CHARACTERISATION OF ENVIRONMENTAL POLLUTION BY GC-MS ANALYSIS OF POLYCYCLIC AROMATIC COMPOUNDS IN WATER AND SOIL

By

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Submitted in partial fulfilment of the requirements for the degree

Doctor of Philosophy
Applied Science

In the Faculty of Natural, Agricultural and Information Science
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Pretoria

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SUMMARY

Polycyclic aromatic hydrocarbons (PAHs) have long been known to pose health risks in humans and have become one of the major environmental issues. Coal tar products, refined petroleum products and lubricating oils are among the anthropogenic sources, which contain highly toxic substances of which benzo[a]pyrene and dibenz[a,h]anthracene are the most potent carcinogens. Sensitive and reliable chemical analyses of contaminated soil and water are imperative for health risk assessments and chemical fingerprinting. The development of techniques that can determine the pollution source is motivated in part by the cleanup costs, legal fees, and fines incurred by the polluter.

In this thesis, direct solid-phase microextraction (DISPME), followed by capillary gas chromatography (GC) and mass spectrometry (MS) in the selected ion storage (SIS) mode was investigated for the determination and characterisation of PAHs in aqueous samples. The SPME method of extraction is also compared to a traditional liquid-liquid extraction method that was based on USEPA method 8270. It was found that several factors affected the extraction efficiency with a single stage SPME extraction, such as the degree of alkylation, fiber condition, absorption time, sample pH, sample matrix, sample temperature, agitation method, etc. The technique of multiple extractions (MESPME) was investigated and found to compensate for variations in analytical conditions or sample matrix. The suitability of the method for health risk assessments was investigated. The results were acceptable for this purpose because the limits of detection were estimated at the pg/cm^3 levels that were considerably lower than the health risk based guideline concentrations (10^{-6} cancer risk) for drinking water specified by the United States Environmental Protection Agency (USEPA). The guideline concentration for dibenz[a,h]anthracene (the most potent carcinogen) is for example 0.0092 ng/cm^3 compared to a detection limit of 0.0045 ng/cm^3 achieved with the SPME-GC/MS method. Detection limits for the other carcinogenic PAHs were also found to be lower than the USEPA guideline concentrations. The method was also developed to include the quantification of alkyl-PAHs, which is important for interpretative methods such as chemical

fingerprinting (source identification). For this purpose detection limits of at least 0.01 ng/cm^3 are required for individual PAHs. The SPME extraction method used in conjunction with GC/MS was found to be sensitive enough for this purpose with detection limits lower than 0.01 ng/cm^3 for all the PAHs. The method was in many respects superior to traditional extraction methods.

A headspace SPME (HSSPME) method, followed by GC/MS, was developed for the screening of soil samples. Vapor pressures of target analytes were determined using a capillary GC method to identify environmentally important components with a sufficiently high vapor pressure to be analyzed in the headspace mode. The method was optimized under non-equilibrium conditions with simplicity and automation in mind and does not require any extraction procedure or sample preparation, other than grinding, drying and homogenizing. The analytical performance and the significance of the results for the purpose of chemical characterisation, source discrimination, determination of individual isomer distributions and the calculation of source and weathering ratios, are discussed. The SPME method of extraction was also compared to the relatively new extraction technique known as Pressurised Liquid Extraction (PLE). HSSPME was found to be a very efficient and sensitive technique for the confirmation of PAHs of up to four-ring structures and suitable for a tiered and adaptive approach.

The selective extraction and analysis techniques that have been developed in this thesis were finally used to develop diagnostic ratios, which can be used to trace contamination in the environment to its source. The successful use of the analytical data to match the chemical patterns of target analytes with potential sources was shown.

KARAKTERISERING VAN OMGEWINGSBESOEDELING IN GROND EN WATERMONSTERS DEUR GC/MS EN DIE ANALISE VAN POLISIKLIESE AROMATIESE VERBINDINGS

DEUR

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SAMEVATTING

Die gesondheidsrisiko wat polisikliese aromatiese koolwaterstowwe (PAHs) vir mense inhou is lankal reeds bekend en het in een van die mees belangrikste omgewingskwessies ontwikkel. Besoedelstowwe soos koolteer, petroleum produkte en smeermiddels bevat heelwat giftige en karsinogene verbindings waarvan benso[a]pireen en dibenso[a,h]antraseen die giftigste is. 'n Sensitiewe en betroubare chemiese analise van grond- en watermonsters word vir die ondersoek na PAH en ge-alkileerde PAH besoedeling, gesondheids gebaseerde risikobepalings en chemiese karakterisering benodig. Kostes verbonde aan opruiming, regskoste en boetes is deels die motivering vir die ontwikkeling van metodes wat besoedelingsbronne kan identifiseer.

Die toepassing van direkte vastestof mikroekstraksie (solid-phase micro-extraction - DISPME), gevolg deur kapillêre gaschromatografie (GC) en massaspekrtometrie (MS) in die geselekteerde ioon (selected ion storage - SIS) mode is vir die bepaling en karakterisering van PAHs in watermonsters ondersoek. Die SPME ekstraksiemetode is ook met die tradisonele vloeistof-vloeistof ekstraksiemetode, gebasseer op die USEPA metode 8270, vergelyk. Daar is gevind dat die effektiwiteit van 'n enkelstap SPME-ekstraksie deur verskeie faktore beinvloed word, soos byvoorbeeld die graad van alkilering, die SPME vesel se toestand, absorpsietyd, monster pH, monstermatrys, monster temperatuur, ens. Die tegniek van veelvuldige ekstrasies (MESPME) is suksesvol ondersoek om vir die variasies in analitiese kondisies en monstermatrys te kompenseer. Deteksielimiete vir individuele PAHs was in die pg/cm^3 gebied wat aansienlik laer is as die riglynkonsentrasie (10^{-6} kanker risiko), soos deur die USEPA (United States Environmental Protection Agency) voorgekryf. Die riglynkonsentrasie vir benso[a]pireen is voorbeeld 0.0092 ng/cm^3 in vergelyking met 'n deteksielimiet van 0.0045 ng/cm^3 wat met die SPME-GC/MS metode verkry is. Deteksie limiete vir die ander karsinogene PAHs was ook almal laer as die USEPA riglynkonsentrasies. Die metode is ook vir die kwantitatiewe bepaling alkiel-PAHs aangepas. Hierdie analietkomponente is belangrik vir

interpreteringsmetodes, soos gevorderde chemiese karakterisering (bron-allokering). Vir hierdie doel word 'n deteksielimiet van 0.01 ng/cm^3 vir al die PAHs vereis. Die SPME ekstraksiemetode, gevolg deur GC/MS, het aan hierdie vereistes voldoen en deteksiemiete van laer as 0.01 ng/cm^3 is vir al die PAHs verkry. Die metode was in baie opsigte beter as die tradisionele metodes is.

'n Dampruim SPME (HSSPME) metode, gevolg deur GC/MS, is vir die siftingsprosedure van PAHs in grondmonsters ontwikkel. Die dampdrukke van analietkomponente is met 'n kapillêre GC metode bepaal om vas te stel watter komponente in die dampruim geanaliseer kan word. Die metode is onder nie-ewewigskondisies geoptimiseer met eenvoud en outomatisasie in gedagte, terwyl geen spesiale monstervoorbereiding anders as droog, maal en homogenisering vereis word nie. Die betroubaarheid van die metode en die geskiktheid van die resultate vir chemiese karakterisering, bronallokering, bepaling van isomeer verspreidingspatrone en die bepaling van bron- en verouderingsverhoudings is ondersoek. Die metode is ook met die relatief nuwe ekstraksie metode, naamlik "Pressurised Liquid Extraction (PLE)" vergelyk. Daar is gevind dat HSSPME 'n baie effektiewe en sensitiewe metode vir die bepaling van PAHs tot en met vier-ring-strukture is.

Die selektiewe ekstraksie- en analise-metodes wat in hierdie studie onwikkel is, is uiteindelik vir die ontwikkeling van diagnostiese verhoudings tussen twee analiete gebruik. Hierdie verhoudings kan gebruik word om plaaslike besoedeling aan 'n besoedelingsbron te koppel. Daar is ook aangetoon dat die analitiese data suksesvol gebruik kan word om die chemiese patrone van analietkomponente in omgewings-monsters aan potensiële bronne te koppel.

ACKNOWLEDGEMENTS

I would first like to sincerely and especially thank my promoter, Prof. Egmont Rohwer. He helped me consistently and constructively the entire way. Throughout my studies, he continually assisted me in constructing and composing this thesis and always responded back to me in a professional and constructive manner. Without his involved assistance every step of the way I am sure I would not have been able to construct the thesis you now see here.

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A very devoted and unique thank you goes to Dr. Abie van Wyk. Without his encouragement, support and trust over many years, providing a spur to my confidence, I would not have been able to complete this study. I thank him so much for being a great coach and an even better friend.

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Saving the best for last, I want to thank my wife Elize for standing by my side. From when the thesis was only a frightening seed of dread in my tummy to the finished product I handed in, she provided me with undying friendship, emotional support, and constructive criticism. More than anyone, Elize has seen the emotional and intellectual ups and downs that this thesis has put me through. I can never thank her enough for her support through this struggle towards something I can finally be proud of.

Thank You

Willie

GLOSSARY AND ABBREVIATIONS

ACF	-	Advanced chemical fingerprinting
Alkyl-PAHs	-	Alkyl substituted polycyclic aromatic hydrocarbons
Anthropogenic	-	Pollution caused by humans
ASE	-	Accelerated solvent extraction
ATSDR	-	Agency for Toxic Substances and Disease Registry
Carcinogenicity	-	Ability of a substance to cause cancer.
Coal tar	-	Heterogeneous mixture of various classes of compounds
CRM	-	Certified reference material
DCM	-	Dichloromethane
DISPME	-	Direct solid phase microextraction
DL	-	Detection limit
DNAPL	-	Dense non-aqueous phase liquid
DQO	-	Data quality objectives
Fugacity	-	Relative escaping tendency
GC	-	gas chromatography
HSSPME	-	Headspace Solid Phase Microextraction
HPLC	-	High performance liquid chromatography
K_{oc}	-	Sorption coefficient on soil/sediment
K_{ow}	-	Octanol-water partition coefficient
LNAPLS	-	Light Non Aqueous Phase Liquids
m/z	-	Mass over charge
MCL	-	Maximum contaminant level
MDL	-	Method detection limit
MESPME	-	Multiple extraction solid phase microextraction
MQL	-	Method quantification limit
MS	-	mass spectrometry
NAPL	-	Non-aqueous phase liquid
ng	-	Nanogram
PAH	-	Polycyclic aromatic hydrocarbons
PDMS	-	Poly dimethylsiloxane
pg	-	Picogram
PLE	-	Pressurised liquid extraction
P^0_L	-	Vapor pressure
psi	-	Pounds per square inch
QA	-	Quality assurance
QC	-	Quality control
QL	-	Quantification limit
R^2	-	Regression coefficient
RI	-	Temperature programmed retention index
RRF	-	Relative response factor
RSD	-	Relative standard deviation
S/N	-	Signal to noise ratio

Sediment	-	Mud and debris
SIM	-	Single ion monitoring
SIS	-	Selected ion storage
SPME	-	Solid Phase Microextraction
SRS	-	Standard reference soil
STD	-	Standard
S_w	-	Water solubility
t_R	-	Retention time
USEPA	-	Unites States Environmental Protection Agency
Weathering	-	Dissolvation, evaporation, bio-degradation, photo oxidation

CHEMICAL COMPOUNDS

A	-	Anthracene
AC	-	Acenaphthene
AE	-	Acenaphthylene
BA	-	Benzo[a]anthracene
BB	-	Benzo[b]fluoranthane
BI	-	Biphenyl
BP	-	Benzo[ghi]perylene
BAP	-	Benzo[a]pyrene
BTEX	-	Benzene, toluene, ethyl benzene and xylenes
C1-		Methyl group
C2-		Methyl-methyl or ethyl group
C3-		Trimethyl, methylethyl or propyl group
C4-		Tetramethyl, ethylethyl, methylpropyl or butyl group
C	-	Chrysene
C1-C	-	C_1-Chrysene
C1-D	-	C_1-Dibenzothiophene
C1-F	-	C_1-Fluorenes
C1-N	-	C_1- Naphthalenes
C1-P	-	C1-Phenanthrene/anthracenes
C2-C	-	C_2-Chrysene
C2-D	-	C_2-Dibenzothiophene
C2-F	-	C_2-Fluorenes
C2-N	-	C_2- Naphthalenes
C2-P	-	C_2-Phenanthrene/anthracenes
C3-C	-	C_3-Chrysene
C3-D	-	C_3-Dibenzothiophene
C3-F	-	C_3-Fluorenes
C3-N	-	C_3- Naphthalenes
C3-P	-	C_3-Phenanthrene/anthracenes
C4-N	-	C_4- naphthalenes
C4-P	-	C_4-Phenanthrene/anthracenes
D	-	Dibenzothiophene
DA	-	Dibenz[ah]anthracene
DI	-	Dibenzofuran

F - Fluorene
FL - Fluoranthene
IP - Indeno[123-cd]pyrene
N - Naphthalene
P - Phenanthrene
PY - Pyrene

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Chapter 1

INTRODUCTION

POLYCYCLIC AROMATIC HYDROCARBONS AND RELATED COMPOUNDS

During the last five years the spill of coal tar has become a major issue in the South African iron and steel industry, while it has been an issue in other countries for at least thirty years. Continuous spills and discards of coal tar products, refined petroleum products and lubricating oils over a few decades have degraded the quality of water, soil and sediments. These dense non-aqueous phase liquids (DNAPLs) have formed pools of "toxic blobs" in the geosphere, and due to their low solubility in water they can continue releasing small quantities of contaminants into the groundwater for centuries. Groundwater is a source of potable water for many households and farming activities nearby industrial areas and chemical releases of coal tar and petroleum products into the soils have become a serious environmental problem. The investigation into the occurrence and fate of polycyclic aromatic hydrocarbons (PAH) and related compounds in the environment is, therefore, essential. Experts see the cokemaking process as one of steel industry's areas of greatest environmental concern. Coal tar is a by-product in the iron making process and is a heterogeneous mixture of various classes of compounds, such as the poly aromatic compounds. Other products are produced from coal tar because of their stable physico-chemical properties and industrial uses. An example of such a product is creosote, which is used as a wood preservative, fuel, animal dipping agent or lubricant. The US Environmental Protection Agency (USEPA) has classed some of the compounds that occur in coal tar and its products as probable human carcinogens. In 1999, one of the PAH compounds (benzo[a]pyrene) was ranked no 8 by the Agency for Toxic Substances and Disease Registry (ATSDR). Most of the parent PAH compounds are also listed among the other 275 compounds. The environmental laboratory at Research & Development, Iscor Limited, is concerned with the study of PAHs and is responsible for the development of analytical methods. The interpretation of analytical data, using techniques such as chemical fingerprinting, is imperative. Chemical fingerprinting is an important technological tool for companies facing major liability claims for environmental damages or clean-up costs under local regulations. Every chemical mixture that leaks into water or soil leaves behind a characteristic pattern, which can be used to trace contaminants to their source. An advanced chemical fingerprinting (ACF) strategy includes a suite of sampling, chemical analysis and data interpretation methods to enable chemists to differentiate among multiple contaminant sources.

