a detector (MSD).

Other methods of identification included TLC using silica gel plates and GC retention indices (RI) on a 30m x 0.25mm i.d. DB-5 capillary column. The TLC method was based upon that of Lederer and Lederer,⁷⁴ described in more detail in chapter 1.5.2.

Lee et. al.⁸¹ used picene (2,3-naphthophenanthrene) to represent the RI of 500,00. This compound was not available for this work and was substituted by 1,2;6,7-dibenzanthracene. To cover the full range of higher molecular mass PAH, 3,4;8,0-dibenzopyrene was used as additional reference. To this was assigned a RI of 600,00.

4.2 Experimental

4.2.1 Equipment

A glass developing tank (Merck, twin trough chamber, catalogue no 25258, 20cm x 22cm x 5cm) with a metal lid was used to develop TLC chromatograms on silica gel plates (Merck, catalogue no 5724, 5cm x 20cm, precoated without fluorescence indicator). A hairdryer (1000W power) was used to dry the plates after removal from the tank.

The equipment and reagents used in preceeding chapters were also used here.

4.2.2 Reagents

Premixed PAH compounds in 1:1 methanol-methylenechloride were obtained from "Supelco Inc." through "Anatech Instruments (Pty) Ltd., Durban, Natal, catalogue no 610-M(4-8743). This reagent contained the following: naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, 1,2-benzanthracene, 1,2--benzophenanthrene, 3,4- benzofluoranthene, 2,3-benzofluoranthene, 3,4-benzopyrene, 2,3-indenopyrene, 1,2;6,7-dibenzanthracene and 4,5;5,6;9,10-tribenzanthracene.

4.2.3 Procedure

4.2.3.1 Identification by gas chromatography coupled to a mass-spectrometer

A sample of pitch was ultrasonically extracted in cyclohexane for 30 minutes, and filtered to remove insoluble residue. The pitch extract was run through anhydrous sodium sulphate to remove moisture. A solution of the ten PAH standards, shown in table 4.1 was made up in cyclohexane as well. Both solutions were transferred to 2 x 2cm³ volume glass vials and sealed with septum caps. They were submitted to "The Department of National Health and Population Development, Health Chemical Laboratory, 110 Joubert Street, Braamfontein, Johannesburg" for a GC/MS analysis.

The following instrument conditions were used:

i. Column

The length of the column was 12.5 metres and was coated with a cross-linked silicone film of 0.33 micron thickness. It was a Wall Coated Open Tubular (WCOT) column and the stationary phase was equivalent to a non-polar OV-101. Helium was used as the carrier gas at $50\text{cm}^3\text{min}^{-1}$.

ii. Method of injection

The splitless injection technique was used for 1 minute, after which the septum was purged with helium at the rate of $50\text{cm}^3\text{min}^{-1}$.

iii. Temperature program

Upon injection the column was at 100 degrees centigrade which was held for one minute. It was increased at a rate of 10 degrees per minute to 300 degrees centigrade.

iv. Detector mass range

The PAH with the highest molecular weights were 1,2- and 3,4-benzopyrene of 252.32. To accommodate this, the detector was set on an atomic mass unit (amu) range of 20 to 600. This detector had an accuracy of 0.9 amu. The instrument scanned through 20 to 600 amu, each scan equivalent to 644 digital values. The instrument was therefore set on 1.7 scans per second.

4.2.3.2 Thin-layer chromatography

A solution containing about 200 mg of each of the solid PAH compounds available was made up in benzene to give a concentration of about 400ug cm⁻³ total PAH.

A spot of this solution was applied using a 10ul syringe to a thin-layer silica gel plate 0,5cm from the bottom and 0,5cm from the side. After drying under a hairdryer, the plate was placed into a glass developing tank containing 50cm³ of a mobile phase and covered with a metal lid.

The first mobile phase used was one containing 0,05% by volume of N,N-dimethylformamide (DMF) in hexane.

The resulting solvent strength was calculated using equation 4.1.

$$\begin{array}{l} (x/100 \times E^\circ) + (100/y \times E^\circ) = \text{resultant } E^\circ \dots \text{equation 4.1.} \\ \text{minor component} \quad \text{major component} \\ \text{i.e. DMF} \quad \quad \quad \text{i.e. hexane} \end{array}$$

Where x and y represents the volume (cm³) per 100cm³ of mixture of DMF and hexane respectively. E° represents the solvent strength of individual DMF and hexane. Literature values of E° for these two substances were obtained from Yost et. al.³⁰.

After the solvent front had moved about 15cm, the plate was removed from the tank and dried with a hairdryer. The separated compounds were viewed under shortwave UV light in a darkroom. The Rf values and colours of the spots were noted.

This procedure was repeated using 0.10%, 1.00%, 2.00% and 5.00% (V/V) DMF in hexane. Results are presented in table 4.3.

About 4mg of ground pitch and 2g of ground petroleum coke and pitch coke were ultrasonically extracted into hexane for 30 minutes. The hexane was evaporated off under nitrogen gas to dryness. A volume of 1ul fresh hexane was added and a spot of this was applied to a new silica gel plate continuing as above.

4.2.3.3 Retention index

The methanol-methylene chloride containing the premixed PAH was evaporated off under gaseous nitrogen to dryness. The residue was taken up in 1cm³ of hexane to make the solution compatible with the samples.

The retention times of naphthalene, phenanthrene, 1,2-benzophenanthrene and 1,2;6,7-dibenzanthracene were noted and were given the RI of 200.00, 300.00, 400.00 and 500.00 respectively for calculating those of the other peaks using equation 4.2.

Lee et. al.,²¹ used a SE-52 capillary column to determine the retention indices of 209 PAH and related compounds relative to the retention of four PAH compounds (see 1.5.2.2.1).

The following equation, described by Lee et. al.,²¹ was used to calculate R.I. of an unknown PAH.

$$R.I. = 100 \times \frac{(\text{tr of unknown}) - (\text{tr of CZ})}{(\text{tr of CZ} + 1) - (\text{tr of CZ})} + 100\% \text{ equation 4.2}$$

Where:

- (i) (tr of CZ) is the retention time in minutes of the PAH standard which elutes before the peak that is to be identified.
- (ii) (tr of CZ + 1) is the retention time in minutes of the PAH standard which elutes after that peak that is to be identified.
- (iii) Z is the number of aromatic rings in the PAH standard that elutes before the peak of interest.

A 5ul aliquot of the PAH solution made up from solid compounds was injected to obtain the retention time 3,4:8,9-dibenzopyrene which was assigned the RI of 600.00.

4.3 Results and discussion

The chromatogram of the ten PAH compounds obtained on the OV-101 capillary column by GC/MS is displayed in figure 4.1. Once the retention times of each peak were noted, the intensity of the molecular fractions were compared to those resident in the computer's library. The molecular ion peak was the most abundant in each case, but the smaller fractions assisted in identifying the compound. The spectra were generally very similar.

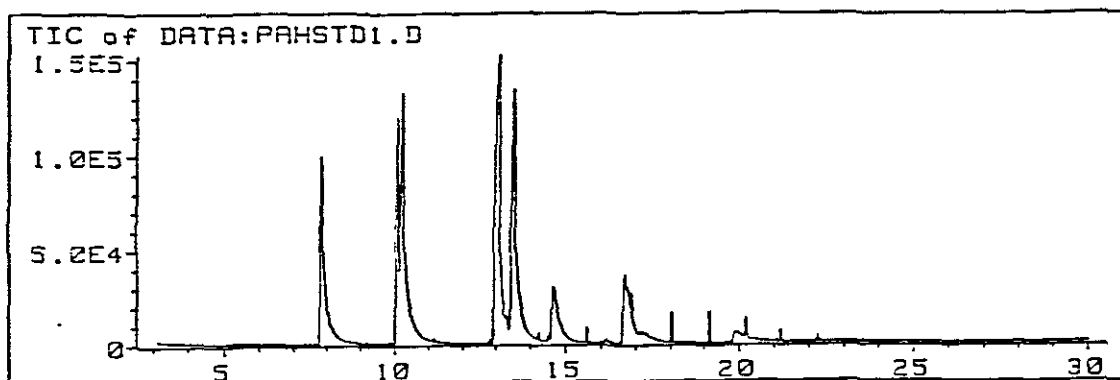


FIGURE 4.1 GAS CHROMATOGRAM OBTAINED OF THE PAH STANDARD SOLUTION CONTAINING TEN COMPOUNDS USING AN OV-101 CAPILLARY COLUMN

Table 4.1 displays the retention time of each compound in the standard solution. This was a new file created and saved into the computer under the file name "PAH".

TABLE 4.1 RETENTION TIMES OF THE TEN PAH STANDARDS CHROMATOGRAPHED ON THE OV-101 COLUMN OF WHICH THIRTEEN COMPOUNDS WERE IDENTIFIED BY THE MSD. THIS FILE WAS CALLED "PAH" AND IS REFERRED TO IN THE TEXT

LIBRARY NUMBER	COMPOUND NAME	RETENTION TIME (MINS.)
1	Fluorene	7.861
2	Phenanthrene	10.099
3	Phenanthrene isomer (anthracene)	10.251
4	Fluoranthene	13.054
5	Fluoranthene isomer	13.113
6	Pyrene	13.556
7	1-methylpyrene	14.528
8	2,3-benzofluorene	14.660
9	1,2-benzofluorene	14.709
10	1,2-benzonaphthol-1,2-thiophen	16.153
11	1,2-benzophenanthrene	16.682
12	3,4-benzofluoranthene	19.955
13	3,4-benzopyrene	20.145

The computer allocated sample peaks to compounds if match qualities were within 99,00%.

Peaks on the chromatograms could be identified further on the basis of mass spectra stored in the computer's own library under "priority pollutants".

Phenanthrene and anthracene, with retention times 10,099 minutes and 10,251 minutes respectively were not resolved well on the column. The mass spectra of these two PAH were practically indistinguishable (figure 4.2).

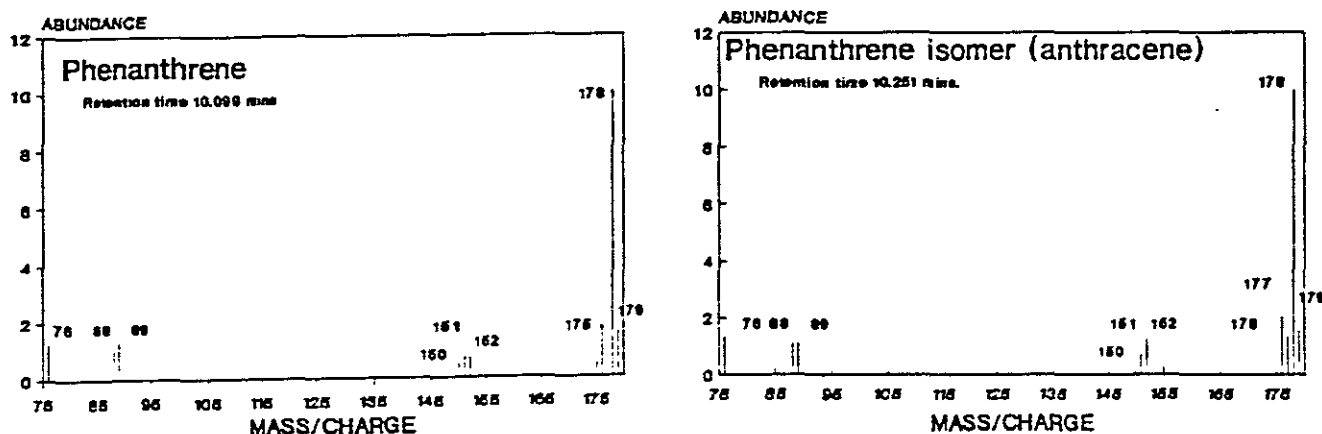


FIGURE 4.2 THE MASS SPECTRA OBTAINED FOR PHENANTHRENE AND ANTHRACENE

Mass spectra of fluoranthene and pyrene (figure 4.3) were also indistinguishable. Identification was only possible by retention time.

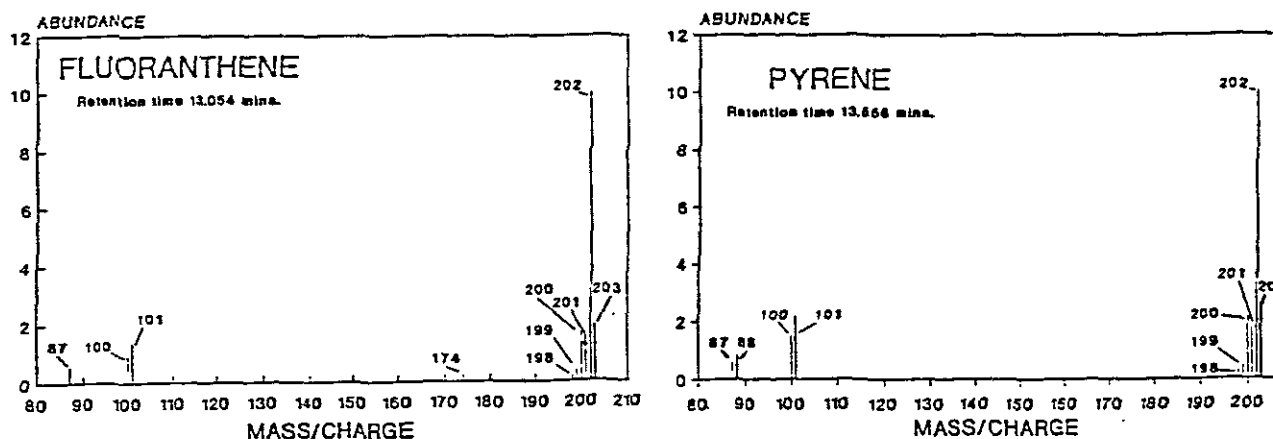


FIGURE 4.3 MASS SPECTRA FOR FLUORANTHENE AND PYRENE

The compounds 1,2-benzophenanthrene and 2,3-benzanthracene were not resolved on the OV-101 column and their mass spectra were also similar.

The gas chromatogram of the pitch extract is displayed in figure 4.4 this chromatogram resembled that of long-chain alkyl benzene sulphonates. Their presence was confirmed by MSD.

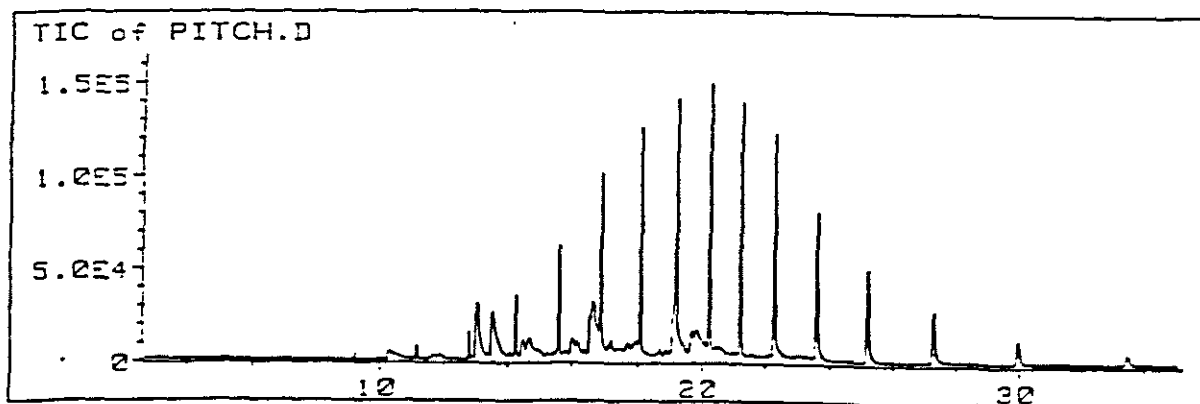


FIGURE 4.4 GAS CHROMATOGRAM OBTAINED ON THE OV-101 CAPILLARY COLUMN OF PITCH EXTRACT

Peaks identified by retention time were manually selected and the mass spectra were compared to those stored in the computer's database.

In some cases, the match of mass spectra between unknowns and standards were very close. The PAH identified in the pitch sample this way, are given in table 4.2.

TABLE 4.2 THE PAH IDENTIFIED IN PITCH USING MATCH
QUALITY AND RETENTION TIMES

RETENTION TIME OF PEAK	PERCENT MATCH QUALITY	COMPOUND	RETENTION TIME OF THIS COMPOUND IN STANDARD
10,272	99,07	Anthracene	10,251
13,023	99,50	Fluoranthene	13,054
13,518	99,68	Pyrene	13,556

Poor match of 1-methylpyrene and 1,2-benzofluorene with the standards rendered their presence in pitch uncertain, though their presence was indicated by their retention times.

3,4-Benzopyrene could not be resolved at all from one of the sulphonic acid peaks at all. The fact that the mass spectrum of 3,4-benzopyrene was indistinguishable from that of 3,4-benzofluoranthene and 2,3-benzofluoranthene complicated matters further.

The compounds 1,2-benzopyrene and 3,4-benzopyrene were not resolved on the column and could not be identified by retention time or by their mass spectra.

The results by TLC on silica gel plates using DMF-hexane mixtures as the mobile phase are summarized in table 4.3.

**TABLE 4.3 A COMPARISON BETWEEN DIFFERING DMF-HEXANE MIXTURES
FOR RESOLVING PAH ON SILICA GEL TLC PLATES**

Mobile phase	Resulting solvent strength *	Separation notes
Hexane	0.0100	Low Rf values, poor separation More polar compounds did not migrate from origin. Run time was 30 mins.
0.05% DMF in hexane	0.0104	Larger Rf values and improved separation. Some compounds remained at origin. No change in run time.
0.10% DMF in hexane	0.0107	
1.00% DMF in hexane	0.0172	
2.00% DMF in hexane	0.0244	Much improved separation. The more polar compounds separated. No change in run time.
5.00% DMF in hexane	0.0460	Maximum resolution achieved. All compounds separated well. No change in run time. Mobile phase too viscous for chromatography.

* calculated using equation 4.1

Based on these results a mobile phase of 2 percent by volume of DMF in hexane was selected for the determination of Rf values for the PAH. These are shown in table 4.4.

TABLE 4.4 RF VALUES AND FLUORESCENT COLOUR UNDER SHORT WAVE UV, 254NM, OF PAH AFTER THIN-LAYER CHROMATOGRAPHY WITH 2% V/V DMF IN HEXANE

COMPOUND	Rf	COLOUR
Dibenzopyrrole	0,02	Pale blue
3,4;8,9-dibenzopyrene	0,26	Pale green
4,5;9,10-dibenzanthracene	0,31	Bright blue
Hexabenzobenzene	0,34	Pale purple
1,2-Benzophenanthrene	0,35	Bright blue
3,4-Benzofluoranthene	0,35	Bright blue
1,2-Benzopyrene	0,35	Blue
3,4-Benzopyrene	0,38	Yellow/green
1,2-Benzofluorene	0,38	Pale purple
9,10-Benzophenanthrene	0,40	Bright blue
2,3-Benzanthracene	0,42	Pale green
2-methylphenanthrene	0,47	Pale blue
1-Methylphenanthrene	0,48	Pale blue
Pyrene	0,55	Bright green
Fluoranthene	0,58	Pale blue
Phenanthrene	0,66	Pale blue
Anthracene	0,67	Bright blue
Fluorene	0,72	Turquoise
Naphthalene	-	Not visible

The Rf values and the colour of the compound under shortwave UV light of each PAH shown in table 4.4 were used to identify PAH in hexane extracts of pitch and coke. These results are indicated in table 4.5.

TABLE 4.5 IDENTIFICATION OF PAH IN DIFFERENT SAMPLE TYPES BY THIN-LAYER CHROMATOGRAPHY AFTER ULTRASONIC EXTRACTION INTO HEXANE

Rf found in:					
(a) Pitch	(b) Petroleum	Colour, UV light, 254nm	Suspected PAH	Rf expected	
0,22		feint green	unknown	-	
0,27		feint blue	unknown	-	
0,38		yellow/green	3,4-benzo- pyrene	0,38	
	0,42	pale blue	9,10- or 1,2-benzo- phenanthrene	0,40	
0,44		bright blue	"	0,40-0,35	
0,57	0,57	green	pyrene	0,55	
	0,67-0,79	pale blue	anthracene	0,67	
			phenanthrene	0,66	
			and/or fluo- ene	0,72	

The retention indices of all the PAH standards available were normalized (equation 4.2) to an RI=200,00 naphthalene, RI=300,00 phenanthrene RI=400,00 1,2-benzophenanthrene, RI=500,00 1,2;6,7-dibenzanthracene, and RI=600,00 3,4;8,9-dibenzopyrene. A plot of RI versus the RI's of Lee et. al.²¹ is shown in figure 4.5.

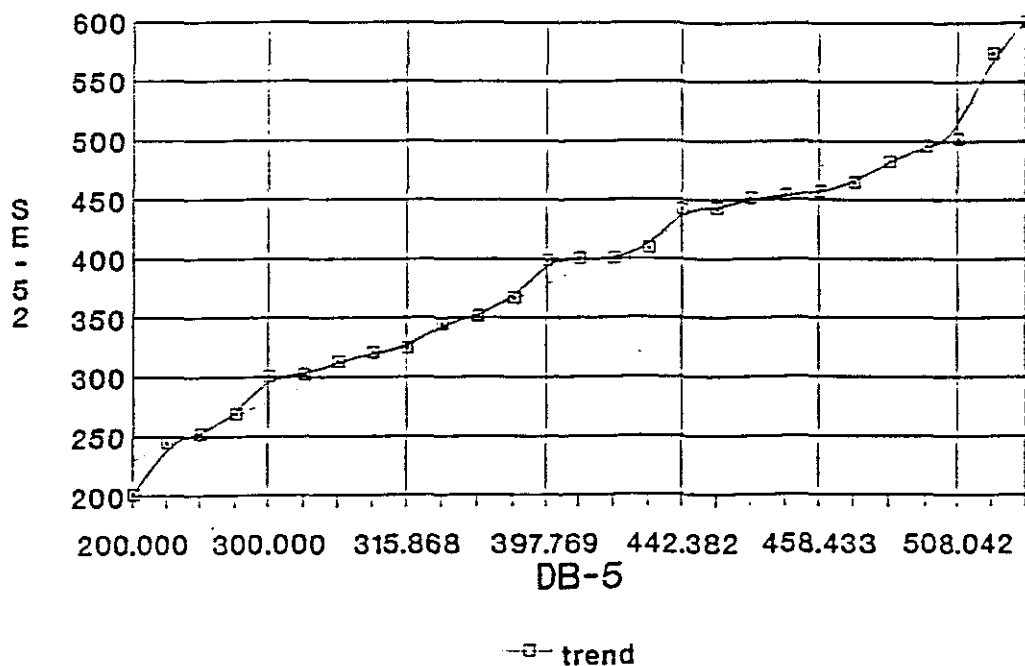


FIGURE 4.5 COMPARISON OF RETENTION INDICES ON DB-5 AND A SE-52 CAPILLARY COLUMN

Comparison of the two plots shows that the retention indices given by Lee et. al.,⁸¹ for their SE-52 capillary column could be used with confidence to identify PAH on the DB-5 capillary column used here.