SCOPE AND PURPOSE OF THE THESIS

Several technical and research papers have been reported in the last couple of decades concerning the chemical analysis of PAHs. Various authors have developed analytical methods with the following purposes:

- Identification of sources
- Obtaining insight into the transport, fate, distribution, degradation and toxic effects of PAHs in the environment
- Risk assessments
- Effective risk management strategies to reduce environmental contamination.

Analytical methods developed require sophisticated instrumentation and skilled analysts. The work presented in this thesis has the following objectives:

- To review available information regarding analytical methods and data interpretation methods
- To investigate the physico-chemical properties of PAHs and related compounds
- To develop more sensitive, faster and more efficient analytical methodology for the extraction and determination of PAHs and related compounds in water and soil samples
- To investigate the suitability of methods for hazard identification, health risk assessments and chemical fingerprinting.
- To use stringent quality control (QC) measures to improve the quality of results
- To validate methodologies that were developed or modified during this study
- To investigate the occurrence and concentration of PAHs in water and soil samples that have been submitted to our laboratory for a PAH analysis
- To develop advanced chemical fingerprinting techniques that can be used to link contaminants to their source
- To recommend strategies for future research in the field of chemical analysis.

APPROACH AND PRESENTATION

This thesis describes the development of methodology for the determination of polycyclic aromatic hydrocarbons in water and soil samples, with emphasis on data interpretation strategies. In **Chapter 2**, a general introduction into the nature of coal tar pollution and the dense non-aqueous phase liquid problem is given. The toxicity of PAHs, drinking water standards, health advisories and exposure limits are considered. An overview is also given on currently available analytical methods that are used to determine PAHs in water and soil samples. Conventional extraction techniques, Accelerated Solvent Extraction, Solid Phase Microextraction pre-concentration steps, matrix clean-up procedures and gas chromatography/mass spectrometry are discussed. The potentials and limitations of these methods are considered. The need for analytical methods suitable for Advanced Chemical Fingerprinting is emphasised and recent advances in this field are summarised. The importance of reliable analytical results for these purposes is shown.

In **Chapter 3** the criteria are set for analytical methods investigated and developed in this study. A set of data quality objectives is discussed that can improve the quality of results and ensure reliable results.

Knowledge of physico-chemical properties is necessary to forecast partitioning of PAHs into the environment and for modelling the multiphase distributions. Properties of the selected target analytes for this study are discussed in **Chapter 4**. As data on some of the compounds are unavailable, vapor pressures were determined for a number of compounds using gas chromatography and determining the Kovats retention index of each compound.

Currently available USEPA methods for the extraction and determination of PAHs in water and soil samples were refined to be better suited for chemical characterisation. The nature of the refinements and results are discussed in **Chapter 5**. An alternative method was developed using the technique of Solid Phase Microextraction (SPME), first introduced by Pawliszyn in 1989. The results of this investigation are discussed in **Chapter 6,** focussing on efficiency, specificity, selectivity, sensitivity, matrix interference and representativeness. The suitability of this technique for health risk assessments and chemical fingerprinting is also discussed. For the purpose of health risk assessments a detection limit of 0.0092 ng/cm^3 is required for the most potent carcinogens benzo[a]pyrene and dibenz[a,h]anthracene, based on a one in a million non-cancer hazard. A detection limit of at least 0.01 ng/cm^3 for all the PAHs is required for advanced chemical fingerprinting applications. The essence of the work reported in **Chapters 4 and 6** was written up as a research paper and accepted for publication in the Journal of Analytical Environmental Chemistry. The manuscript is included in **Appendix 1**. The work covered in this publication was also presented as a paper during the 3rd Euroconference on Analytical Environmental Chemistry in, Chalkidiki, Greece. The abstract is included in **Appendix 2**. The application of the SPME-GC/MS technique for Advanced Chemical Fingerprinting was presented as a paper during the Chromatography/Mass Spectrometry Conference at Warmbaths, October 2000. The abstract is included in **Appendix 3**.

For the extraction of PAHs from soil and sludge samples, the technique of Accelerated Solvent Extraction was investigated in **Chapter 7**. The suitability of this technique for chemical fingerprinting is discussed. A fast screening technique was developed by sampling PAHs in the headspace of a soil sample using headspace SPME. The analytical performance of this method is discussed in **Chapter 8**, focussing on extraction efficiency, selectivity and suitability for chemical fingerprinting. This work was written up as a research paper and accepted for publication in the Journal of Chromatography A. The manuscript is included in **Appendix 4.**

In **Chapter 9**, the data generated by the analytical methods that were developed in the previous chapters, are used to develop diagnostic ratios. These ratios are used to trace the contamination in the environment to its source and to follow weathering processes. An improved method was developed for this purpose, based on single isomer-to-isomer ratios, instead of using the sum of the grouped isomers in an alkyl homologue. The detection limits of isomers that are used for this purpose are discussed. The use of PAH distribution patterns is illustrated to differentiate between coal tar and petroleum sources.

In the general discussion presented in **Chapter 10**, consideration is given to the reliability of the analytical methods and data interpretation techniques that were developed during this study. Future needs in the field of analytical methodology are considered and recommendations are made with respect to the scope and strategy of new developments.

Chapter 2

GENERAL ASPECTS OF COAL TAR POLLUTION, CHEMICAL ANALYSES AND CHEMICAL FINGERPRINTING

INTRODUCTION

Environmental policies in various industries are based upon comprehensive analysis of air, water and soil pollution and aim to protect the environment. Regulatory bodies, such as the United States Environmental Protection Agency (USEPA), ensure that industry complies with regulations before considering to issue permits for the facilities and activities[1]. The central concepts driving the new policy direction are that pollution releases to each environmental medium (air, water and

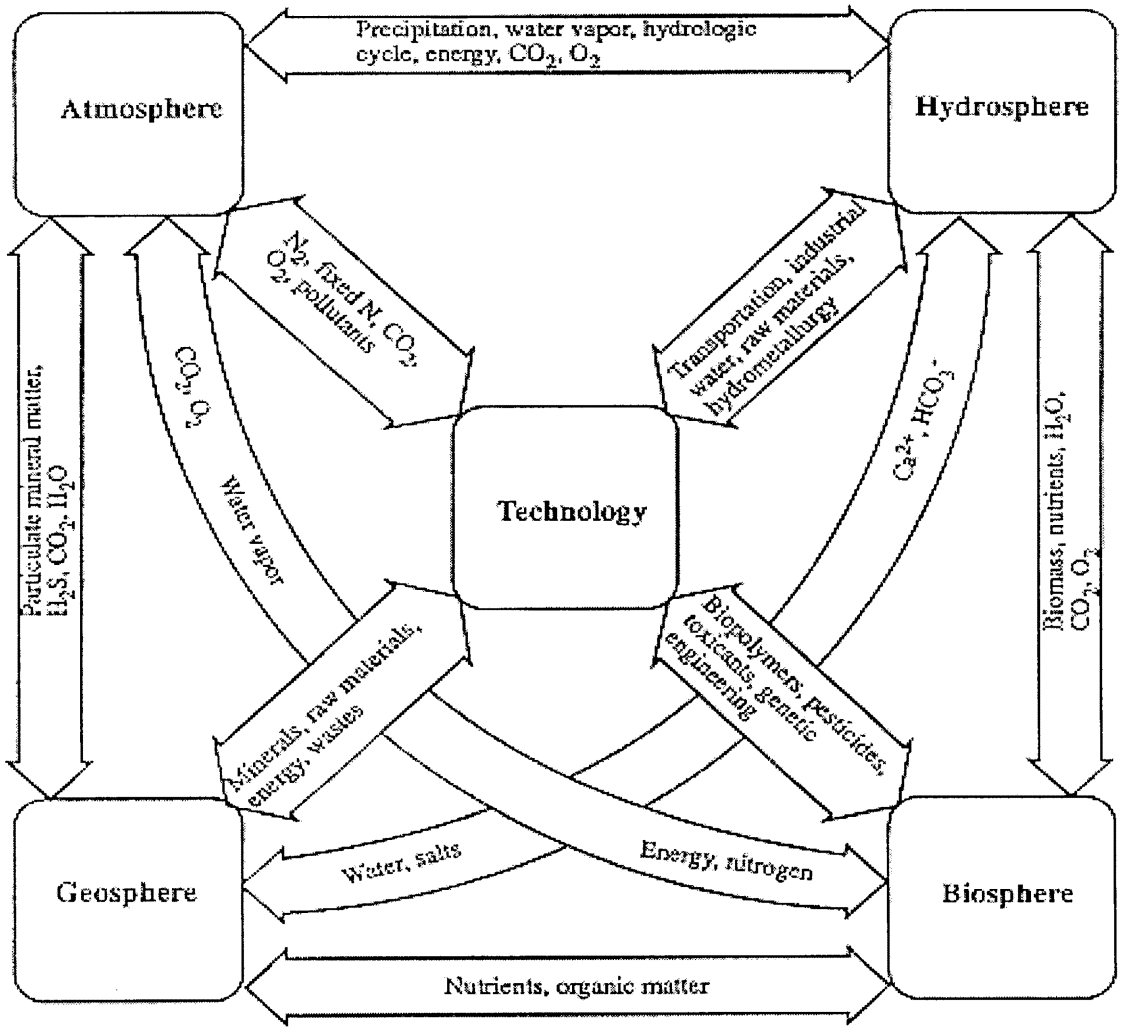

Figure 2.1 : Illustration of the close relationship among the air, water and earth environments with each other and with living systems, as well as the tie-in with technology.

land) affect each other. Environmental strategies must actively identify and address these interrelationships by designing policies for the "whole" facility.

The iron and steel industry produces iron and steel mill products, such as bars, strips, and sheets, as well as formed products such as wires, rods and pipes. Blast furnace products also include coke, coke gas and products derived from chemical recovery in the coking process such as coal tar and distillates. In the by-products recovery process, volatile components of the coke oven gas stream, such as naphthalene, ammonium compounds, crude light oils and sulphur compounds, are recovered. Coal tar is a heterogeneous mixture of various classes of compounds, as illustrated in **Figure 2.2,** where the compounds of most frequent occurrence in coal tar is shown. These compounds can be divided into two groups:

- LNAPLs [Light Non Aqueous Phase Liquids] containing compounds such as benzene, ethyl benzene, toluene and xylenes.

- DNAPLs [Dense Non Aqueous Phase Liquids] containing compounds such as the PAHs and alkyl-PAHs

The analysis of these compounds is important because of their toxicity and the wealth of information that can be obtained from the quantitative results of the PAHs and their alkyl homologues. The most frequent interpretative uses of the analytical results include advanced chemical finger-printing and hazard identification. The production and transportation of coal tar and light oil in the steel industry has been subject to many accidents involving spills. Experts see the cokemaking process as one of steel industry's areas of greatest environmental concern.

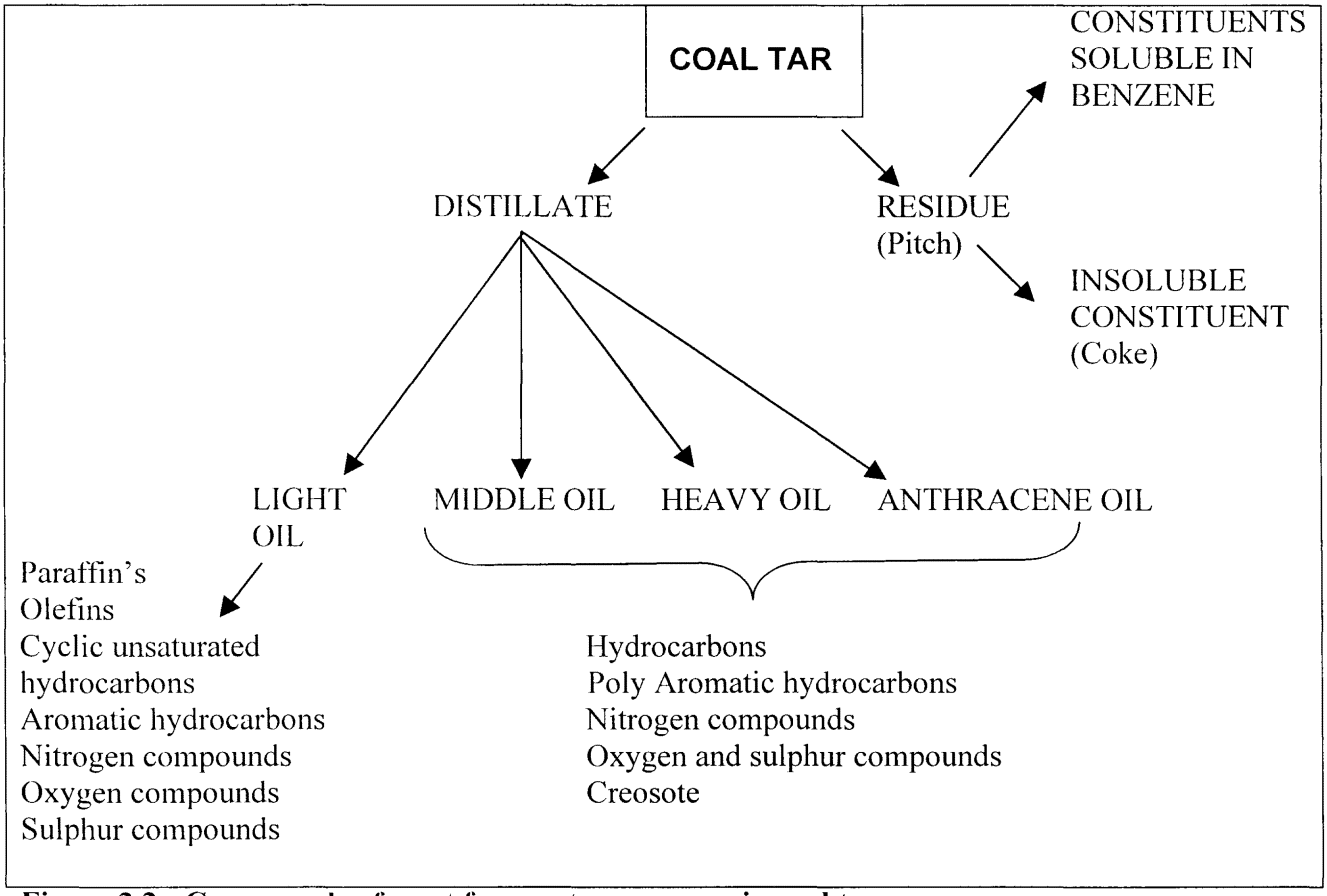

Figure 2.2: Compounds of most frequent occurrence in coal tar

Benzo[a]pyrene, benzo[b]fluoranthene and dibenz[a,h]anthracene are individual PAHs that occur in coal tar related products and are listed as part of the "Top 20 Hazardous Substances" by the ATSDR/USEPA. The focus in this study is, therefore, to investigate the analytical methods that can be used to analyse DNAPL components in soil and water samples and the usefulness of the analytical data obtained for interpretative methods.