This method proved to be very useful for identifying PAH and related compounds in hexane extracts of pitch, cokes and particulate matter. In some cases however, more than one compound fell within one standard deviation of the average retention index determined by Lee et. al.⁸¹. Other instrumental techniques such as those outlined in section 1.5.2.3 of this dissertation would be required to differentiate between these compounds, but these were not available for the present work.

The PAH compounds 9,10-benzophenanthrene and 1,2-benzophenanthrene were poorly resolved. Each had a RI of 400.00 on the SE-52 used by Lee et. al.²¹ On the DB-5 column, these two compounds were partially resolved with RI's of 399.34 and 400.00 respectively. The corresponding chromatograms are shown in figure 4.6.

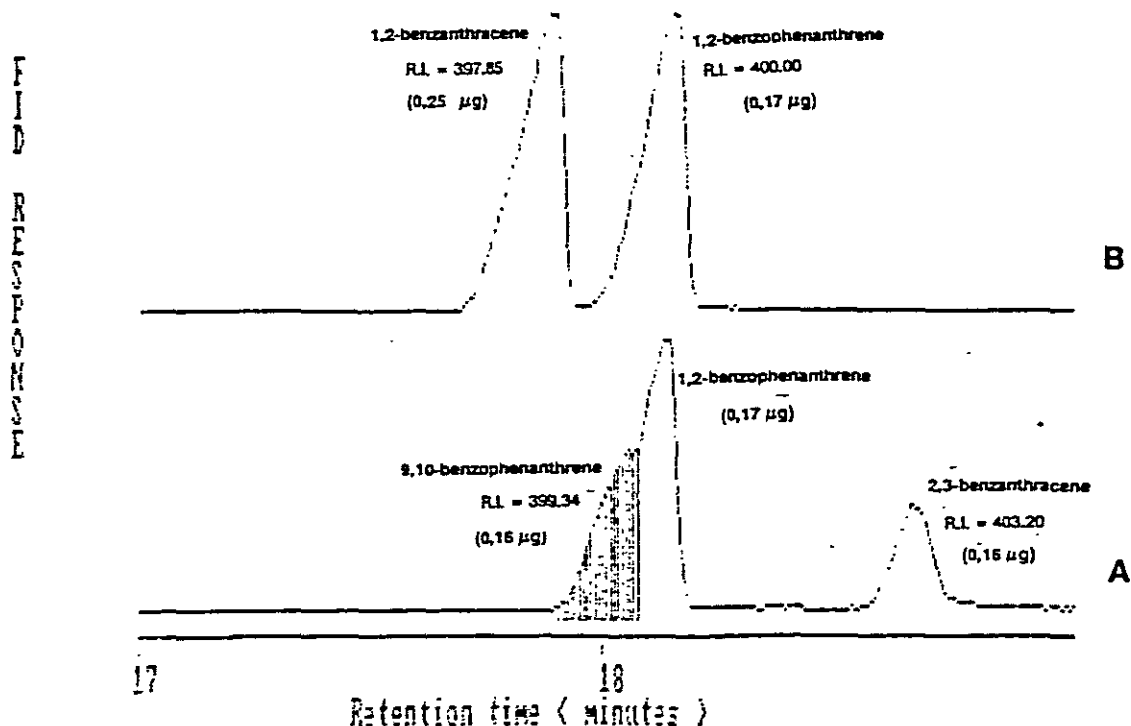


FIGURE 4.6 CHROMATOGRAMS TO DEMONSTRATE THE PARTIAL RESOLUTION OF 9,10-BENZOPHENANTHRENE AND 1,2-BENZOPHENANTHRENE ON A DB-5 COLUMN.

B= RESOLUTION OF 1,2-BENZANTHRACENE FROM 1,2-BENZOPHENANTHRENE WITH REFERENCE TO B: A= POOR RESOLUTION OF 9,10-BENZOPHENANTHRENE FROM 1,2-BENZOPHENANTHRENE

Similarly, the compounds 3,4-benzofluoranthene and 2,3-benzofluoranthene which had retention indices of 442.88 and 444.01 respectively on the

DB-5 column were almost baseline separated as shown in figure 4.7. On the SE-52 column the RI's were 441.71 and 442.56 respectively indicating poorer resolution.

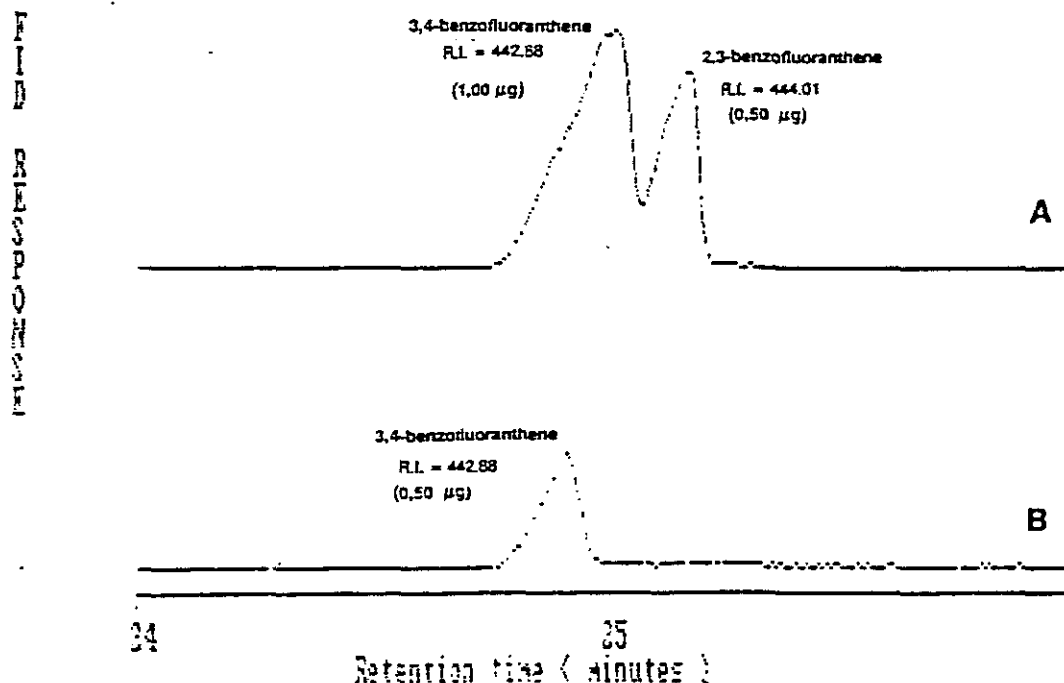


FIGURE 4.7 THE RESOLUTION OF 3,4-BENZOFLUORANTHENE FROM 2,3-BENZOFLUORANTHENE ON THE DB-5 COLUMN,
A = RESOLUTION OF 3,4-AND 2,3-BENZOFLUORANTHENE.
B = 3,4-BENZOFLUORANTHENE WITHOUT ISOMER

The high molecular mass compounds hexabenzobenzene and 3,4:8,9-dibenzopyrene which had DB-5 retention indices of 572.97 and 600.00 assigned respectively were not included in the work by Lee *et. al.*⁸¹

4.4 Conclusion

GC-MS on a non-polar OV-101 capillary column gave poor PAH resolution. The mass spectra were of little help because overlapping compounds gave virtually identical mass spectra.

Of the mobile phases investigated for TLC on silica gel, 2% DMF in hexane gave the best PAH separations, but crowding and the relatively large quantities required for detection did not make this method suitable for the analysis of environmental samples.

The DB-5 capillary column was shown to give excellent resolution of PAH. Published RI could be used with confidence to identify PAH up to RI of 500.00. Because of a lack of published data for PAH with RI > 500.00 circumvented positive identification of compounds such as hexabenzobenzene and 3,4:8,9-dibenzopyrene.

CHAPTER 5

QUANTIFICATION OF POLY-CYCLIC AROMATIC HYDROCARBONS BY GAS CHROMATOGRAPHY

5.1 Introduction

Bjorseth¹¹ injected 2ul of a particulate matter extract containing between 7 and 16ug of individual PAH into a GC with an FID. He obtained a coefficient of variation on nine parrallel determinations of less than 10% for each of the 15 PAH they investigated regardless of whether they were present as major or minor components.

Bagheri and Creaser¹² injected between 1 and 3 ul of untreated samples of white spirit, kerosene and petrol into a GC with a fluorescence detector. The coefficient of variation was 8.5% for the two-and three-ring aromatic hydrocarbons. Detection limits varied from one nanogram (ng) for fluorene to 100ng for the naphthalenes.

Because of the limited information then available it was decided to test the reproducibility of 2ul and 5ul injections on the 30m x 0.25mm i.d. capillary column.

1,3,5-triphenylbenzene was selected as IS for quantifying PAH (see 1.5.3.1). It was considered necessary to measure the response to PAH

relative to that for the IS before and after exposure to ultrasound was compared. This would indicate whether the IS should be added to the extract or the untreated sample.

Relative response factors (RRF) were calculated by the computer for each pure PAH standard from peak areas and mass of IS to the compounds. The coefficient of variation of nine consecutive RRF are reported.

The minimum detectable level (MDL) of propane has been determined using a FID at $10^{-12}\text{g(C)sec}^{-1}$ ⁵⁴. Such values are not available for PAH. The MDL was determined for each PAH by injecting a dilute solution of PAH in hexane. This solution was successively diluted until the peaks produced were twice the height of the peak-to-peak noise divided by half the width of half height of the peak. All measurements are in seconds (see 1.5.3.3).

5.2 Experimental

5.2.1 Equipment

The 2cm³ glass vials with septum caps described in 2.1.2.1 were used to store standard solutions previously prepared in 50cm³ glass volumetric flasks. All equipment reagents used in previous chapters were used here.

5.2.2 Reagents

1,3,5-triphenylbenzene (IS) was 92% pure and was recrystallized from cyclohexane before use.

5.2.3 Procedure

A solution of the ten PAH compounds used in chapter 2.1.2.1 was made up in hexane containing 60 to 70ug of each in a 50cm³ volumetric flask and 70ug of recrystallised IS.

2ul of this solution were injected successively four times using the splitless injection technique. This procedure was repeated using a 5ul injection volume. The GC conditions were those given in 2.1.2.3.3.

A 100ul volume of the PAH solution described above was transferred into a glass test-tube containing 5cm³ of hexane. It was placed into the ultrasonic bath and the power was switched on for 30 minutes. After 30 minutes, the hexane was distilled off under nitrogen gas to dryness. The residue was taken up in 100ul of fresh hexane and a 5ul volume of this solution was injected into the GC in duplicate.

A solution containing about 6ug cm⁻³ of the compounds which eluted up to and including pyrene, and about 20ug cm⁻³ of the higher molecular mass compounds was made up in hexane.

This solution was successively diluted with hexane and aliquots were injected into the GC until the peak produced by each compound was at the MDL (see 1.5.3.3). The MDL was determined for each PAH and expressed as grams of carbon per second (g(C)sec⁻¹).

5.3 Results and discussion

The coefficient of variation was calculated from the four sets of results obtained from the 2ul and 5ul injections. These are displayed in table 5.1.

TABLE 5.1 THE COEFFICIENT OF VARIATION BETWEEN THE 2UL AND 5UL INJECTION OF THE PAH MIXTURE

PAH	Conc.ug cm ⁻³	Coefficient of variation %	
		2ul injection	5ul injection
Fluorene	64	14.3	10.8
Phenanthrene	66	17.9	12.4
Anthracene	66	18.4	12.6
Fluoranthene	82	25.8	14.0
Pyrene	60	27.7	13.8
1,2-benzofluorene	72	35.8	14.5
1,2-benzophenanthrene	60	41.8	15.1
2,3-benzanthracene	82	66.5	20.3
1,2-benzopyrene	58	46.1	23.1
3,4-benzopyrene	58	58.5	22.7
I.S.	66	52.0	21.3

As expected, an increase in the injection volume from 2ul to 5ul decreased the coefficient of variation for each PAH as indicated above in table 5.1.

The effect of ultrasound on the IS relative to the PAH compounds is illustrated by comparing the peak area ratio of each PAH to that of the IS. The results are indicated in table 5.2.

TABLE 5.2 A COMPARISON BETWEEN THE PEAK AREA RATIOS OF EACH PAH AGAINST THE INTERNAL STANDARD BEFORE AND AFTER ULTRASONIC PRETREATMENT

PAH	Conc.ug cm ⁻³	Peak area Ratio of $\frac{\text{PAH}}{\text{IS}}$	
		No ultrasonic pretreatment	After 30 mins. ultrasound
Fluorene	64	2.69	4.26
Phenanthrene	66	2.74	7.34
Anthracene	66	2.70	8.15
Fluoranthene	82	3.51	9.99
Pyrene	60	2.05	5.74
1,2-benzofluorene	72	1.55	3.95
1,2-benzophenanthrene	60	1.35	2.83
1,2-benzanthracene	82	0.06	0.04
1,2-benzopyrene	58	0.78	0.92
3,4-benzopyrene	58	0.65	0.80
I. S.	66	1.00	1.00

The results in table 5.2 show that during ultrasonic pretreatment in an open vessel for 30 minutes the IS was lost more rapidly than PAH. The substantially higher ratios of the lower molecular mass PAH to those higher in molecular mass indicated that the former were presumably volatilised in preference to the latter. Consequently the IS had to be added to the sample extract after extraction.

The average RRF of fifteen PAH compounds were determined relative to 1,3,5-triphenylbenzene from nine Sul injections together with their coefficient of variation. These are displayed in table 5.3.

TABLE 5.3 THE RELATIVE RESPONSE FACTORS OF FIFTEEN PAH AND THE COEFFICIENT OF VARIATION CALCULATED FOR NINE SUCCESSIVE SUL INJECTIONS

PAH	RRF (AVERAGE OF 9)	COEFFICIENT OF VARIATION, %
Naphthalene	3.95	53.5
Fluorene	4.39	35.3
Phenanthrene	3.82	54.2
Anthracene	4.74	34.0
Dibenzopyrrole	3.95	52.4
2-methylphenanthrene	2.74	51.4
1-methylphenanthrene	3.53	50.5
Fluoranthene	3.30	44.3
Pyrene	3.03	42.9
1,2-benzofluorene	2.18	36.9
3,4-benzofluoranthene	1.04	2.6
1,2-benzopyrene	1.90	4.7
3,4-benzopyrene	1.88	5.2
4,5;9,10-dibenzanthracene	1.14	10.5
Hexabenzobenzene	1.65	33.8

The IS eluted near 4,5;9,10-dibenzanthracene and the pair 1,2 benzo-pynene and 3,4-benzopynene, hence their low coefficient of variation.

The MDL expressed in g(C)/sec are shown in table 5.4. The relatively low solubilities of 2,3-benzanthracene and 3,4;8,0-dibenzopyrene in hexane are reflected in their MDL's.

TABLE 5.4 THE MINIMUM DETECTABLE LEVEL FOR PAH BY PROPOSED METHOD (See text).

PAH	ng	g(C)s ⁻¹
Naphthalene	2,13	5 x 10 ⁻¹⁰
Fluorene	3,27	5 x 10 ⁻¹⁰
Phenanthrene	2,17	5 x 10 ⁻¹⁰
Anthracene	2,04	6 x 10 ⁻¹⁰
Dibenzopyrrole	3,00	3 x 10 ⁻⁹
2-Methylphenanthrene	2,16	3 x 10 ⁻¹⁰
1-methylphenanthrene	2,33	4 x 10 ⁻¹⁰
Fluoranthene	2,27	3 x 10 ⁻¹⁰
Pyrene	2,71	3 x 10 ⁻¹⁰
1,2-benzofluorene	3,57	4 x 10 ⁻¹⁰
9,10-benzophenanthrene/		
1,2-benzphenanthrene	6,67	7 x 10 ⁻¹⁰
2,3-benzanthracene	31,70	5 x 10 ⁻⁹
3,4-benzofluoranthene	4,81	1 x 10 ⁻⁹
1,2-benzopyrene	8,33	1 x 10 ⁻⁹
3,4-benzopyrene	8,92	2 x 10 ⁻¹⁰
4,5;9,10-dibenzanthracene	9,89	2 x 10 ⁻⁹
1,3,5-triphenylbenzene	4,09	1 x 10 ⁻¹⁰
Hexabenzobenzene	13,10	1 x 10 ⁻⁹
3,4;8,9-dibenzopyrene	552,00	4 x 10 ⁻⁹

5.4 Conclusion

The compound 1,3,5-triphenylbenzene was selected as the IS for quantifying PAH in pitch, coke and particulate matter samples. A lower response for this compound was obtained after ultrasonic extraction. It was therefore added to the sample after extraction.

A 5ul injection volume was found to give an acceptable coefficient of variation. The poorer reproducibility with less than 5 ul were not considered acceptable.

The MDL decreased with increasing molecular weight with the exception of 2,3-benzanthracene.

CHAPTER 6

APPLICATION OF THE METHOD

6.1 Introduction

Bjorseth et.al.,¹² and Anderson et.al.,⁶⁷ took both stationary and personal air samples (see 1.6) in metallurgical process plants to determine the amount of PAH liberated to test their analytical technique.

Tables 6.1 reproduces some of their results which may be regarded as more or less typical.

Under otherwise comparable conditions, Anderson et. al.,⁶⁸ recovered totals of 95ug, 5ug and 3ug of PAH from particulate matter taken with a personal sampling pump in a coke plant, a paste electrode reduction plant, and a creosote plant respectively.

TABLE 6.1 TYPICAL RESULTS OBTAINED BY BJORSETH ET. AL.,¹²⁾

PAH	ANODE MATERIALS	
	UNGRAPHITIZED PASTE ELECTORDE (GC-FID)	GRAPHITE ELECTRODES (HPLC)
	ug	ug
Dibenzothiophene	2.05	-
Phenanthrene	33.21	-
Anthracene	6.97	-
Dibenzopyrrole	9.84	-
Methylphenanthrene}		
Methylanthracene }	4.92	-
Fluoranthene	122.59	1.95
Pyrene	101.68	1.30
1,2-benzofluorene	37.31	-
2,3-benzofluorene	23.37	-
1-methylpyrene	12.30	-
1,2-benzophenanthrene	32.39	-
1,2-benzanthracene	61.50	1.30
3,4-benzophenanthrene}		
9,10-benzophenanthrene}	123.41	1.45
3,4-benzofluoranthene}		
2,3-benzofluoranthene}	110.29	1.40
1,2-benzopyrene	50.02	0.45
3,4-benzopyrene	36.90	0.25
4,5:9,10-dibenzanthracene	9.84	-
4,5:5,6:9,10-tribenzanthracene	22.55	-
TOTAL PAH	820.41ug	8.10ug

To test the present method in practical terms, several different samples were obtained and processed by the proposed method.

6.2 Experimental

6.2.1 Equipment

All equipment and reagents used in previous chapters were also used here.

6.2.2 Sampling sites

6.2.2.1 Site A

A represented the vicinity of an electrolytic pot containing a large mass of a hot, "ungraphitized" mixture of pitch and pitch coke paste.

The sample was collected as dust on a glass-fibre filter paper using a sampling pump.

6.2.2.2 Site B

B was in an exhaust duct, ahead of the electrostatic precipitator (ESP). An isokinetic sampling device was used.

The sample was collected as dust on a glass-fibre filter paper using a sampling pump.

6.2.2.3 Site C

C represented the material captured by electrically polarised plates in the ESP and was collected by hand at the main dust settling tank under the ESP.

The sample was collected as dust on a glass-fibre filter paper using a sampling pump.

6.2.2.4 Site D

D represented a site in a process plant where graphite electrodes were used which had been pre-baked.

The sample was collected as dust on a glass-fibre filterpaper using a sampling pump.

6.2.3 Procedure

About 40mg of recrystallized IS was accurately weighed to the nearest 0.01mg and dissolved in 100cm³ of hexane in a volumetric flask. 5cm³ of this was pipetted into another 100cm³ flask and made up to volume with hexane. The glass-fibre filters from sites A, B, and D and the precipitated dust from site C were ultrasonically extracted into hexane for 30 minutes. The extracts were passed through anhydrous sodium sulphate into a second glass test tube. A volume of hexane containing 20ug IS (1,3,5-triphenylbenzene) was added (from the stock

solution prepared above) to the extracts from sites A, B, C and one containing 10ug IS to that for site D.

The extracts were evaporated to dryness under nitrogen at room temperature in 2cm³ glass vial. For the samples from sites A, B and C, the residues were taken up in 100ul of fresh hexane. The residue from site D was taken up in 50ul of fresh hexane. The vials were then sealed with a septum cap, and were placed into a refrigerator.