The DNAPL problem[2]

Due to continuous spills over a few decades the DNAPLs will form pools or "toxic blobs" of coal tar in the geosphere. DNAPLS also have been called "sinkers" because they are heavier than water and sink until they hit an aquitard, a change in soil type or density. DNAPL movements are directed more by gravity than the flow of groundwater. If the base of the aquifer slopes in one direction, then the DNAPL will flow in the same direction seeking the lowest point. Once they reach the low point of their descent, these pools of toxic waste will slowly dissolve in the surrounding water in the form of small contamination plumes. Since DNAPLs have low solubility points, they can continue releasing small quantities of contaminants into the groundwater for centuries. What makes DNAPLs so dangerous is the fact that they all degrade to other compounds, which might be even more insidious. The formation of DNAPL pools is illustrated in **Figure 2.3**.

Warning signs of a DNAPL problem[2]

Although all forms of NAPLs share low solubility points to varying degrees, only DNAPLs are heavier than water, which make them very difficult to find and to effectively remediate. Typically, the first indication that a site may have a potential DNAPL problem occurs during a phase 1 site assessment. A key element of a Phase 1 assessment is a detailed review of the site's history and use, including a record of all chemicals that may have been released on the site (see **Figure 2.13**). Even after a determination is made that DNAPL compounds were released, the likelihood of a DNAPL groundwater problem will still depend on such factors as the total quantity of the release, the period of time over which the release occurred, and the make-up of the saturated soils. If the site history reveals significant releases of DNAPL compounds, then the next phase of site characterisation should include actual soil and groundwater tests to determine if DNAPLs are present in the soil. Once a determination has been made that a DNAPL problem appears likely, then more invasive procedures are required to measure the severity and extent of contamination. The most common techniques include borings and drilling of monitoring wells at various strategic points and at different depths on the site. Computer modelling of groundwater and contaminant flows at the site and "behavioural" characteristics of the DNAPL can assist in estimating the location and migration of the pool and resulting plume without additional invasive testing. Modelling also helps to further focus sampling efforts to intersect the most likely pathways of contamination and perhaps even to locate the pools of DNAPL. The LNAPLs (light non-aqueous phase liquids) are also useful for modelling purposes and contain compounds such as benzene, toluene, ethyl benzene and xylenes (BTEXs).

Sources and occurrence of PAHs in natural waters

The discharge of coal tar products, refined petroleum products and lubricating oils into the environment is among the common anthrapogenic sources that have degraded the quality of water and sediment, impacting on health and biota. As indicated previously, coal tar contains a wide variety of chemical components that can pollute the hydrosphere.

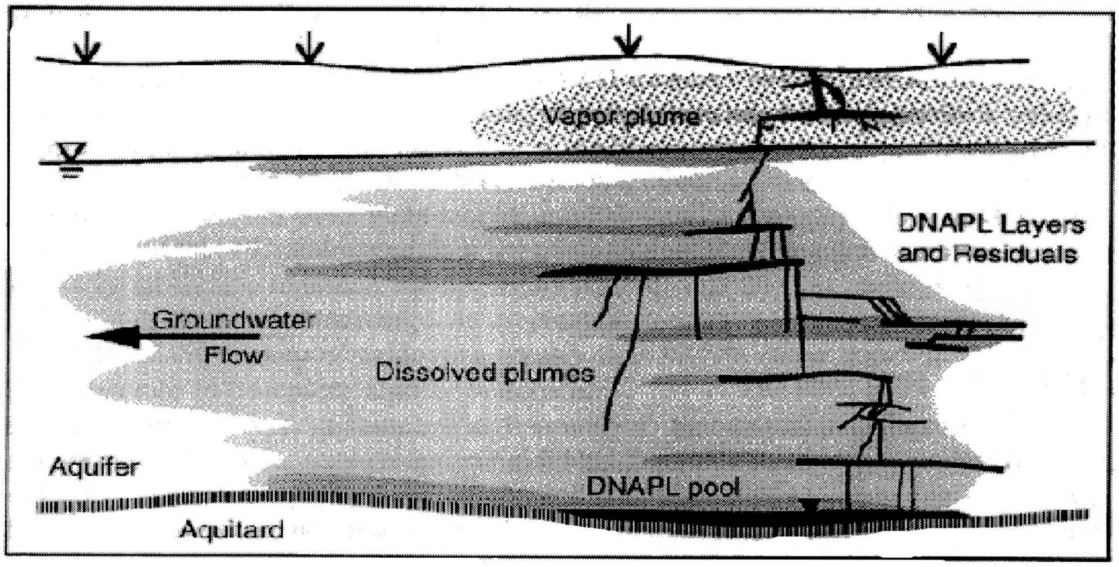

Figure 2.3 : Contaminant Plume with Residual and Pooled DNAPL present (Zoller, 1994)[2]

The concentration of coal tar components in aqueous samples is often in the low part per billion (ng/cm^3) to part per trillion (pg/cm^3) range due to the low solubility of heavy PAHs and partitioning of all PAHs back into stream sediments. Certain aromatic compounds have the potential to damage resources at low levels and can affect the health of animals and humans in a contaminated area. The European Community directive 80/778/EEC states a maximum level for PAHs in drinking water of 0.2 ng/cm^3. Fluoranthene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene were used as indicators to arrive this standard. This is a generic figure that is used for overall assessment of contaminant levels to identify a hazard, but it cannot be used as such for health risk assessments. For that purpose the individual levels of PAHs must be known because individual PAHs each has a different relative potency.

CHEMICAL ANALYSIS TECHNIQUES

During the past decade environmental laboratories have put considerable effort into the development of analytical methods for the determination of PAHs in environmental soil and groundwater samples, and the use of the analytical chemical data in interpretation techniques. These methods mainly rely on a solvent extraction step to isolate the target analytes from the soil or water matrix, followed by a concentration step and finally an instrumental analysis technique. High Performance Liquid Chromatography (HPLC) methods are often preferred for the determination of low levels of PAHs in water samples, due to the sensitivity of the method. A disadvantage of the EPA HPLC method 8310 is its dependence on retention time for compound identification. Another technique that is frequently used by the USEPA is the Infrared Spectroscopy Method 418.1 (EPA, 1983), which is designed to determine the Total Recoverable Petroleum Hydrocarbons, using Soxhlet or sonication extraction. Douglas and co-workers[3] reported that negative method bias may result when samples are analysed by this method

because of:

- Poor extraction efficiency of freon for high molecular weight hydrocarbons
- Loss of volatile hydrocarbons during extract concentration
- Differences in molar absorptivity between the calibration standard and product type
- Fractionation of soluble low-IR-absorbing aromatic hydrocarbons in groundwater during water washout
- Removal of 5- to 6-ring alkylated aromatics during silica cleanup procedure
- Preferential biodegradation of n-alkanes

They also showed that other EPA methods are used for identifying and quantifying certain hydrocarbons present in petroleum products. EPA method 602 (EPA, 1983), 624 (EPA, 1983), and 8240 (EPA, 1986) for analysing volatile hydrocarbons are adequately sensitive, but identify only a limited number of components in petroleum, thus making it difficult to identify the source. To be suitable for advanced chemical fingerprinting, the method must also include the identification and quantification of compounds that are target specific indicators.

Many laboratories have modified EPA and American Society for Testing and Materials (ASTM) protocols to be better suited for the chemical fingerprinting of environmental samples. The combined technique of high-resolution capillary GC and MS is normally ideal for this purpose and is discussed below.

Gas Chromatography/Mass Spectrometry

Sauer and Boehm[4] showed that the identification of a single PAH compound, using EPA Method 8270, is difficult when petroleum hydrocarbons are present in the sample. The method also lacks chemical selectivity (i.e. types of constituents analysed) and chemical sensitivity (i.e. analytical detection limits). These deficiencies yield a larger problem, namely the inability to interpret the data for scientifically defensible environmental damage assessments[4]. Detection limits of 10 pg/cm^3 for individual PAHs are normally required for chemical fingerprinting. Douglas[5] reported an improvement in the detection limit of USEPA Method 8270 from parts per million to the parts per trillion level, by basically:

- using the mass spectrometer in the single ion monitoring (SIM) mode
- concentrating the final extract to 250 µl
- increasing the sample size.

Through this approach the contaminants from petroleum and coal tar sources (PAHs and volatile aromatic hydrocarbons) can be quantified at very low (ppt) levels. Analysis by GC/MS is necessary to enable analysts to focus on complex PAH patterns and to determine concentrations of specific PAHs, including their alkylated homologues and isomers. The complexity and uniqueness of these compounds that contain a wealth of "fingerprintable" information at trace levels can only be studied using a more selective and sensitive analytical method, such as GC/MS.

Solid Phase Microextraction (SPME)

The technique of SPME was introduced by Pawliszyn[6] in 1989 and has shown advantages such as solvent free extraction, relatively short analysis turnover time and possibilities for automation. Typically a fused silica fiber, coated with a thin layer of polymeric stationary phase, is submerged into a water sample or in the headspace of a soil sample to extract the analytes. Once the analytes are adsorbed the fiber is inserted into the injection port of a gas chromatograph for thermal desorption. Phases such as polydimethylsiloxane (non-polar) and polyacrylate (polar) are currently commercially available. Applications of these phases for the analysis of a variety of

volatile components, including PAHs [7,8] have been reported. Liu et. al.[9] and Zhang and Pawliszyn[10] showed the potential of applying headspace SPME for analysing organic compounds in a variety of matrices, including soils and sludges. PAHs can be extracted from aqueous samples with SPME using a non-polar phase fiber such as the 100µm polydimethylsiloxane. The technique has since been developed for a variety of compound classes and has earned a reputation for its simplicity, speed, high sensitivity and selectivity. The extraction of organic compounds using the SPME technique eliminates most drawbacks to extracting organics and detection limits in the pg/cm^3 range can be achieved. SPME is suitable to extract PAHs directly from a water matrix or in the headspace of a soil sample. A schematic diagram of the technique is shown in **Figure 2.4**.

The basic theory behind SPME has been detailed in previous publications[11,12]. It has also been reported[13] that the distribution coefficient (K) of alkyl substituted compounds vary with different degrees of alkylation. This is because PAHs with side chains are more soluble in the hydrophobic stationary phase, improving the partitioning into this phase. This is an advantage for chemical characterisation purposes because it will result in an increase in the detection limits of alkyl-PAHs, which is ideal or the purpose of this study. Due to the absence of standards, however, the quantification of alkyl-PAHs is complex, especially when using a equilibrium technique such as SPME. This is due to the differences in extraction efficiencies with a single extraction step, which will introduce errors when using the parent PAH response factors and internal standards. Typically, an enhanced profile will be obtained for compounds with a higher degree of alkylation. It is possible to overcome this problem by using the technique of multiple extraction MESPME. This technique calculates the total area of an analyte in solution by using the data of two consecutive extractions and, therefore, allows for differences between the extraction efficiency of parent and alkyl-PAHs.