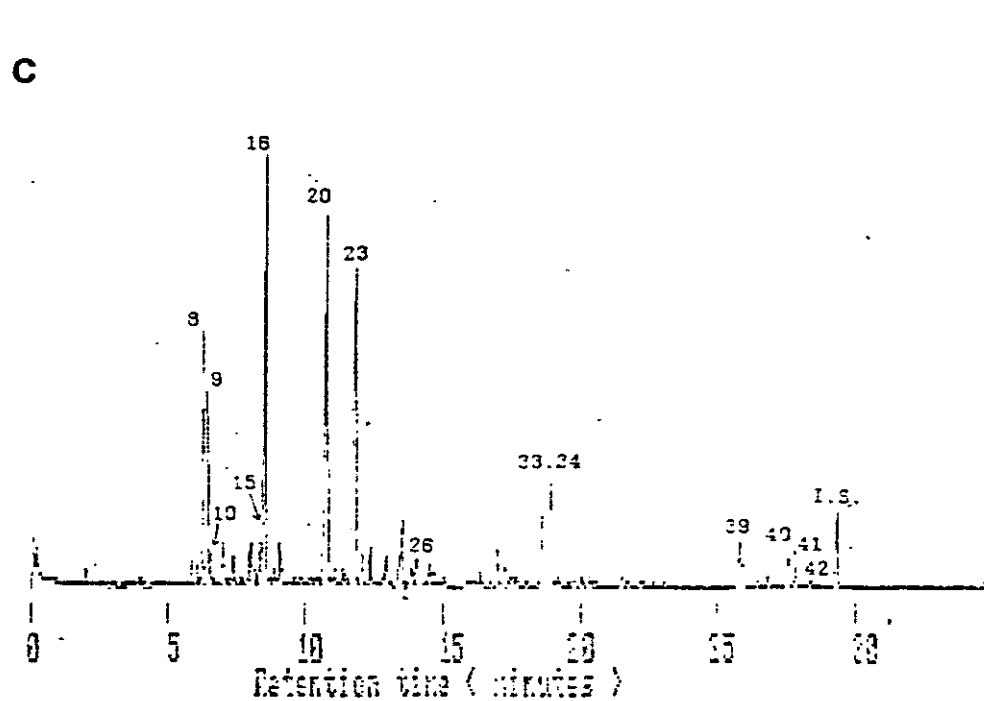
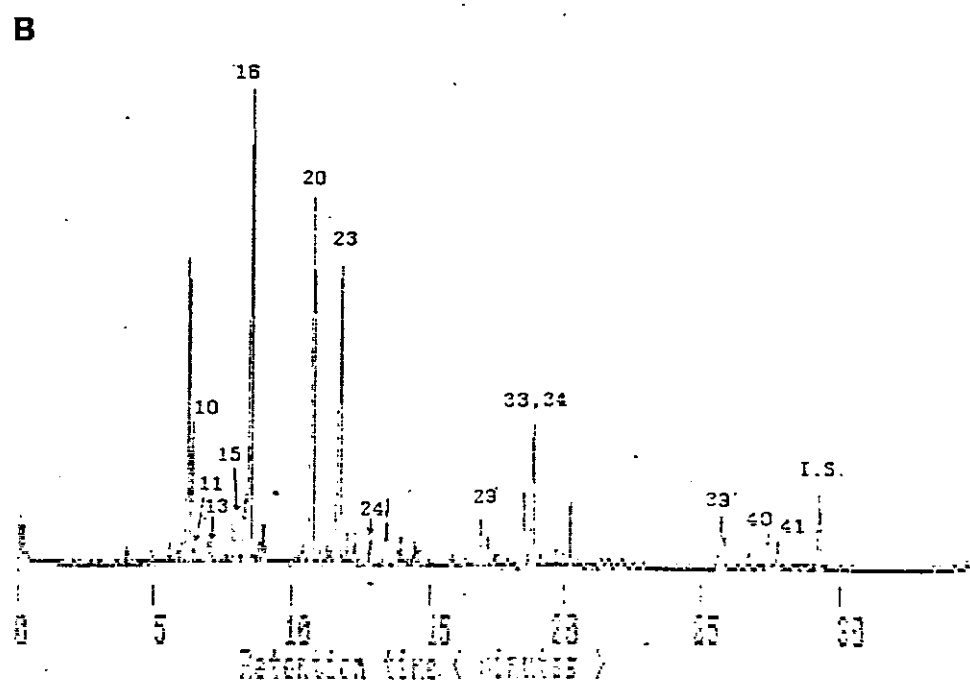
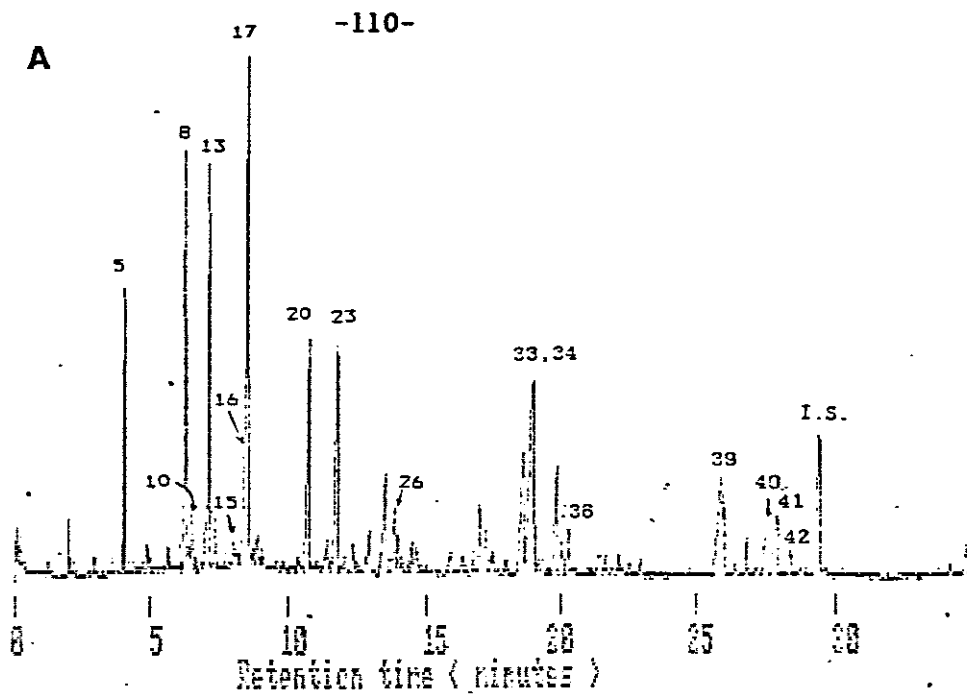
Once the DB-5 capillary column was conditioned and preliminary runs indicated reproducible PAH retention times, a 5ul aliquot of the PAH standard solution was injected into the GC. The peak areas of the PAH were normalised against the IS and the RRF of each PAH were calculated by the computer.

5ul Aliquots of each sample were then injected into the GC. The computer acquired the data for each injection and saved the chromatogram on a floppy disk. It integrated the peaks and calculated the mass of each PAH identified on the basis of retention times.

These data were imported onto a "Lotus 1-2-3" spreadsheet, for the calculation of RI and masses of PAH in original samples.

6.3 RESULTS

The gas chromatograms obtained from one sample taken at each of the four sites are displayed below in figures 6.1 to 6.4. The annotated peaks correspond to those identified by retention times or if a standard was not available, by retention index.



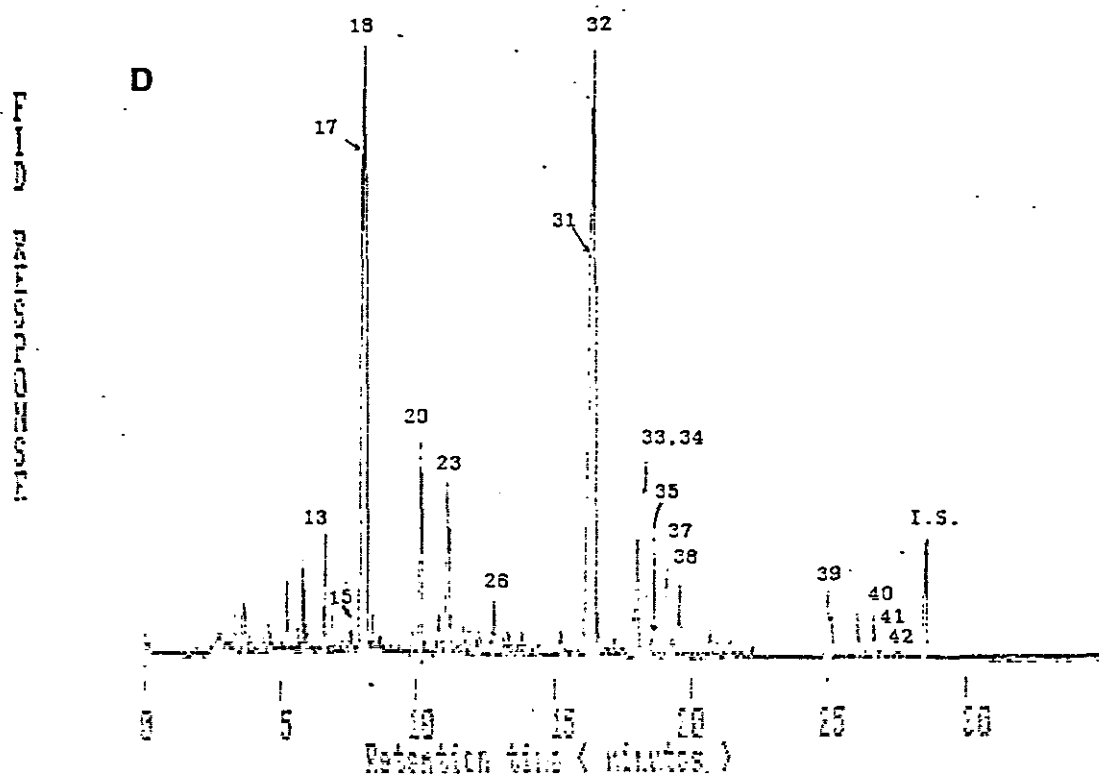


FIGURE 6.1 GAS CHROMATOGRAM OF PAH FOR PARTICULATE MATTER TAKEN AT SITES A,B,C AND D. PEAK NUMBERS CORRESPOND TO APPENDIX 1.

The results of the quantitative analyses are shown in table 6.2.

The compounds listed in table 6.3 were identified at sites A, B, C and D. In this table, retention indices determined by Lee et. al.⁶¹ are compared with those calculated here.

TABLE 6.2 MASS OF EACH PAH DETERMINED AT THE FOUR SITES

Assigned Peak No. *	PAH compound	Mass recovered, ug			
		Site A	Site B	Site C	Site D
1	Naphthalene	<0.002	<0.002	<0.002	<0.002
6	Fluorene	0.05	0.03	0.08	<0.01
10	Phenanthrene	0.62	1.28	3.59	<0.01
11	Anthracene	<0.002	<0.002	<0.002	0.04
13	Dibenzopyrrole	5.66	0.14	0.82	1.16
15	2-methylphenanthrene	0.32	<0.002	1.79	0.21
17	1-methylphenanthrene	0.48	0.23	<0.002	9.34
20	Fluoranthene	5.62	10.44	18.78	2.60
23	Pyrene	6.30	9.67	16.31	1.74
26	1,2-benzofluorene	2.15	0.87	0.91	0.31
33	9,10-benzophenanthrene and				
34	1,2-benzophenanthrene	0.53	8.86	15.18	0.84
35	2,3-benzanthracene	30.96	64.37	52.24	0.99
39	3,4-benzofluoranthene	3.74	5.32	4.60	3.25
40	1,2-benzopyrene	2.74	2.65	2.72	1.22
41	3,4-benzopyrene	1.86	1.66	0.99	0.94
42	4,5:9,10-dibenz- anthracene	0.83	0.34	0.58	<0.01
43	Hexabenzobenzene	<0.01	<0.01	<0.01	<0.01
44	3,4:8,9-dibenzo- pyrene	<0.55	<0.55	<0.55	<0.55

* cf. Appendix 1

TABLE 6.3 POLYCYCLIC AROMATIC COMPOUNDS IDENTIFIED BY RETENTION INDEX ON PARTICULATE MATTER TAKEN AT THE FOUR SITES

Assigned Peak No.*	Compound Name	R.I.	Literature R.I.+	Site Identified at
2	3-methylbenzo- 2,3-thiophene	220.90	221.02	D
5	Dibenzofuran	257.27	257.17	A
8	1,2,3,4-tetrahydrophen anthrene	297.13	297.21	A+C
9	9-fluorenone	299.36	299.77	C
16	9-ethyl-dibenzopyrrole	313.66	313.97	C+A
18	1,2,3,10b-tetrahydro- fluoranthene	316.46	316.37	A+D
24	9-n-propylphenanthrene	350.15	350.30	B
25	9,10-dimethylantracene	355.12	355.49	A
29	9-phenylcarbazole	382.05	382.09	B
30	2,7-dimethylpyrene	386.07	386.34	D
31	11-benzo-1,2-fluorene	386.91	386.41	D
36	3,4-benzo-9-oxodihydro- anthracene	406.33	406.54	A
37	9-phenylphenanthrene	406.84	406.90	D
38	2,3-benzo-dibenzopyrrole	409.66	410.12	D

* cf. Appendix 1

+ Ref. No. 13, table 7.2.

The compounds identified by retention index in the raw materials used for the processes at the time of sampling at sites A, B, C and D are shown in table 6.4.

TABLE 6.4 THE POLYCYCLIC AROMATIC COMPOUNDS, RELATED TO PAH, IDENTIFIED IN THE RAW MATERIALS BY RETENTION INDEX. THE PEAK NUMBERS CORRESPOND TO THE ANNOTATED PEAKS IN FIGURES

Assigned Peak No. *	Compound Name	R.I.	Literature R.I. +	Origin
3	1,5-dimethylnaphthalene	244.85	244.98	Pitch
4	2,2'-bipyridyl	245.81	245.48	Pitch
5	Dibenzofuran	257.27	257.17	Coke
7	1,2,3,4,5,6,7,8-octahydro-phenanthrene	296.10	292.03	Pitch
12	9,10-dihydroacridine	304.42	304.33	Pitch
14	5,6-benzoquinoline	310.22	309.25	Pitch
16	9-ethyl-dibenzopyrrole	313.60	313.97	Pitch
18	1,2,3,10b-tetrahydro-fluoranthene	316.35	316.37	Coke
19	2-phenylnaphthalene	332.63	332.59	Coke
21	3,6-dimethylphenanthrene	338.36	337.83	Coke
22	6-phenylquinoline	341.82	342.45	Coke
27	5,12-dihydro-2,3-benzanthracene	380.42	381.56	Pitch and Coke
28	9,10-dimethyl-3-ethyl-phenanthrene	381.84	381.85	Coke
29	9-phenyl-dibenzopyrrole	382.55	382.09	Pitch
32	1,2-benzacridine	398.66	398.74	Pitch

* cf Appendix 1

+ Ref. No. 13, table 7.2.

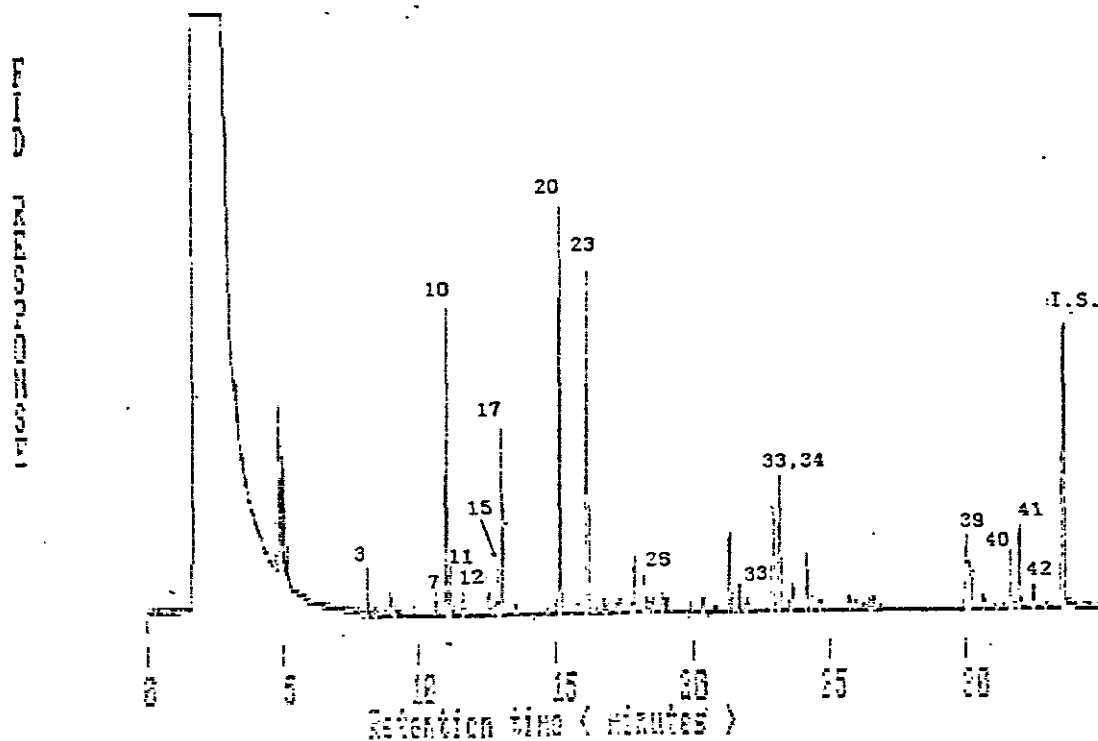


FIGURE 6.2 GAS CHROMATOGRAM OF AN EXTRACT OF PITCH AS USED IN THE "UNGRAPHITIZED" ANODES INSTALLED AT SITE A

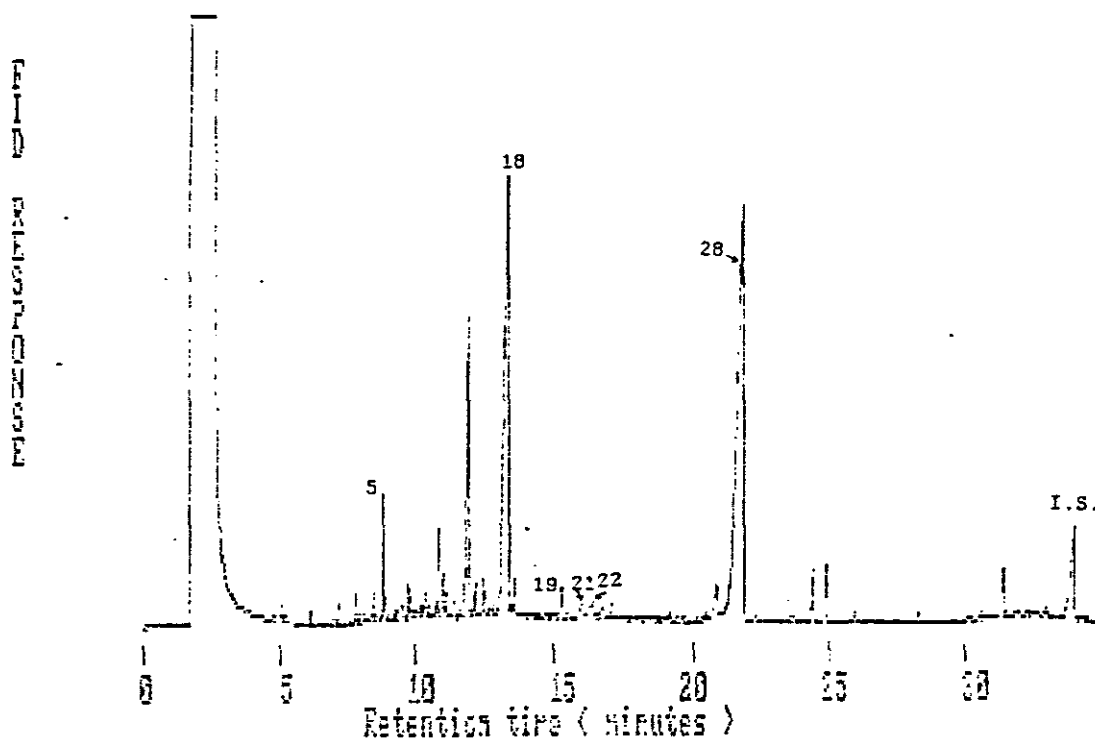


FIGURE 6.3 GAS CHROMATOGRAM OF AN EXTRACT OF PITCH COKE ISOLATED BY COLUMN CHROMATOGRAPHY ON SILICA GEL. THIS COKE WAS USED AS AGGREGATE MATERIAL IN THE ANODES INSTALLED AT SITE A.