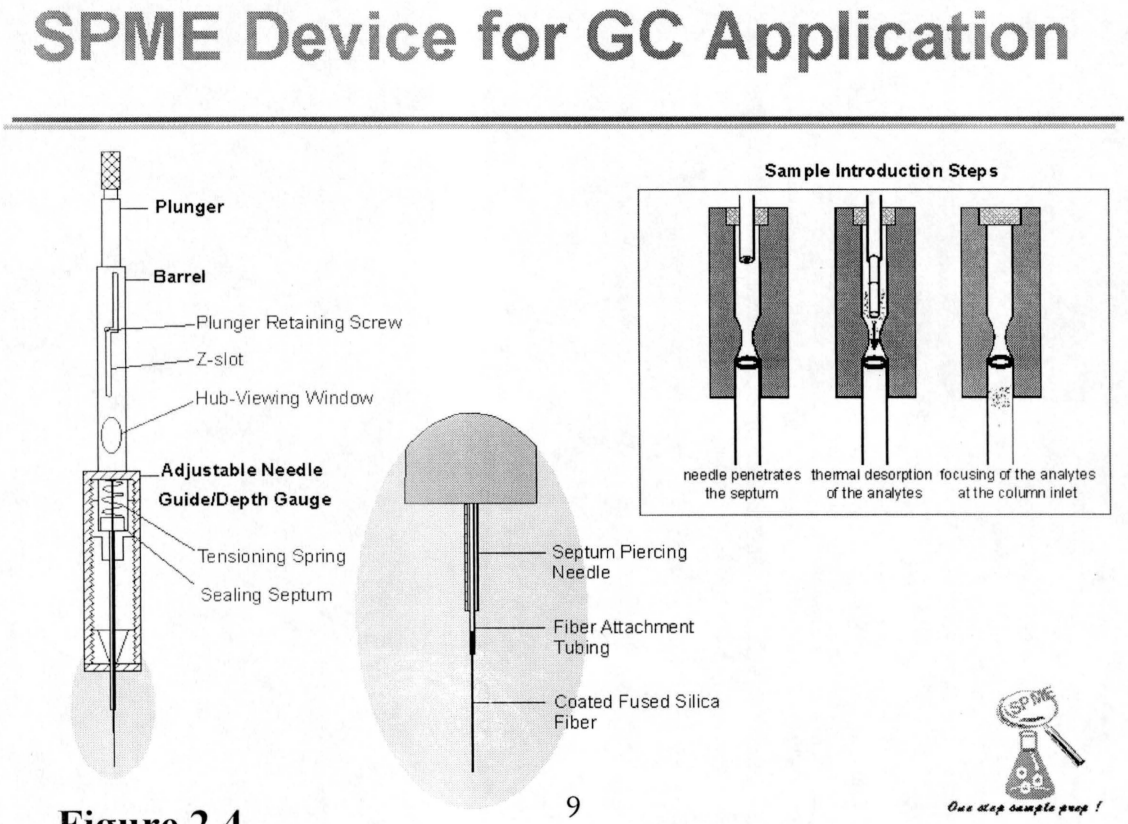

Figure 2.4

Accelerated Solvent Extraction

Pressurised Liquid Extraction (PLE), also known as Accelerated Solvent Extraction[14] (ASE™), is a relatively new extraction technique. The method is based on the principle that a solvent is pumped into an extraction cell that contains the soil sample, which is then brought to an elevated temperature and pressure. A schematic diagram of the technique is shown in **Figure 2.5**. This method replaces the traditional Soxhlet extraction technique. The advantages of PLE are the use of less solvent, convenience, efficiency and analysis speed. Typically, a 10gram sample can be extracted in about 15 minutes with a total solvent consumption of about 15 cm^3. PAH recoveries are reported to be equivalent to traditional methods and meet the requirement for the extraction of solid waste as described in USEPA[15] method 3545. Following the extraction step, the extract is transferred from the heated cell to a standard collection vial for clean-up, pre-concentration and analysis. For a quantitative determination of individual PAHs, the extraction step is then followed by a GC/MS analysis.

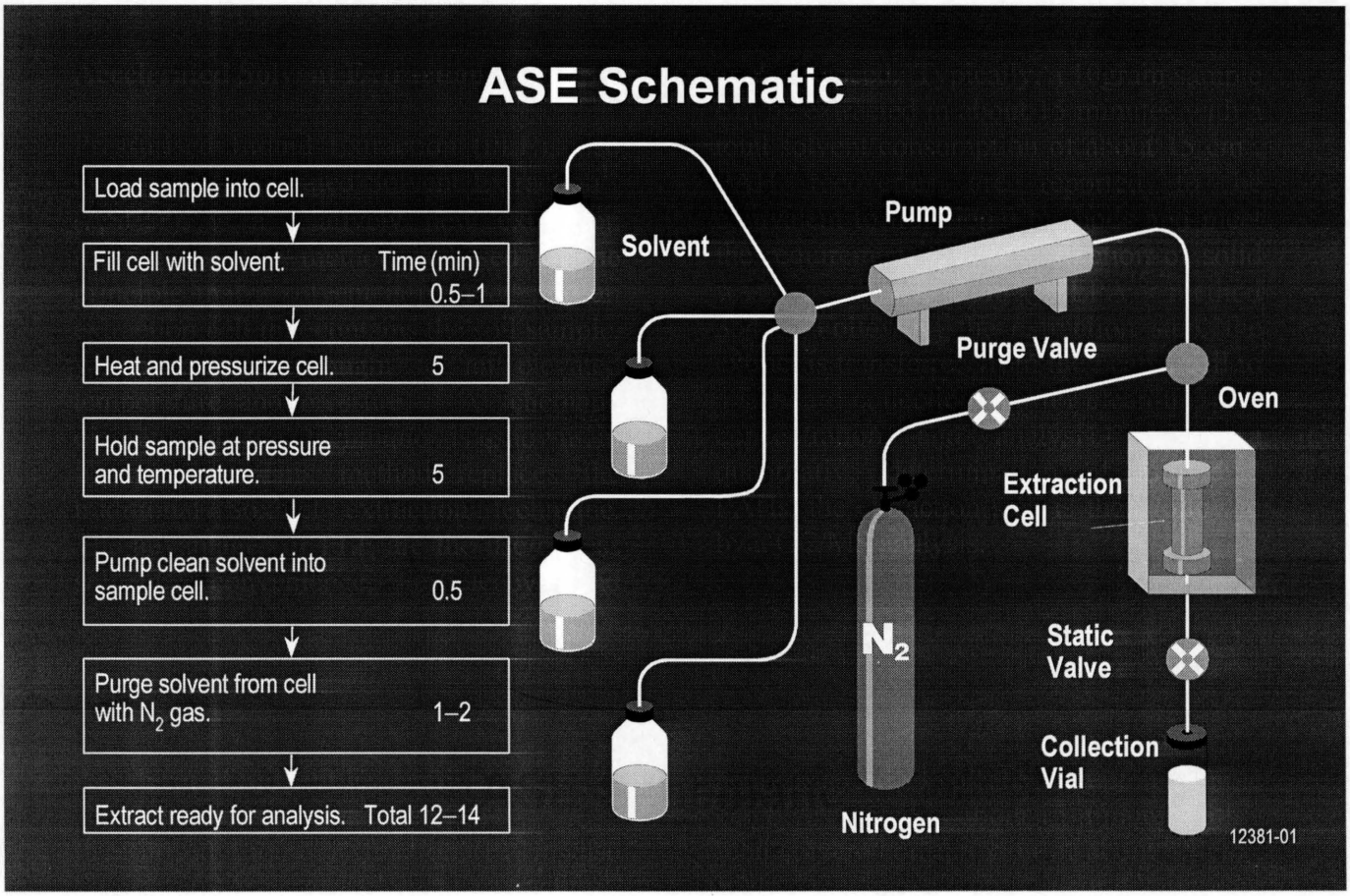

Figure 2.5: ASE Schematic Diagram

CHEMICAL CHARACTERISATION

The development of Chemical Fingerprinting Techniques

In the following paragraph a review about hydrocarbon fingerprinting, which was published by Page et. al.[16], is discussed. They indicated that most work conducted in organic geochemistry before the 1960s focused on the exploration of fossil fuels. Petroleum chemistry and hydrocarbon fingerprinting developed further in the 1970s with the passage of certain environmental regulations in the US (e.g. the clean water act). GC was one of the earliest techniques to examine alkane distributions in fresh oils. The application of alkane fingerprinting was very limited because the GC patterns changed over time due to the effects of evaporation, biodegradation, dissolution and photo-oxidation. Although GC analyses of alkanes are still in use, they represent only part of fingerprinting methodology. The GC methods have since been replaced by more advanced techniques such as GC/MS, which focus on other classes of compounds, especially the alkyl-PAHs. Fingerprinting of hydrocarbons is made possible by the variety of individual PAH compounds found in hydrocarbon sources and in the great variability in the relative abundances of these compounds among different sources. PAH analyses were first applied to oil spills to determine the composition of the more toxic fraction of petroleum and to examine the weathering of hydrocarbons. After the Exxon Valdez tanker incident on the 24th of March 1989 and the release of 11 million gallons of oil into Prince William Sound, a need existed for advanced method of chemical characterisation. It was necessary to investigate the rates of weathering of the oil, the changes that occurred during these weathering processes and to differentiate between petroleum sources and coal tar sources.

Chemical Fingerprinting objectives

The interpretation methods that were developed during the *Exxon Valdez* investigations[17], serve as a basis for environmental pollution characterisation. Hydrocarbon fingerprinting involves the comparison of specific chemical patterns that will distinguish potential sources from each other and from background levels. For example, conventional gas chromatograms of diesel fuel, lubricating oil, crude oil and coal tar can reveal the presence of PAHs in all cases, but they exhibit different chromatographic profiles. Chemical mixtures that leak into the water leave behind a characteristic pattern. A suit of sampling, chemical analysis and data interpretation strategies enables chemists to identify specific contaminant sources and to link a wide range of pollutants to their sources. Advanced chemical fingerprinting is the appropriate technique for land-based and aquatic site contamination assessment and cost allocations for remediation of problems associated with crude oil releases. This approach employs chemical analysis technology to identify the constituents of complex chemical mixtures, and/or unique chemical markers, then matches the patterns of those constituents against chemical patterns of potential sources. As indicated in the review by Page et.al.[16], chemical fingerprinting has, over the last two decades, evolved into a science by which original source(s) of complex chemical mixtures (e.g. petroleum or coal tar) can often be identified. They showed that the relative abundance of key individual compounds (especially two to four ring PAHs, and three ring heterocyclic dibenzothiophenes) forms a chemical pattern that can be used for source identification. There are two major objectives[5] in the chemical characterisation of contamination in environmental samples:

Short-term : To characterise the hazard and to determine the concentration of the environmentally important hydrocarbon constituents in the contaminated samples. These constituents include those that are immediately toxic to organisms and those

that would be considered carcinogenic to organisms. The intent is to determine the potential toxicity of the coal tar components as it is transported in the water and to help estimate what components would be available to affect a particular habitat.

Long-term : The application of advanced chemical fingerprinting to determine the concentration of major hydrocarbon constituents that would be valuable as source indicators and of the fate and weathering of the coal tar in the environment. Concentrations of key individual components or reference compound are used to evaluate the coal tar's behaviour and its toxicity as it persists in the environment. The following advances in chemical fingerprinting techniques have been reported:

Source discrimination based on the hydrocarbon distribution pattern

The compounds that are commonly measured for these studies include the 16 U.S. EPA priority pollutant PAHs, their associated alkylated homologues and selected heterocyclic compounds. A list of analytes and abbreviations are given in **Table 2.1**. The method used for source discrimination involves profiling the *alkyl substituted homologous series*[16], e.g. C_0- C_4 naphthalenes, C_0 - C_4 phenanthrenes, C_0 - C_4 fluorenes and C_0 - C_4 chrysenes. The results are normally presented as an analyte profile histogram and accurate quantitative data for each alkyl homologue is necessary for this purpose. The parent PAH is accurately quantified with the help of internal standards and the alkyl homologue concentrations are then calculated, assuming the same response factor for each respective molecular ion signal. All the isomers within an alkyl homologue are grouped together for this purpose. The fundamental differences in the distributions of PAHs are used to distinguish between different sources. The characteristic profiles of various sources of pollution, which were obtained from AD Little Inc, Acorn Park, Cambridge, are illustrated below:

Petrogenic hydrocarbons (Figure 2.6): These sources are characterised by their distributions of alkylated homologues of naphthalene (N), fluorene (F), phenanthrene (P), dibenzothiophene (D) and chrysene (C), where the parent PAH for each series is least abundant[18].

Pyrogenic hydrocarbons (Figure 2.7): These sources are combustion related that produce PAH distributions dominated by the parent compounds of two to four ring PAHs and containing large quantities of fluoranthene (FL) and pyrene (PY)[18]. The characteristic profiles are used to establish chemical matches between one "suspect" oil and the petroleum in an environmental sample, and to distinguish between petrogenic and non-petrogenic sources[3].

Degraded oil (Figure 2.8): The profile of degraded oil is typical petrogenic and dominated by phenanthrenes, dibenzothiophenes and chrysenes. A build-up of heavy PAHs and C_3 - C_4 alkyl PAHs is observed in degraded samples. The build-up of C_4-P > C_3-P > C_2-P can, for example, be observed in the figure. It is also evident that the C_1- to C_4-chrysenes are very resistant towards weathering as only a slight change in the relative abundances of alkylated chrysenes can be observed.

Diesel oils (Figure 2.9): The characteristic profile of typical diesel oil is dominated by the two and three ringed structures, with the phenanthrenes showing a typical petrogenic profile. Also note the absence of heavy PAHs in the profile.

Atmospheric deposition (Figure 2.10): A characteristic profile is mainly dominated by heavy PAHs (four to six ring structures). Atmospheric deposition normally occur near airports or industry where aerosols fall to the ground.

Creosote (Figure 2.11): Anthracene, phenanthrene, chrysene, fluoranthene and pyrene dominate the profile (naphthalenes and other light PAHs are absent).

Table 2.1: Analytes measured for source discrimination based on hydrocarbon distribution patterns showing abbreviations

Naphthalene	N
C_1- Naphthalenes	C1-N
C_2- Naphthalenes	C2-N
C_3- Naphthalenes	C3-N
C_4- Naphthalenes	C4-N
Acenaphthylene	AE
Acenaphthene	AC
Biphenyl	BI
Dibenzofuran	DI
Fluorene	F
C1-Fluorenes	C1-F
C2-Fluorenes	C2-F
C3-Fluorenes	C3-F
Phenanthrene	P
Anthracene	A
C1-Phenanthrene/anthracenes	C1-P
C2-Phenanthrene/anthracenes	C2-P
C3-Phenanthrene/anthracenes	C3-P
C4-Phenanthrene/anthracenes	C4-P
Dibenzothiophene	D
C1-Dibenzothiophene	C1-D
C2-Dibenzothiophene	C2-D
C3-Dibenzothiophene	C3-D
Fluoranthene	FL
Pyrene	PY
Benzo[a]anthracene	BA
Chrysene	C
C1-Chrysene	C1-C
C2-Chrysene	C2-C
C3-Chrysene	C3-C
Benzo[b]fluoranthane	BB
Benzo[a]pyrene	BAP
Benzo[ghi]perylene	BP
Dibenz[ah]anthracene	DA
Indeno[123-cd]pyrene	IP