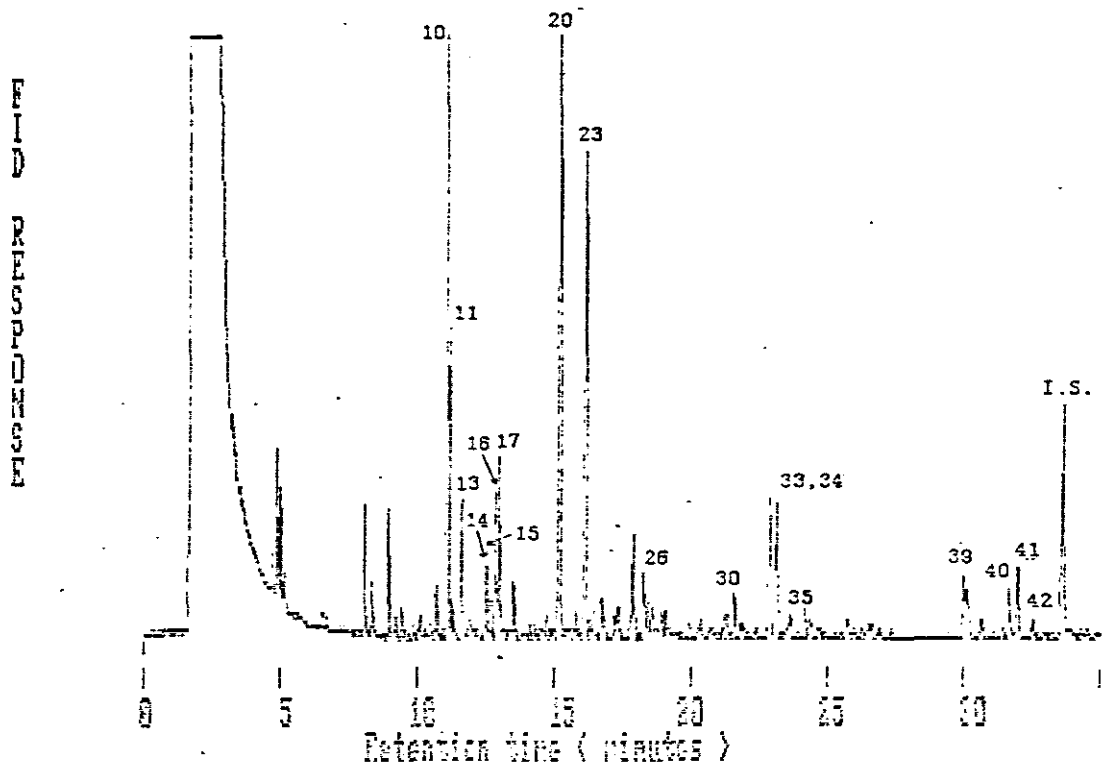


FIGURE 6.4 GAS CHROMATOGRAM OF AN EXTRACT OF PITCH AS USED IN "GRAPHITIZED" ANODES INSTALLED AT SITE D

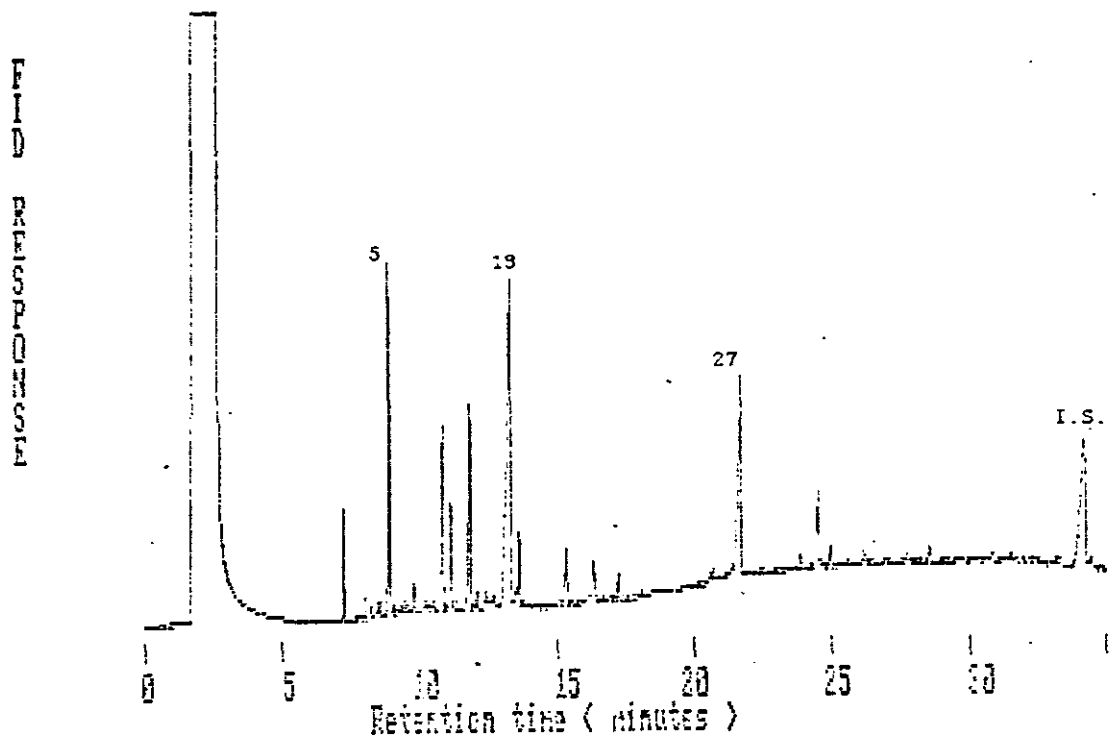


FIGURE 6.5 GAS CHROMATOGRAM OF AN EXTRACT OF PETROLEUM COKE ISOLATED BY COLUMN CHROMATOGRAPHY ON SILICA GEL. THIS COKE WAS USED AS AGGREGATE MATERIAL IN THE ANODES INSTALLED AT SITE D.

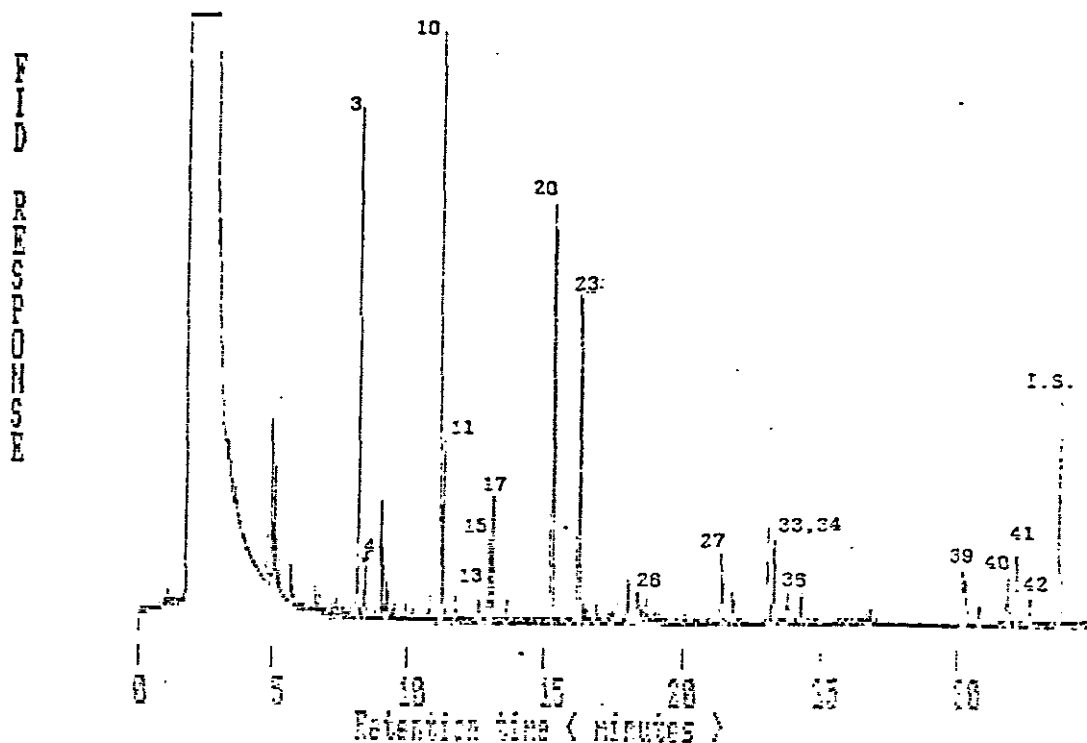


FIGURE 6.6 GAS CHROMATOGRAM OF AN EXTRACT OF PITCH USED FOR
"RAMMING PASTE" AT SITE D.

6.4 DISCUSSION

Generally the chromatograms of the PAH fraction extracted from particulate matter represented the condensed higher molecular mass fraction of the pitch. This suggested that the lower molecular mass PAH in air did not occur adsorbed on particulate matter.

For example, phenanthrene (RI = 300.00) was a major compound of the PAH in pitch but on particulate matter, its contribution was much less.

The PAH analogue dibenzofuran (RI = 257.27) on the other hand was identified in comparable quantities in pitch coke as well as on the

particulate matter sampled at site A.

Many PAH compounds were found on dust taken at site B. This indicated that they were stable even at the high temperatures in the electrolytic cell prior to their removal by the ESP at site C.

Peak 17 (1-methylphenanthrene RI=316,00) and peak 18 (1,2,3,10b-tetrahydro- fluoranthene RI=316,46) which were identified in the pitches and cokes respectively, were poorly resolved by the DB-5 capillary column. Peak 18 (RI=316,46), peak 31 (11-benzo-1,2-fluorenone RI=386,91) and peak 32 (1,2-benzacridine RI=398,66) were found at site D (graphite electrodes installed) but not at site A (ungraphitized electrodes). These compounds therefore could be used as a fingerprint device to differentiate one from the other.

Peak 18 originated from coke material used to make the graphite electrodes at site D (see figure 6.5). It was not found in the air sampled at site A.

Peak 31 and 32 were identified at site D, but not in the raw materials used for the anodes or ramming paste. It could be deduced therefore that these were manufactured during the graphitizing process and subsequently released, or released by the gradual baking or graphitizing of the ramming paste.

Fluoranthene (RI=334.20) and pyrene (RI=342.25) were recovered in approximately equal amounts at all four sites (see table 6.2).

1,2-benzopyrene (RI=426,41) and 3,4-benzopyrene (RI=464,90) were recovered at each of the four sites in a ratio of approximately 2:1.

The high molecular mass PAH hexabenzobenzene (RI=587,7) and 3,4;8,9-dibenzopyrene (RI=600,00) were not detected at any of the four sites.

6.5 CONCLUSION

A number of PAC and PAH were identified at the four sites. For some of them, the results suggest that they originate from the raw materials used for the electrodes. The chromatogram of extract from the "ungraphitized" anode working area (site A) was dissimilar from that taken in the vicinity of a graphitized anode (site D).

Application of the proposed method on particulate matter taken at sites A and D produced similar chromatograms with the exception of three large peaks. These were identified at site D by retention index.

The PAH fingerprint for the pitches was also evident in the chromatograms obtained at the four sites. The three peaks identified at site D resulted in some differences from those of the other sites.

The pitches provided more PAH and PAC than the coke materials in the air around the electrolytic reduction cells. It is difficult to say what the fate of the compounds were.

PAH could be quantified in sub-microgram amounts provided that a high volume sampling pump be used to collect enough sample.

CHAPTER 7

DISCUSSION AND CONCLUSIONS

Ultrasonic extraction of PAH into hexane gave more quantitative recoveries than a soxhlet thimble technique. Benzene and acetone appeared to be less efficient and cyclohexane tended to form emulsions. PAH could be separated from a coke matrix into hexane using silica gel by absorption chromatography. Of the four separation techniques chosen, this method gave the best recoveries of the PAH investigated.

Because of the low concentrations of PAH expected in particulate matter and cokes, a splitless injection was mandatory for resolving PAH by gas chromatography. This excluded a 100 μm i.d. capillary column. Helium maintained lower values of HETP than nitrogen for a 250 μm i.d. capillary column and was used as the carrier gas for resolving PAH.

This capillary column gave a good correlation between calculated and published retention indices (Lee *et. al.*¹³) relative to four PAH standards, viz. naphthalene, phenanthrene, 1,2-benzophenanthrene and 1,2:6,7-dibenzanthracene. For this work, the latter was substituted for picene. An attempt to extend this by incorporating 3,4:8,9-dibenzopyrene was of little use because of the lack of intermediate retention data.

The active carcinogen 1,2-benzophenanthrene (R.I. = 400,00) was only partially resolved from its inactive isomer 9,10-benzophenanthrene (R.I. = 399,34). R.I. of these two on the SE-52 used by Lee et. al.¹¹ were both 400,00 indicating that they were not resolved.

A TLC identification method using 2% (v/v) DMF in hexane was of limited use because of crowding of the many PAH in samples.

A gas chromatograph using the 250 um i.d. capillary column was therefore used to resolve and identify PAH in samples from the selected four sites. The result can be concluded as the following.