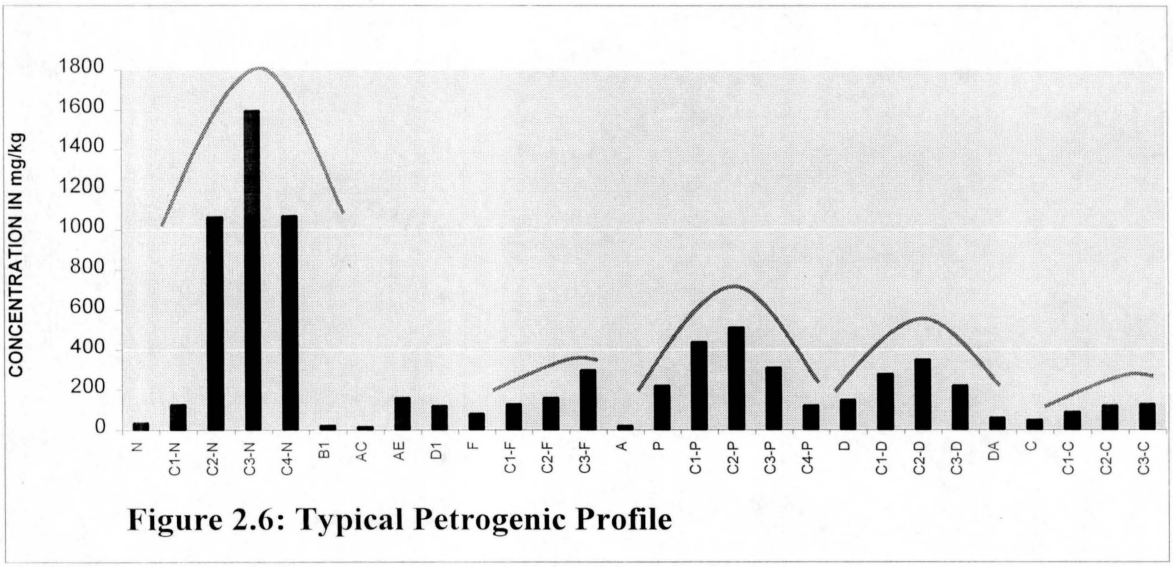

Figure 2.6: Typical Petrogenic Profile

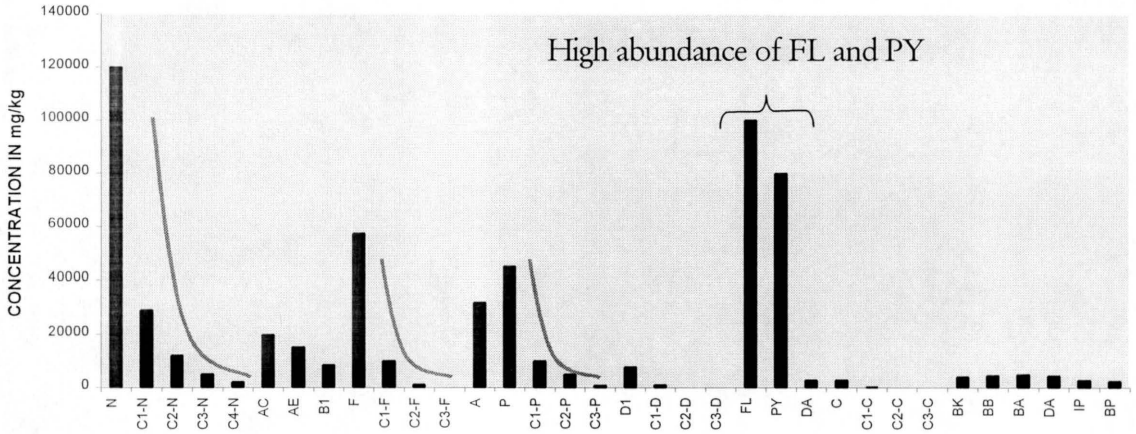

Figure 2.7: Typical Pyrogenic Profile

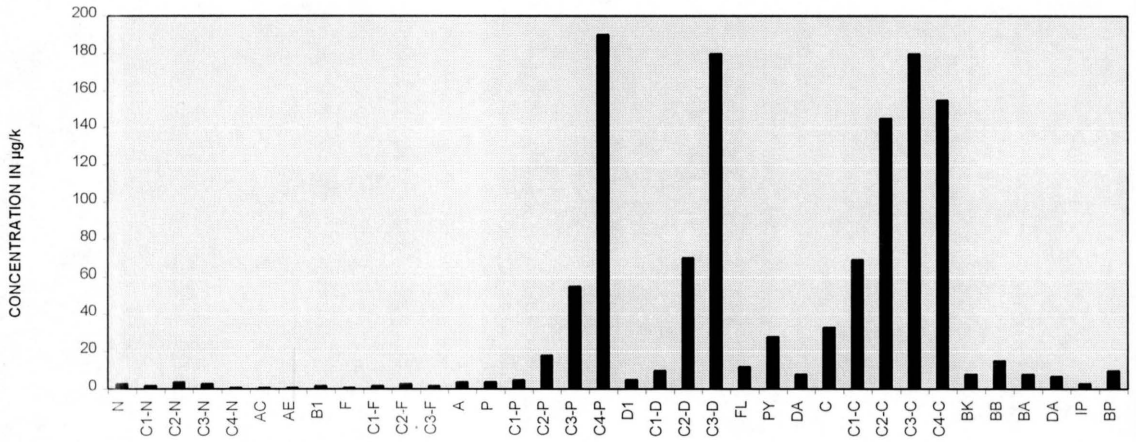

Figure 2.8: Typical Degraded Heavy Oil

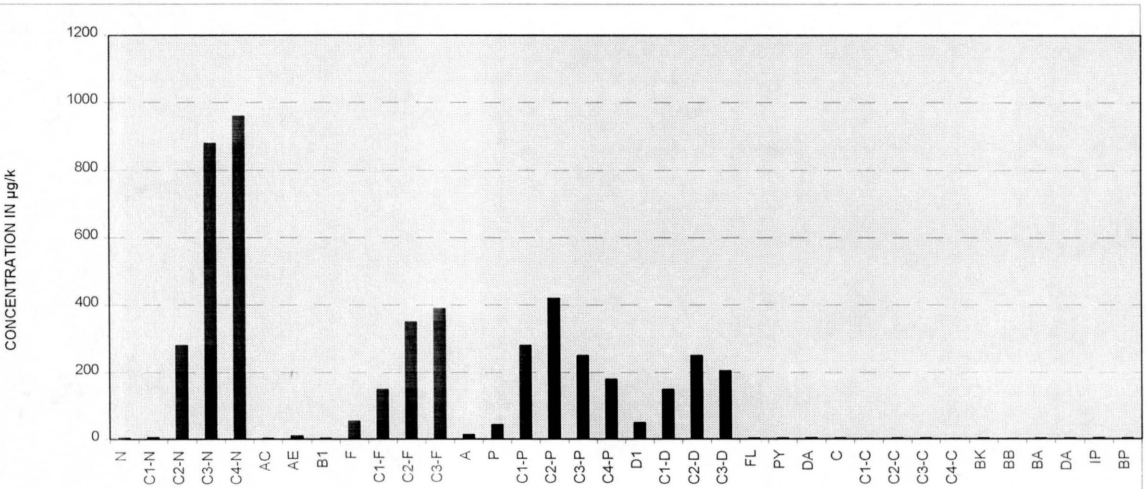

Figure 2.9: Typical Diesel Profile

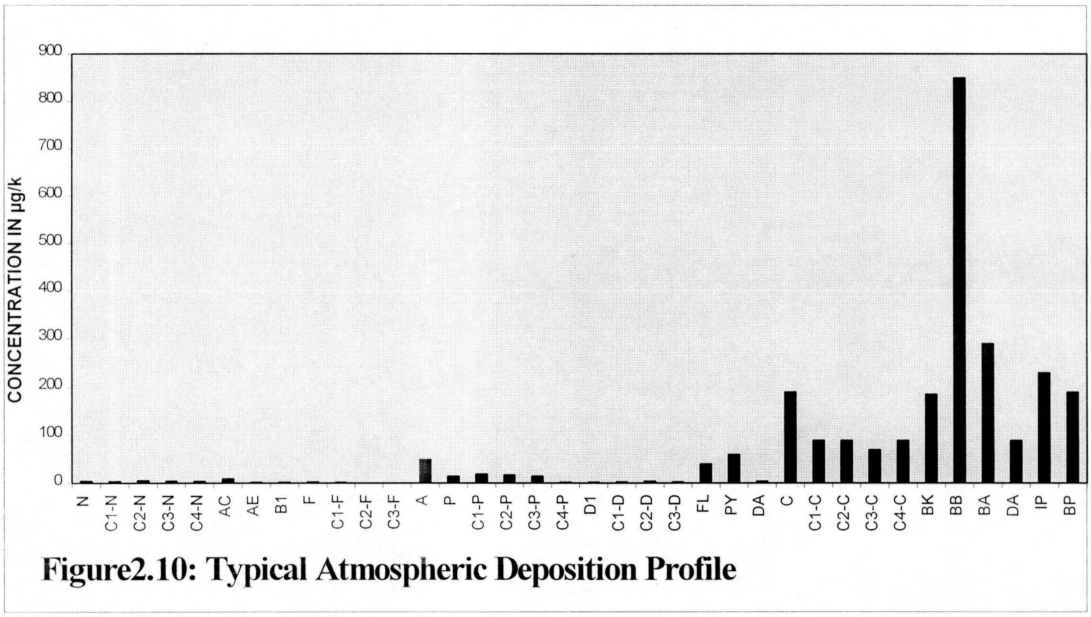

Figure2.10: Typical Atmospheric Deposition Profile

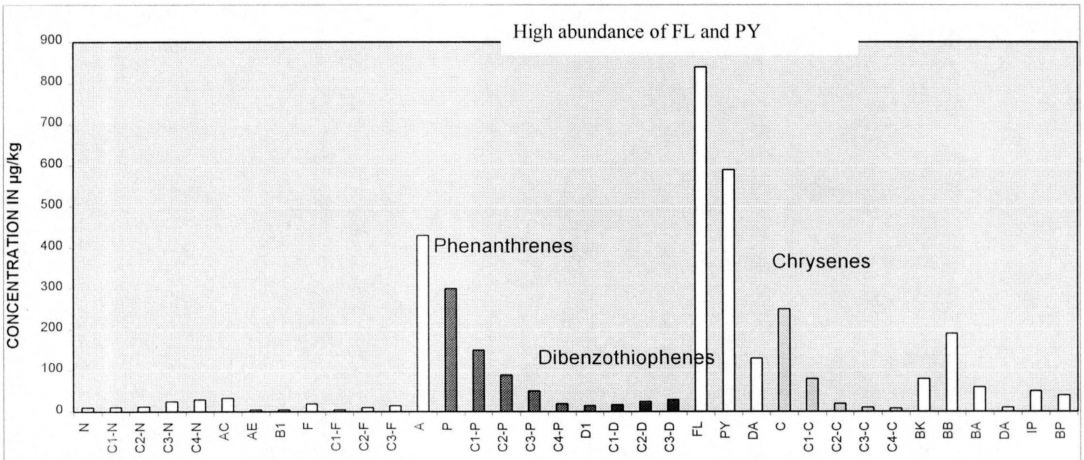

Figure 2.11: Typical Creosote Profile also showing the relative abundances of P- D- and C-homologues

Relative amounts of phenanthrenes, dibenzothiophenes and chrysenes

The relative amounts of these compounds in an environmental sample are used to differentiate among different crude oils, petroleums and refined petroleums[16,19]. In crude oil, for example, similar abundances of phenanthrenes and dibenzothiophenes are found, with the chrysene series largely absent in some cases (e.g. Exxon Valdez crude oil)[16]. Major differences in the PAH fingerprints between petroleum sources have previously been found in the relative amounts of dibenzothiophenes[18]. Creosote, on the other hand, contains significant amounts of five to six ringed PAHs with a low relative abundance of dibenzothiophenes. The relative amounts of phenanthrenes, dibenzothiophenes and chrysenes in creosote are shown in **Figure 2.11**.

The use of source ratios

A source ratio is a ratio between two characteristic analytes or group of analytes in a source, which must be ideally unique to that particular source. For the ratio to stay constant the particular compounds must degrade at similar rates and have similar

chemical and physical properties. Page et. al.[16] reported that selected alkyl-PAH homologues are (1) relatively resistant to weathering influences and (2) occur in relatively different concentrations in different petroleum sources. Douglas et. al.[20] reported that the ratios of C_2-dibenzothiophenes to C_2-phenanthrenes (C_2-D/C_2-P) and ratios of C_3-dibenzothiophenes to C_3-phenanthrenes (C_3-D/C_3-P) stay relatively constant, even when weathering has degraded up to 98% of the total PAHs. They have also demonstrated the stability and usefulness of the source ratio over a wide range of weathering and biodegradation of different oils using double ratio plots of C_3-D/C_3-C (weathering ratio) versus C_3-D/C_3-P (source ratio). The dibenzothiophene group of compounds (C_0-D to C_4-D) was found to vary the most widely in different sources, as their concentrations reflect the sulphur content of the source[20]. The resistance to weathering, combined with the source specific nature of the C_3-D/C_3-P ratio in spilled oil, makes them especially useful for the identification of multiple sources of hydrocarbons[20].

The use of weathering ratios

Ratios of compounds that change substantially with weathering and biodegradation are termed "weathering ratios". Weathering is the combined effect of dissolution, biodegradation and photo-oxidation. The bacterial degradation within a PAH homologous series is[19]:

C_0-PAH > C_1-PAH > C_2-PAH > C_3-PAH > C_4-PAH

During a study of hydrocarbon sources following the Exxon Valdez oil spill, Page and co-workers[16] reported the following major compositional changes in sediments and soils:

- Pronounced decrease in naphthalenes (N) relative to other PAHs, which occurs rapidly in the first few days of exposure to the atmosphere.
- Development of a "water-washed" profile for each of the petrogenic groups so that each group has the distribution: Parent (C_0)<C_1<C_2<C_3.
- Gradual build-ups in the relative abundances of the phenanthrenes, dibenzothiophenes, and chrysenes as the more soluble components are lost. The chrysenes exhibit the most pronounced relative increase because of their low solubilities in water, and resistance to microbial degradation.

In the study by Douglas and co-workers[20] concerning the environmental stability of petroleum hydrocarbons, they reported that compounds that weather to below their respective detection limits during the early stages of oil degradation cannot provide reliable weathering ratios. Bence and co-workers[21] developed weathering indicators of varying sensitivity for different stages of the weathering process. The ratio of C_3-N/C_2-P is a sensitive ratio and can for example be used for light product degradation such as diesel fuel. A less sensitive weathering ratio such as C_3-D/C_3-C may be used for crude oil degradation.

The use of individual isomer distributions

This method involves the profiling of *isomers* of a certain alkyl homologue[22], e.g. isomers of C_2-phenanthrene or C_3-dibenzothiophene. A typical profile for C3-dibenzothiophene isomers is shown in **Figure 2.12**, illustrating the differences in the relative distribution of individual isomers. For this purpose, an accurate quantitative result is not required for each isomer, but the result is presented as a single ion chromatogram, based on the major ion of the homologue, showing the relative intensities of all the isomers. Page et.al.[16] have shown that the differences in the relative distribution of individual isomers within a homologous series, such as the C_3-dibenzothiophene isomers, present opportunities for fingerprinting similar petroleum hydrocarbon sources.

They indicated that:

- the C_3-dibenzothiophenes as a group, represent more than 20 individual abundance's in oils from different sources
- these isomer distributions reflect the source carbon, depositional environment during formation and the existence of any diatonic sources.

Phases of an advanced chemical fingerprinting Strategy

The chemical characterisation of pollutants in the geosphere and hydrosphere is an integral part of the fingerprinting strategy. A typical Advanced Chemical Fingerprinting (ACF) project[17] is a sequence of separate but strategically related steps that can be explained in the phases shown if **Figure 2.13**.

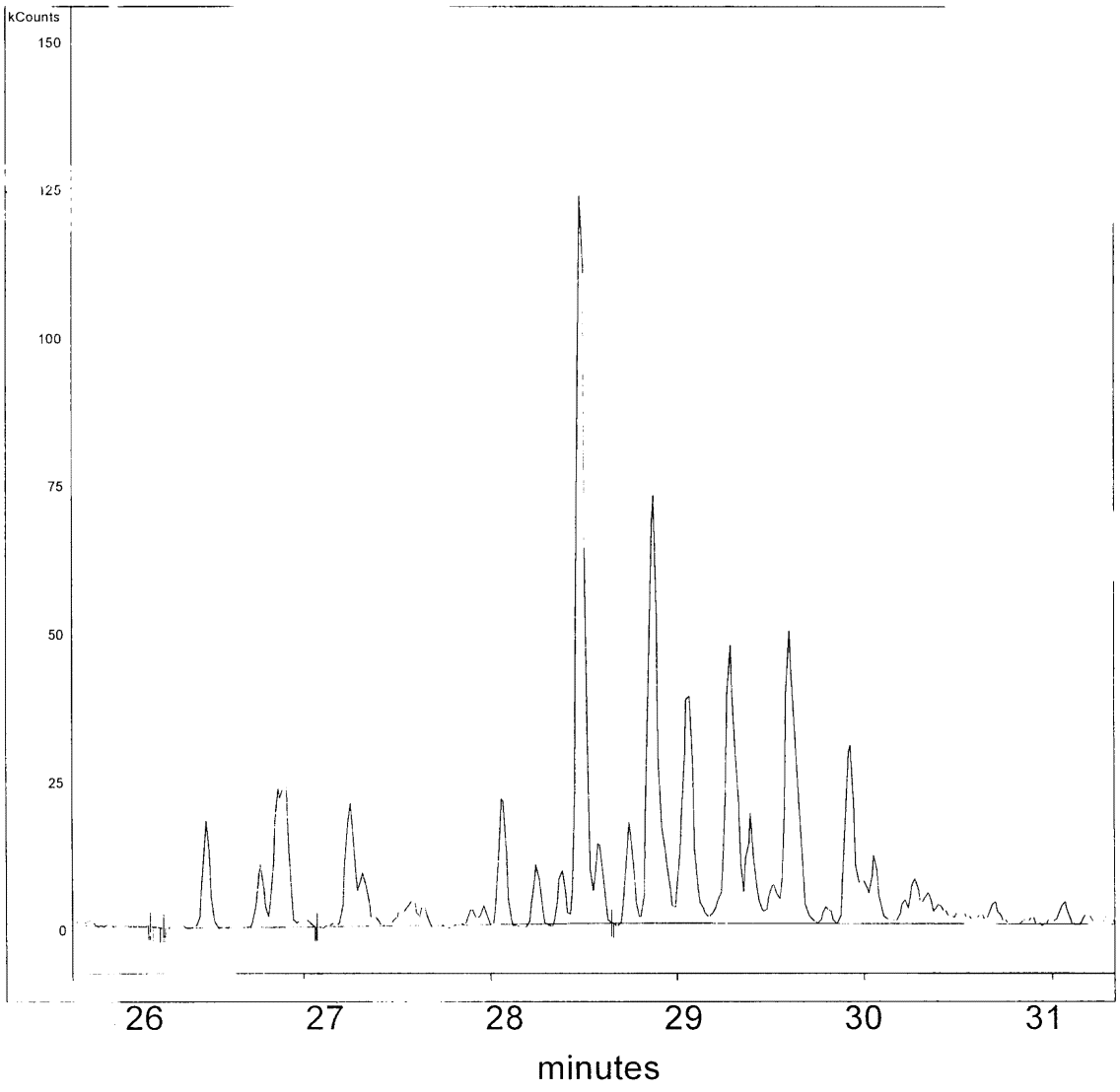

Figure 2.12: Example of a Selected Ion Chromatogram of C3-dibenzothiophene isomers – (m/z = 226 and 211).

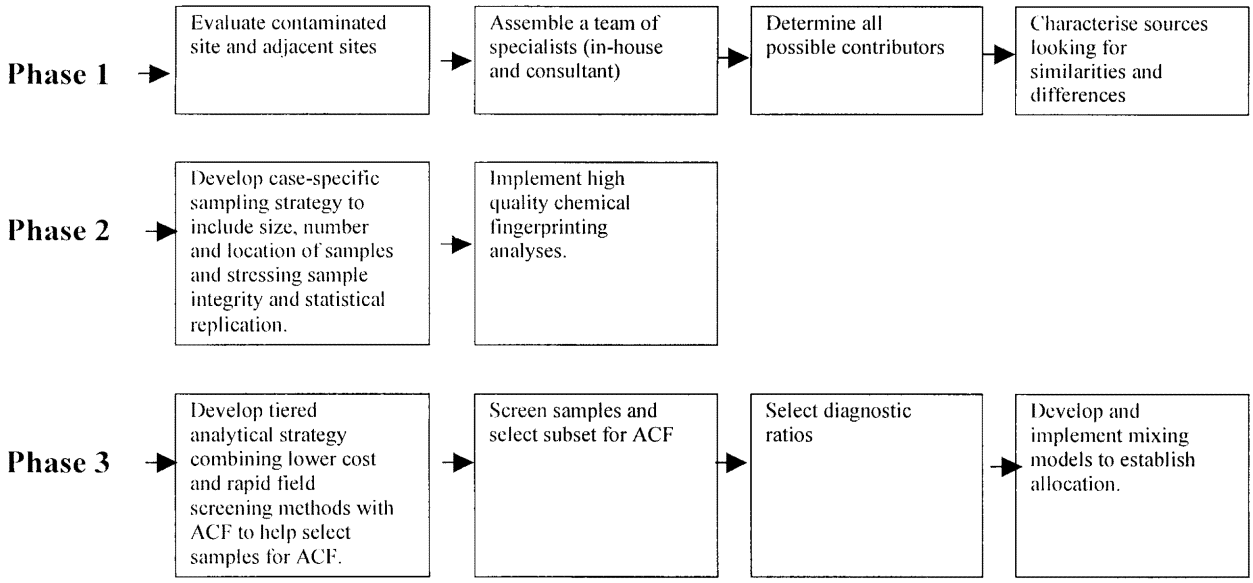

Figure 2.13: Phases of an Advanced Chemical Fingerprinting (ACF) project [17]

Chapter 3

CRITERIA FOR CHEMICAL METHODS DEVELOPED AND INVESTIGATED IN THIS STUDY

ANALYTICAL DESIGN FEATURES

There is a constant demand for screening methods capable to analyse at lower levels, with shorter turnaround times and lower analysis cost. Methods should be reliable enough to characterise the type and source of contamination, as this forms the basis of sound decisions and action required to protect public health and to improve the quality of the environment. High quality environmental measurements are required for a number of purposes, such as:

- Compliance with legislation
- Characterisation of hazardous waste sites
- Monitoring of the effectiveness of measures taken to reduce contamination
- Monitoring of site remediation
- Decisions and actions regarding waste disposal
- Studies related to the degradation of PAHs in the environment

The need for analytical methods that can provide expedited characterisation of hazardous waste sites is critical. Site remediation is often delayed during the site characterisation step because of slow turnaround times of sample analyses. In addition, once a sample is removed from the location, its chemical integrity is always a concern. Methods that minimise sample handling and transport are needed to improve data quality. The analytical methodology developed in this study is designed to fulfil these needs.

To achieve the objectives for a high quality chemical analysis that is essential for a successful fingerprinting strategy, four important features must be taken into account:

1. Selection of the specific constituent target analytes
2. Selection of analytical methods and performance characteristics
3. Data use, interpretation and assessments
4. Quality assurance and quality control

The close relationship between sampling, analytical determinations, data evaluation and interpretation and environmental management is shown is **Figure 3.1**.

Selection of specific constituent target analytes

This study is focused on coal tar polluted water and soil samples, which contains a heterogeneous mixture of PAHs, alkyl-PAHs and heterocyclic compounds. The analytes targeted for this study are those listed in **Table 2.1.** In the case of the alkyl-PAHs a C_1-PAH indicates a single methyl group attached to the specific PAH, a C_2-PAH the sum of all dimethyl or ethyl isomers and a C_3-PAH the sum of all trimethyl, methylethyl and propyl isomers.

Selection of analytical methods and performance objectives

Contaminated coal tar samples can also contain refined petroleum products (diesels, mineral oils, fuel oils, and lubricating oils). These compounds are co-extracted with the PAHs because they are non-polar and can cause matrix interference.

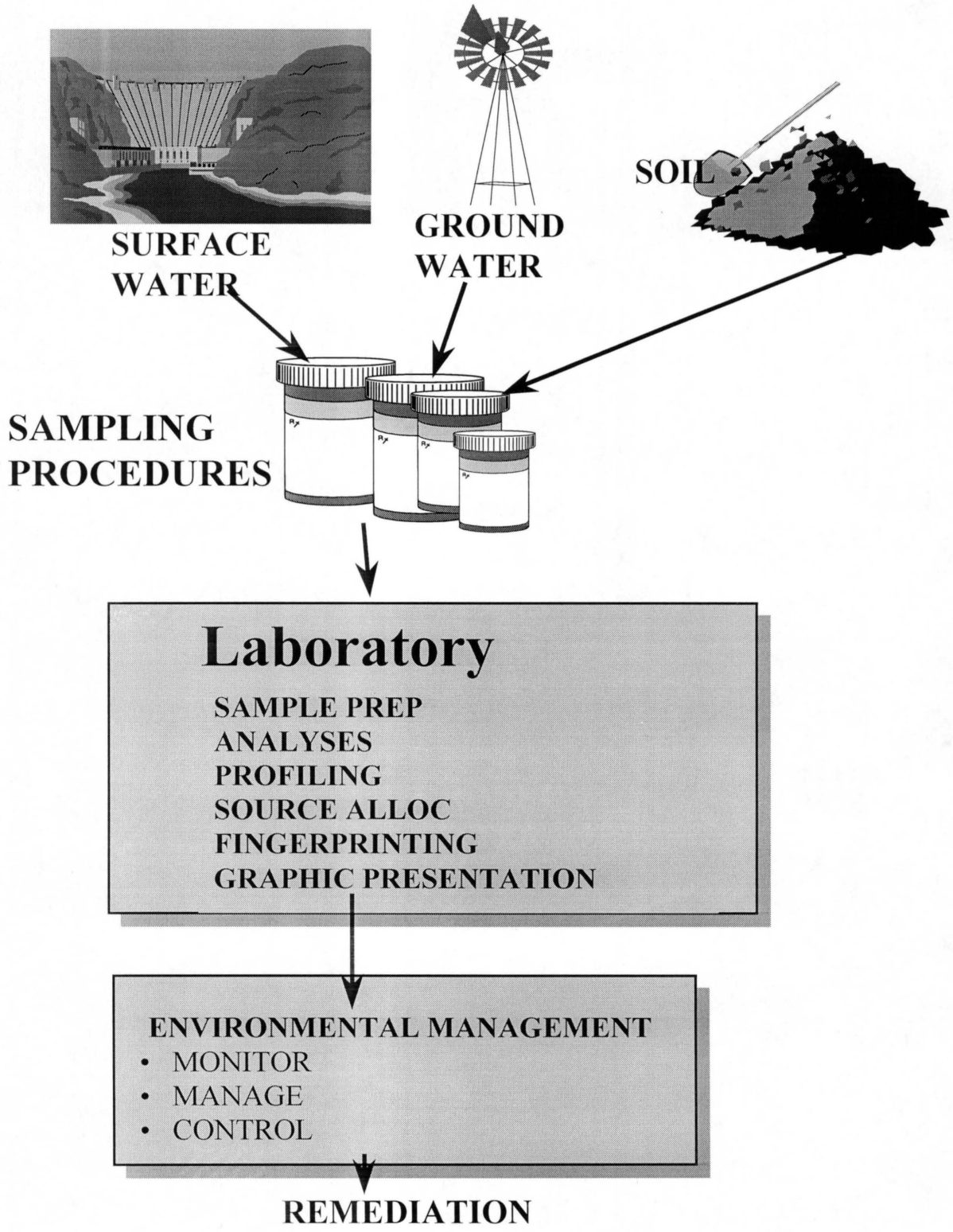

Figure 3.1: Relationship between sampling, the laboratory and Environmental Management

Because the range of matrices in environmental samples is very large it is difficult to develop a "tailor made" strategy for each case. A basic requirement from a quality point of view is that the overall trueness and precision must be adequate for the objective of the measurement. The selection of the analytical method then also depends on the regulatory requirements and other data interpretation objectives. The existing USEPA method were used as a guideline for this study, but considering the inadequacies that were discussed in **Chapter 2**, attention was given to specific modifications and refinements for methods to be more suitable for the characterisation of coal tar pollution. New methods were developed using SPME-GC/MS, mainly because of the advantages associated with this technique, namely simplicity, efficiency, selectivity and sensitivity. Modified and newly developed methods were validated to ensure that it is fit for the intended purpose and a range of performance characteristics was investigated for this purpose. Traceability to a recognised reference (pure substance or certified reference material) was demonstrated where possible.

Criteria for Data Interpretation and Assessment Use

Chemical Characterisation

As shown earlier, the detection of C_1-, C_2- and C_3-isomers in an alkyl homologous series plays an important role in the development of source or weathering ratios. Another assessment use of isomer data is to compare the chemical composition and concentration of spilled, unweathered coal tar with the composition and concentrations of the residual coal tar in the environment. Analytical data obtained from these comparisons allow the analyst to trace the fate, weathering, and environmental partitioning of different fractions of the tar and predict the potential long-term impact of the spilled tar. Reliable determination of trace level contamination is required for these purposes. The objective was, therefore, to achieve a high degree of specificity to distinguish the isomers in an alkyl homologue from other interfering analytes or other compounds, with the required sensitivity.