Chromatographic fingerprints obtained for particulate matter extracts were similar to those of pitch. This led to the conclusion that PAH were evaporated or volatilized from the heated pitch during the processes, and condensed onto particulate matter.

Small amounts of alkylated PAH were identified in pitch chromatograms. Similar amounts were found on particulate matter. Similar proportions of alkylated PAH to PAH were evident on the chromatograms of particulate matter collected at the ESP. The high temperatures which the sample was exposed to (about 1000°C) before entry into the ESP, suggested that PAH tended not to form derivatives.

A number of "new" compounds were identified both in raw materials and on particulate matter. In some cases those identified in the raw materials were not found on the particulate matter. Likewise, some of the same compounds identified in the working air were not detected in the electrode's matrix.

A number of PAC identified in the cokes after isolation of the fraction by column chromatography (silica gel), were also identified in particulate matter. The amount of PAH found in the cokes were so low that they were considered not to contribute towards the total load of PAH in the electrodes.

The reduced response of the internal standard (1,3,5-triphenylbenzene) after ultrasonic extraction led its addition being made to sample extracts using this technique the following trends in quantification were found.

Low molecular mass PAH ($<192\text{g mol}^{-1}$) were generally present in submicrogram amounts at all four sites investigated. This contrasted with the proportion found in pitch. It was concluded that the lower molecular mass PAH were partially in the gaseous state during sampling and passed through the filter. Loss of these compounds in another way could not be determined by this method.

Fluoranthene and pyrene were present in approximately equal amounts at all four sites. 1,2-Benzopyrene was recovered in slightly greater amounts than its carcinogenic isomer 3,4-benzopyrene.

The present method was characterized by a quick and selective extraction procedure, good resolution and fast quantification of microgram amounts of 3,4-benzopyrene and other high molecular mass PAH. Previously, submicrogram levels of PAH could only be determined by a HPLC technique.^{12, 67}

Time taken per analysis was approximately two hours, of which, ultrasonic extraction and subsequent concentration using hexane as medium were the steps prior to injection into the GC.

7.1 SUGGESTIONS FOR FURTHER WORK

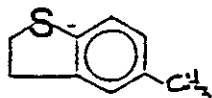
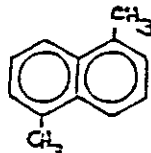
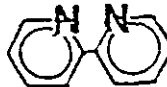
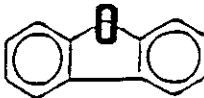
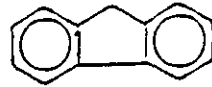
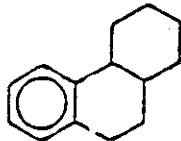
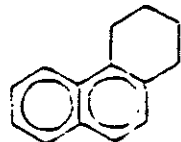
The method presented in this dissertation for PAH was applied to air samples and was quick and specific.

Such a method is required for determining PAH in effluent water.¹³³ Bagheri and Creaser¹³⁴ suggested that fluorescence and HPLC with fluorescence detection be used to determine PAH in water after concentrating its extract.

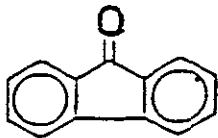
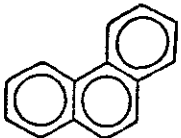
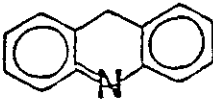
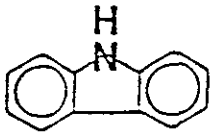
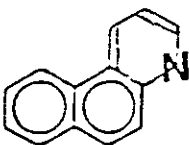
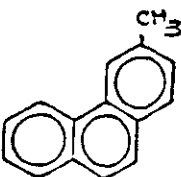
Rigorous levels of PAH set by the "World Health Organisation" (WHO) and the EPA in domestic and effluent waters necessitates a method for determining individual PAH.¹³⁵ Fluorescence detectors can achieve detection levels below ng L^{-1} .¹³⁶ It is suggested therefore that replacing the FID by a fluorescence detector might be investigated for water samples in which PAH are in smaller amounts than in samples studied here.

Complete resolution of 1,2- and 9,10-benzophenanthrene, which was not possible on the DB-5 column, can be resolved in liquid crystal stationary phases (chapter 1.5.1.2.1) and may require further attention in a generalised PAH analysis. It is further suggested that liquid crystal columns be applied to air and water samples using both GC-fluorescence and GC-FID techniques.

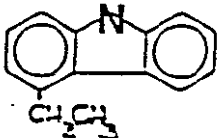
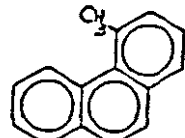
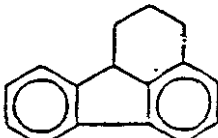
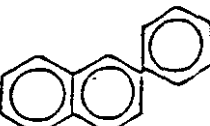
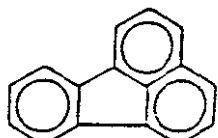
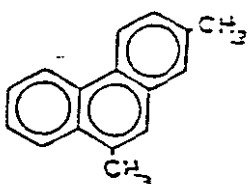
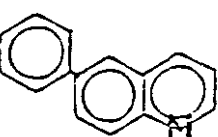
APPENDIX 1

Assigned peak no	Compound name	Structural formula	DB-5 column retention index	Alternative name (if any)
1	Naphthalene		200.00	
2	3-methylbenzo-2,3-thiophene		220.90	3-methylbenzo(b)-thiophene
3	1,5-dimethylnaphthalene		244.85	
4	2,2'-bipyridyl		245.81	2,2'-bipyridine
5	Dibenzofuran		257.27	
6	Fluorene		260.85	
7	1,2,3,4,5,6,7,8-octahydronaphthalene		292.13	
8	1,2,3,4-tetrahydrophenanthrene		297.13	

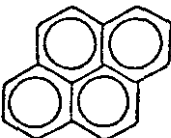
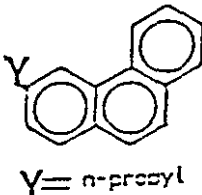
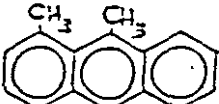
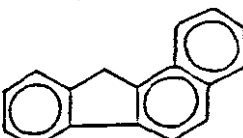
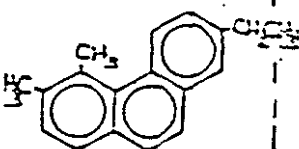
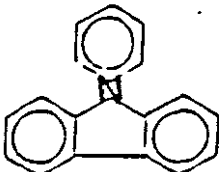
APPENDIX 1 cont'd.

Assigned peak no	Compound name	Structural formula	DB-5 column retention index	Alternative name (if any)
9	9-fluorenone		299.37	
10	Phenanthrene		300.00	
11	Anthracene		301.17	
12	9,10-dihydroacridine		304.42	
13	Dibenzopyrrole		304.90	Carbazole
14	5,6-benzoquinoline		310.22	Benzo(f)quinoline
15	2-methylphenanthrene		312.77	

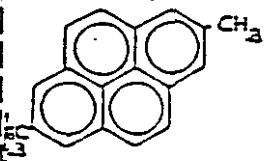
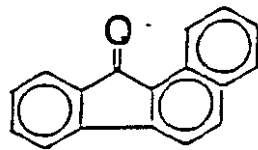
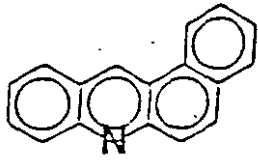
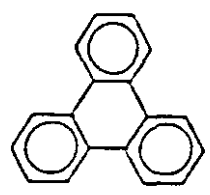
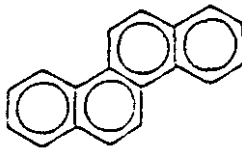
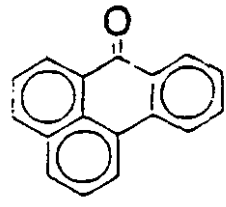
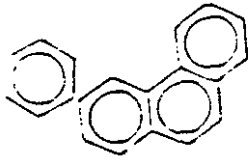
APPENDIX 1 cont'd.

Assigned peak no	Compound name	Structural formula	DB-5 column retention index	Alternative name (if any)
16	9-ethyl-dibenzopyrrole		313.60	9-ethylcarbazole
17	1-methylphenanthrene		316.00	
18	1,2,3,10b-tetrahydro-fluoranthene		316.46	
19	2-phenylnaphthalene		332.63	
20	Fluoranthene		334.20	
21	3,6-dimethylphenanthrene		338.36	
22	6-phenylquinoline		341.82	

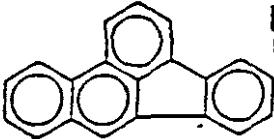
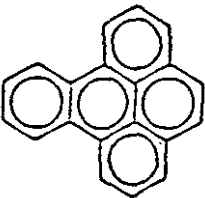
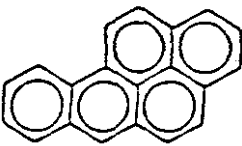
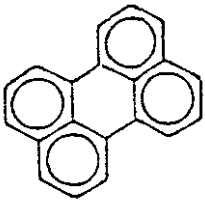
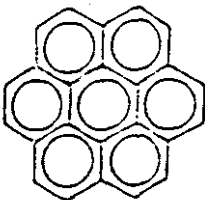
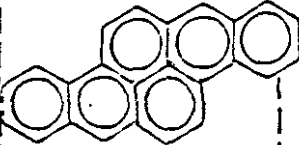
APPENDIX 1 cont'd.

Assigned peak no	Compound name	Structural formula	DB-5 column retention index	Alternative name (if any)
23	Pyrene		342.25	
24	9-n-propylphenanthrene	 Y = n-propyl	350.15	
25	9,10-dimethylantracene		355.12	
26	1,2-benzofluorene		359.48	Benzo(a)fluorene
27	5,12-dihydro-2,3-benzanthracene		380.42	
28	9,10-dimethyl-3-ethylphenanthrene		381.84	
29	9-phenyl-dibenzopyrrole		382.05	9-phenylcarbazole

APPENDIX 1 cont'd.

Assigned peak no	Compound name	Structural formula	DB-5 column retention index	Alternative name (if any)
30	2,7-dimethylpyrene		386.07	
31	11-benzo-1,2-fluorenone		386.91	
32	1,2-benzacridine		398.66	Benz(a)acridine
33	9,10-benzophenanthrene		399.34	Triphenylene
34	1,2-benzophenanthrene		400.00	Chrysene
35	2,3-benzanthracene		404.08	Naphthacene
36	3,4-benzo-9-oxodihydroanthracene		406.33	
37	9-phenylphenanthrene		406.84	

APPENDIX 1 cont'd.

Assigned peak no	Compound name	Structural formula	DB-5 column retention index	Alternative name (if any)
38	2,3-benzo-dibenzopyrrole		409.66	Benzo(b)carbazole
39	3,4-benzofluoranthene		449.62	Benzo(b)fluoranthene
40	1,2-benzopyrene		462.41	Benzo(e)pyrene
41	3,4-benzopyrene		464.90	Benzo(a)pyrene
42	4,5;9,10-dibenz-anthracene		468.54	Perylene
43	Hexabenzobenzene		557.77	Coronene
44	3,4;8,9-dibenzopyrene		600.00	Dibenzo(b,def)-chrysene

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