Hazard Identification

One of the objectives for environmental measurements is to check compliance with legislation. The standard used for hazard characterisation this study is based on the National Primary Drinking Water Regulations and Health Advisories of the USEPA[23] and the Agency for Toxic Substances and Disease Registry (ATSDR)[24]. Health risk based guideline concentrations of PAHs in water can be calculated on an age-weighted exposure distribution. For a lifetime cancer risk of one in a million, the risk-based concentration for benzo[a]pyrene is 0.01 ng/cm^3. For non-carcinogens the guideline concentrations are normally higher, based on exposure to a reference dose (RfD). For naphthalene, for example, the guideline value is 1500 ng/cm^3. Limits for the PAHs that are listed in these regulations are summarised in **Table 3.1.** The table shows data that are available for some parent PAHs, and except for 2-methyl naphthalene, no data are available for alkyl-PAHs. The data was used as a guideline in the development of analytical methodology, where the objective was to achieve a quantification limit of individual PAHs that is lower than the guideline levels specified in the USEPA regulations. For the purpose of a health risk assessment and chemical fingerprinting a high degree of sensitivity and low limits of detection are necessary. Due to the toxicity of, for example, the PAH reference compound benzo[a]pyrene, a detectable concentration of at least 0.01 ng/cm^3 in groundwater samples is required[18]. The methods were therefore developed to meet these sensitivity requirements.

Table 3.1: Drinking Water Regulations and Health Advisories of the USEPA and ATSDR

CARCINOGENS	NONCARCINOGENS	1999 Rank as a ATSDR Priority Hazardous Substance	Cancer Group [a]	Drinking Water Standard MCL ($\mu g/cm^3$) [b]	HEALTH ADVISORIES FOR DRINKING WATER (70 kg Adult)		
					ATSDR MRLs mg/kg/day [c]	USEPA RfD mg/kg/day [d]	USEPA guideline concentration for a 10^{-6} Cancer Risk (ng/cm^3) [e]
	Anthracene	-	D	-	10	0.3	11000
	Acenaphthene	159	D	-	0.6	0.06	2200
	Fluorene	275	D	-	0.4	0.04	1500
	Fluoranthene	101	D	-	0.4	-	1500
	1-methyl naphthalene	-	-	-	0.07	-	-
	2-methyl naphthalene	-	-	-		-	1500
	Naphthalene	75	D	-	0.02	0.02	1500
	Phenanthrene	216	D	-	-	-	1500
Chrysene		115	B2	-	-	-	2.09
Benzo[g,h,i]perylene		-	-	-	-	-	0.42
Pyrene		253	D	-	-	0.03	0.11
Benz[a]anthracene		35	B2	-	-	-	0.092
Benzo[b]fluoranthene		10	B2	-	-	-	0.092
Indeno[1,2,3-cd]pyrene		185	B	-	-	-	0.092
Dibenz[a,h]anthracene		17	B2	-	-	-	0.0092
Benzo[a]pyrene		8	B2	0.0002	-	-	0.0092

Notes:

[a] - Weight of evidence = EPA class designating overall evidence that a substance causes cancer in humans
A = Known human carcinogen
B1 = Probable human carcinogen, limited human data
B2 = Probable human carcinogen, inadequate or no human data
C = Possible human carcinogen
D = Not classifiable as human carcinogen
E = No evidence of carcinogenicity for humans

[b] – Maximum contaminant level (MCL) - The maximum permissible level of a contaminant in water which is delivered to any user of a public water system. MCLs are enforceable standards.

[c] – Minimal Risk Level (MRLs) for Hazardous Substances. An MRL is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse noncancer health effects over a specified duration of exposure.

[d] – Reference Dose (RfD). An estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime.

[e] – Guideline 10^{-6} Cancer Risk. Health risk based guideline for drinking water corresponding to an estimated lifetime cancer risk of 1 in 1,000,000.

[f] – Lifetime Consumption. The concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for a lifetime exposure.

Quality Assurance (QA) and Quality Control (QC) Objectives

The awareness of QA for environmental measurements has increased considerably during the past few years. This is mainly due to the fact that inaccurate environmental analyses can lead to severe economic and social implications, such as undetected hazards or identification of unreal hazards. The analytical methods developed in this study were required to have certain performance characteristics and to conform to the following Data Quality Objectives (DQO), as summarised in **Table 3.2**.

Table 3.2: Data-quality objectives for groundwater and soil studies

PARAMETER	EXPLANATON OF OBJECTIVES	Data Quality Objectives (DQO) required for this study	Comparative Standard Method DQO's (USEPA, 1986, SW 846 Method 8270)
Accuracy or trueness of the measurements	The main objective was to establish the true concentration of contaminants at low levels and in complex matrixes. CRMs were used to determine the recoveries of PAHs in soil extracts. Spiking techniques were used to determine recoveries for water samples, in which case CRMs are unavailable.	80 - 120% recovery for individual parent PAHs	18 – 137% recovery for p-Terphenyl-d_{14}
Precision	To obtain agreement of measurements under specific conditions, using the same instrument, same analyst and analysing samples in batches.	< 15% RSD	N/A
Quantification limit (QL) for individual PAHs	A Quantification limit of ten times lower than the MCL specified by the USEPA was required.	30 pg/cm^3 (water) 3 µg/kg (soil)	-- 660 µg/kg
Method detection limit (MDL)	Detection limits were specified for each individual PAH (see Table 1.1)	10 pg/cm^3 (water) 1 µg/kg (soil)	 66 µg/kg
Procedural blank	Procedural blanks were used to check the background levels. To ensure reliable results, procedural and field blanks were limited to a maximum concentration of ten times the method detection limit.	10 x MDL	MDL
Duplicate precision	Field replicates were used to control the representativeness, with the maximum relative percent of duplicate values within ± 30%.	< 35 % RSD	N/A
Calibration: %RSD of the RFs	In the case of groundwater analysis the instrument calibrated was optimised in the lower concentration range due to the poor solubility of four- and five-ring PAHs. Relative response factors for individual PAHs are required to have a maximum RSD of 30% over the linear range of the calibration.	< 30 % RSD	N/A
Selectivity	The objective was to distinguish the target analytes from matrix compounds that may have concentrations of up to orders of magnitude higher than the target analytes.	No peak overlap from co-eluting compounds giving mass fragments at the selected mass	N/A
Specificity	A differentiation among various isomers is desired.	Baseline separation	N/A

Quality control procedures

The reliability of the GC/MS method was improved by employing the following quality control procedures before every batch of samples.

GC/MS performance validation

The mass spectrometer was tuned regularly for maximum sensitivity and resolution using a standard tuning procedure, which can be summarised by the adjustment of the following parameters:

Resolution: _The optimum resolution was adjusted on the 130 and 131 peaks of the calibration gas mixture of the Saturn 2000 ion trap, by adjusting the axial modulation amplitude.

Sensitivity: The optimum sensitivity was adjusted by setting the RF modulation response to 763 (highest) and 361 lowest, and the filament emission current to 15 μA. The multiplication voltage was tuned automatically by the instrument software to obtain a voltage that is high enough to produce 10^5 electrons from one ion.

Mass calibration: A mass calibration was performed weekly or when the operator manually changes the:

- ionisation time. The ionisation time is normaly computed and set automatically via the automatic gain control (AGC).
- Axial modulation voltage. The A/M voltage must be adjusted to the proper value before a mass calibration. If the voltage is too low, high molecular weight ions will not be observed. If the voltage is too high, the peak width for low molecular weight ions will be broadened and mass misassignments may occur.
- ion trap temperature.

Trap function calibration: This calibration was performed weekly.

SIS calibration: The single ion storage (SIS) amplitude was checked on a regular basis to ensure optimum performance in the SIS mode. SIS eliminates unwanted ions from the trap. Trapped ions exhibit a characteristic frequency of oscillation. This frequency depends on the mass of the ion and the amplitude of the fundamental storage rf field.

After completion of the tuning procedure, the performance verification was then performed using a 40 μg/cm^3 PAH standard. The chromatogram was checked for correct retention times, resolution, peak areas and the mass spectrum was checked for signal to noise ratios and peak intensities.

Instrument calibration and verification procedure

The typical calibration standards for syringe injections were 20, 40, 60, 80 and 160 μg/cm^3 PAHs in water, with 20 μg/cm^3 deuterated PAH internal standards at each calibration level. Calibration standards were run with 2μl injections of each standard containing parent PAH analytes and internal standards. The Calibration data were checked for linearity and relative standard deviation (RSD) and corrections made. The maximum allowable RSD was 30% for the response factors (RF) over the linear range for all target compounds with a minimum RF of 0.05 (response relative to internal standard). The typical calibration standards for SPME analyses were 2, 4, 6 and 8 ng/ml PAHs in water, with 8 μg/ml deuterated PAH internal standards at each calibration level. Calibration standards were run using a sample size of 1.2 cm^3 containing parent PAH analytes and internal standards. The Calibration data were checked for linearity and RSD and corrections made. The maximum allowable RSD was 30% for the response factors over the linear range for all target compounds with a minimum RF of 0.05. A verification standard was run in between samples to check the calibration before and after a

maximum of ten samples using a mid-range standard. Results were checked to be within 30% of the expected values. The software automatically performs the concentration calculations of the verification standard. The instrument was re-calibrated where necessary. Checking the internal standard peak areas for each analysis to be within + 75 and – 75% of those in the daily calibration check, and within a given retention time window of 20 seconds, checked the instrument stability.

Control samples - spiked water sample

A 1000 cm^3 of pure water was spiked with 5 µl of the 2000 $\mu g/cm^3$ PAH standard to obtain a concentration of 10 $\mu g/cm^3$. About 10 cm^3 of methanol was added to keep the PAHs in solution. The control sample was analysed using the standard procedure after every calibration and after every ten samples.

Quantitative analysis using GC/MS

Gas chromatographic separation was carried out using a DB-5 non-polar stationary phase. The mass spectrometer was operated in the full scan mode where all masses between 45 and 450 are acquired or in the SIS mode where only the specified analyte masses are acquired. Quantification of the 16 EPA priority PAHs were performed using:

- the quantification ions specified in **Table 5.1, Chapter 5.**
- response factors (RFs),
- peak areas
- calibrating on the deuterated internal quantification standards
- a linear curve fit, forced through the origin.

The deviation and calibration range tolerance was set at 30%. For the identification of the target analytes, the following criteria were used:

- Retention time window = (±) 0.200 minutes.
- Mass spectrum match threshold = 700
- Minimum peak area = 1000
- Report threshold = 0.10 ng/cm^3
- Signal to noise ratio of the selected ion current = > 3:1
- Maximum uncertainty of the ratio between the molecular ion and qualifier ions = 20%.

Presently alkyl PAH standards for each alkyl group of interest are not commercially available. RFs are, therefore, specified for each degree of alkylation by assignment of the RF of the next closest alkyl homologue group. They are then quantified by grouping the peak areas of individual isomer of each level of alkylation and using the specified RF.

ANALYTICAL CONDITIONS

The following analytical GC/MS conditions were used throughout this study, unless otherwise indicated:

Module: Saturn 2000.40 Mass Spectrometer

Saturn GC/MS Workstation Version 5.2.1
Module Software Version: FF0D
Module Option Keys: EI SIS MS/MS
Setpoints
Trap Temperature: 150 degrees C
Manifold Temperature: 35 degrees C
Transfer Line Temperature: 300 degrees C
Axial Modulation Voltage: 2.8 volts
Air/Water Check
Mass 28 Peak Width: 0.8 m/z
Mass 19 to Mass 18 Ratio: 14.3%
Total Ion Count: 3158 counts
Integrator Zero Set
DAC Setpoint: 100 DACs
Average Counts: 0.5 counts
Electron Multiplier Set
10^5 Gain Value: 2050 volts
Final Gain Value: 2050 volts
RF Full Scale Adjust
DAC Setpoint: 132 DACs
Calibration Ion Used: 614 m/z
Mass Calibration
Method: FC-43

Ion Mass	Apex	Ion Intensity
28	175.8	137
69	433.1	1510
131	822.2	560
264	1658.5	378
414	2601.2	108
464	2916.2	42
502	3155.8	118
614	3865.5	21

Average Calibration Slope: 6.263 DAC/m/z
Standard Deviation: 0.037

Trap Function Calibration
Mass 69 Frequency: 258.900 kHz
Mass 131 Frequency: 257.400 kHz

SIS Calibration
Amplitude Adjust Factor: 60%

Calibration Gas Adjust
Ionization Time: 550 uSeconds
Total Ion Count: 3726 counts

RF Tuning Adjust
Highest Count: 739 counts
Average Count: 351 counts

Segment Number 1:
Description: FIL/MUL DELAY
Emission Current: 0 microamps

Segment Number 2:
Emission Current: 15 microamps
Mass Defect: 0 mmu/100u
Count Threshold: 2 counts
Multiplier Offset: 0 volts
Scan Time: 0.770 seconds
Segment Start Time: 3.00 minutes
Segment End Time: 42.00 minutes
Segment Low Mass: 45 m/z
Segment High Mass: 450 m/z
Ionization Mode: EI AGC
Ion Preparation Technique: NONE

EI-Auto Mode:
Maximum Ionization Time: 25000 µs

Mass Range	Ion. Storage Level	Ion. Time
Scan Segment 1:		
10 to 99	44.0 m/z	100%
Scan Segment 2:		
100 to 199	44.0 m/z	140%
Scan Segment 3:		
200 to 399	44.0 m/z	120%
Scan Segment 4:		
400 to 650	44.0 m/z	35%

Target TIC: 20000 counts
Prescan Ionization Time: 100 µs
Background Mass: 43 m/z
RF Dump Value: 650.0 m/z

Module: 3800 Gas Chromatograph

Front Injector Type 1079

Temp (C)	Rate (C/min)	Hold (min)	Total (min)
300	0	42.00	42.00

Time (min)	Split State	Split Ratio
Initial	On	25

"Advanced Flow Control" for 1 cm^3/min constant flow with pressure pulse injection

Pressure (psi)	Rate (psi/min)	Hold (min)	Total (min)
15.0	0.00	0.10	0.10
7.8	20.00	0.01	0.47
11.8	0.40	0.00	10.47
15.8	0.29	0.00	24.26
19.2	0.34	0.00	34.26
22.6	1.13	4.00	41.27

Column Oven
Stabilization Time: 0.10 min

Temp (C)	Rate (C/min)	Hold (min)	Total (min)
60	0.0	0.01	0.01
130	7.0	0.00	10.01
200	5.0	0.00	24.01
260	6.0	0.00	34.01
320	20	4.80	41.81

Chapter 4

PHYSICO- CHEMICAL PROPERTIES OF COAL TAR COMPONENTS

INTRODUCTION

Compound properties

The global fate of compounds depends on their transport and general distribution, as well as their enrichment and transformation in a specific environmental compartment[25-27]. The environment is usually divided into the major compartments air, water, soil/sediment, biota, plants and particles, as illustrated in **Figure 2.1**. The knowledge of the physico-chemical parameters is necessary to forecast partitioning into the environment and for modeling the multiphase distribution. Mackay[28] used the fugacity approach (relative escaping tendency) to determine the favorite compartment of a compound. The most important physico-chemical properties that are relevant for environmental behavior, are vapor pressure (P^0_L), water solubility (S_w), octanol-water partition coefficient (K_{ow}) and sorption coefficient on soil/sediment (K_{oc}). The K_{ow} is a useful index of compound hydrophobicity, and Log K_{ow} of PAHs reported in literature[26] ranges from 3.36 (naphthalene) to 6.50 (benzo[a]pyrene). This implies that the heavier PAHs (high Log K_{ow}) will partition strongly from water onto soil/sediments due to their low solubility in pure water. The water solubility and volatility of PAH compounds generally decrease with an increase in the number of rings and degree of alkylation. The tendency of a chemical to transfer to and from gaseous environment phases (e.g. the atmosphere) is determined to a large extent by its P^0. This property is critical for prediction of either the equilibrium distribution or the rates of exchange to and from natural waters. Even compounds with very low ambient P^0 are of environmental importance, as these same chemicals have low solubilities in water (high aqueous phase fugacities), and partition appreciably into the atmosphere. The chemical and physical properties of target analytes were hence investigated. The compounds, which occur in coal tar, have a low volatility (boiling points ranges between 200 and 400 °C) and experimental data on vapor pressures of compounds such as the alkyl-PAHs is very scarce.

Knowledge of the physico-chemical properties of target analytes is also important for the development of analytical methods. It is, for example, necessary to identify those components with a sufficiently high vapor pressure to be analysed in the headspace mode. Headspace sampling at room temperature is limited to substances with sufficient vapor pressures. Information of P^0 is useful to understand the behaviour of a given organic compound during the headspace sampling process and to predict the equilibrium distribution between the soil, air and a SPME fiber. Vapor pressure governs the vaporisation of the analyte from soil, and consequently the amount adsorbed onto the SPME fiber. Capillary GC has been reported [26,29] as a

practical method to at least get a good estimate of vapor pressures of low volatility compounds, assuming the subcooled liquid [$P^0(L)$], since the molecules are *dissolved* in the stationary phase. The vapor pressures of selected target analytes were determined using capillary GC.

EXPERIMENTAL

Standards

Chromatograms were obtained using the following certified petrochemical and PAH mixtures:

- Diesel Range Organic Mix, C_{10} - C_{25} , Chem Service Inc.
- Petrochemical Calibration Mix, C_6 - C_{44} Chem Service Inc
- TLC mixture, 2000 ppm each PAH standard, Supelco
- Coal tar sample

GC/MS analytical conditions

The Varian Saturn model 2000 GC/MS was operated under the conditions listed in **Chapter 3.**

Determination of vapor pressures

The Petrochemical Calibration Mixtures obtained from Chem Service Inc., containing n-alkanes from n-hexane (C_6) to n-tetratetracontane (C_{44}) were used as reference compounds with known vapor pressures to calibrate the GC. A high-resolution gas chromatograph equipped with a DB-5 non-polar stationary phase was used under the conditions as stated above. Chromatograms were obtained for the target analytes and the n-alkanes respectively to determine the retention time of each individual component at standard instrumental conditions. These retention times were used to determine the Kovats [30] retention index for each component, using the following equation:

$$RI = 100.n + 100.[t_R(x)-t_R(n)]/[t_R(n+1)-t_R(n)] \quad .....4.1$$

where:
RI = temperature programmed retention index
n = carbon number of n-alkane eluting before substance x
n+1 = carbon number of n-alkane eluting after substance x
t_R = retention time
Using the assumption that vapor pressure is proportional to the retention index the vapor pressures for the target analytes were calculated at 298 K by linear regression [29]:

$$\log P^0_L = a.RI + b \quad .....4.2$$

RESULTS AND DISCUSSION

The results are presented in **Figure 4.1**, showing the linear regression data. The saturated vapor pressure of the PAHs, their alkylated homologous series and heterocyclic compounds are determined using the values in **Figure 4.1**. The results for the determined vapor pressures and the water solubilities obtained from literature are presented in **Table 4.1** and graphically presented in **Figures 4.2** and **4.3.** The P^0_L values obtained (298 K) range from 2.0 x 10^{-3} mm Hg for indene to 9.0 x 10^{-19} mm Hg for benzo[ghi]perylene. The observed rules for the vapor pressure of coal tar components are:

- There is roughly between 1 and 4 orders of magnitude difference between the P^0_L of 2 and 3 ring structures, and between 2 and 10 orders of magnitude difference between 3 and 4 ring structures.
- There is a trend in decreasing P^0_L for each methylene group added

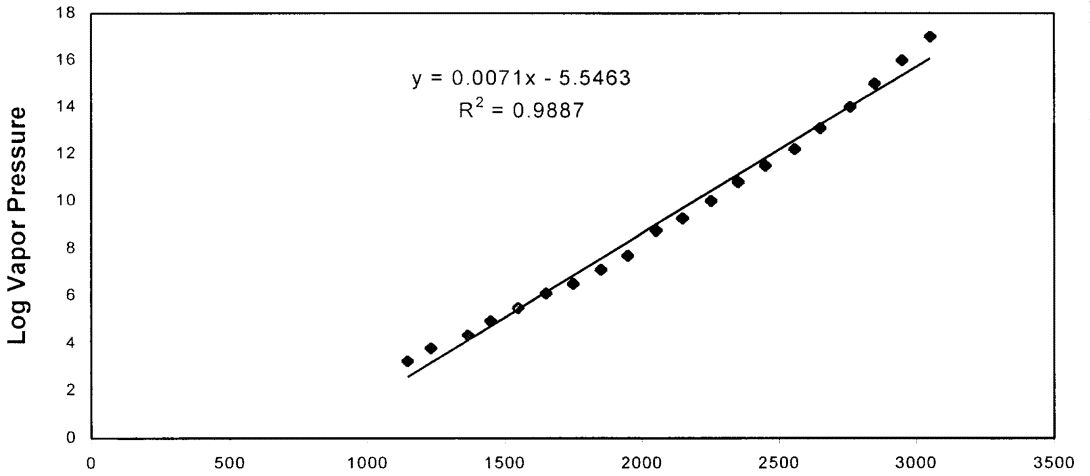

Figure 4.1: Saturated vapor pressure of n-alkanes as a function of Kovats index

TABLE 4.1 : Physical-Chemical Properties of Selected Coal Tar Pollutants – P^0_L determined experimentally

No	COMPOUND	RINGS	KOVATS INDEX	Log P^0_L (mm Hg)	P^0_L (mm Hg)	Log Molar Solubilities[a]	S_W (mg/L)
1	Indene	1	1161	2.70	2.0E-03	-3.034	110
2	Naphthalene (N)	2	1255	3.36	4.3E-04	-3.606	32
3	2-Methyl naphthalene (C1-N)	2	1314	3.78	1.7E-04	-3.748	28
4	1-Methyl naphthalene (C1-N)	2	1330	3.90	1.3E-04	-3.705	25
5	Biphenyl (BP)	2	1397	4.38	4.2E-05	-4.345	6.6
6	1-ethyl-naphthalene (C2-N)	2	1413	4.49	3.3E-05	-4.162	10.7
7	1,3-dimethyl naphthalene (C2-N)	2	1458	4.81	1.6E-05	-4.292	8.0
8	1,5-dimethyl naphthalene (C2-N)	2	1425	4.57	2.7E-05	-4.679	3.3
9	2,3-dimethyl naphthalene (C2-N)	2	1438	4.66	2.2E-05	-4.716	3.0
10	2,6-dimethyl naphthalene (C2-N)	2	1443	4.70	2.0E-05	-4.888	2.0
11	1,2,5-trimethyl naphthalene (C3-N)	2	1556	5.50	3.2E-06	-4.923	2.0
12	Acenaphthylene (AC)	3	1470	4.89	1.3E-05	----	---
13	Acenaphthene (AE)	3	1503	5.13	7.5E-06	-4.594	3.9
14	Dibenzofuran (D1)	3	1537	5.37	4.3E-06	----	---
15	Fluorene (F)	3	1604	5.84	1.4E-06	-4.925	2.0
16	4-methyl dibenzofuran (C1-D1)	3	1639	6.09	8.1E-07	----	---
17	3,4-diethyl-1,1-biphenyl (C2-BP)	2	1692	6.47	3.4E-07	----	---
18	2-methyl fluorene (C1-F)	3	1720	6.67	2.2E-07	----	---
19	2-ethyl fluorene (C2-F)	3	1823	7.40	4.0E-08	----	---
20	Methyl-ethyl fluorene (C3-F)	3	1910	8.02	9.6E-09	----	---
21	Dibenzothiophene (D)	3	1775	7.06	8.7E-08	----	---
22	Phenanthrene (P)	3	1803	7.25	5.6E-08	-5.150	1.30
23	Anthracene (A)	3	1815	7.34	4.6E-08	-6.377	0.08
24	Fluoranthene (FL)	4	2084	9.25	5.7E-10	-5.898	0.26
25	Pyrene (PY)	4	2136	9.62	2.4E-10	-6.176	0.14
26	1,2-Benzanthracene (BA)	4	2476	12.03	9.3E-13	-7.214	0.017
27	Chrysene (C)	4	2486	12.10	7.9E-13	-8.057	0.002
28	3,4-Benzopyrene (BP)	5	2895	15.01	9.9E-16	-7.820	0.004
29	Benzo[k]fluoranthene (BK)	5	2780	14.19	6.4E-15	----	---
30	Dibenz[a,h]anthracene (DA)	5	3243	17.48	3.3E-18	----	---
31	Benzo[g,h,I]perylene (BP)	6	3323	18.05	9.0E-19	-9.018	0.0003
32	Indeno[1,2,3]perylene (IP)	6	3232	17.40	4.0E-18	----	---

[a] - Data from Yalkowsky et. al.[51]

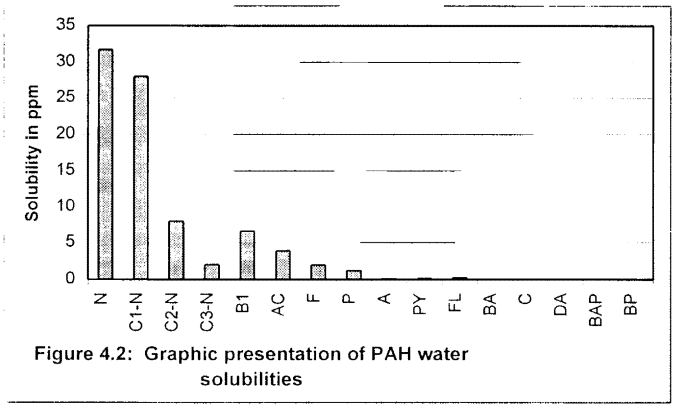

Figure 4.2: Graphic presentation of PAH water solubilities

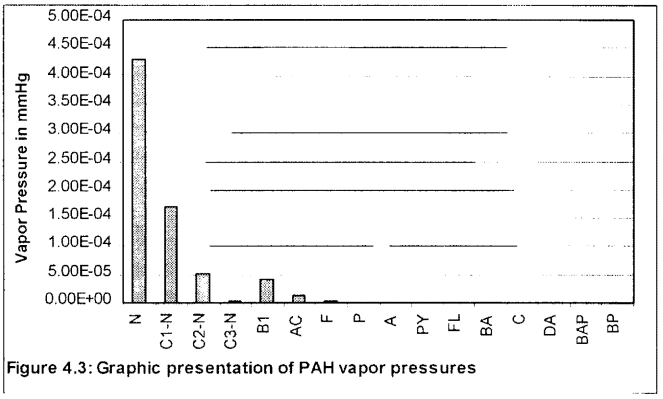

Figure 4.3: Graphic presentation of PAH vapor pressures

Compounds 1 - 25 have been identified as contaminants with sufficiently high vapor pressures to be analysed in the headspace mode using a SPME fiber. Of these compounds, pyrene has the lowest vapor pressure of 2.4 x 10^{-10} mm Hg, which also indicates a relatively low soil to air transfer potential. Compounds with a molecular weight lower than pyrene are of particular interest due to both their high groundwater and air transfer potentials. The conclusion was made that the SPME headspace technique is suitable for two- and three-ring, as well as selected four-ring polyaromatic and heterocyclic compounds.

The results in **Table 4.1** reveal that the 2-ring and some 3-ring PAHs have relatively high solubilities in water ($\mu g/cm^3$ range). The solubilities dropped to the pg/cm^3 levels for 6-ring PAHs. A decrease in the solubility of alkylated compounds was also observed, which was proportional to the degree of alkylation. This is due to the fact that alkylated compounds are more hydrophobic than their corresponding parent compound. The occurrence of 5- to 6-ring PAHs in groundwater is, therefore, expected to be in the very low concentration range, especially those with a high degree of alkylation.

Environmental distribution and fate of PAHs

The environmental distribution and fate of PAHs depends on the physico-chemical properties as depicted in **Table 4.1.** Lower alkyl-PAHs possess greater P^0 (low fugacity in the gas phase) while those with a higher degree of alkylation are less soluble and more hydrophobic (high fugacity in aqueous solution). These differences will, therefore, govern the partitioning processes between soil, air and water. **Figure 4.4** is a diagram which tracks PAHs in the various compartments in the environment and their transfer between and dissipation within those compartments. This diagram shows that the PAHs can degrade (disappear) in many ways. During aerobic degradation bacteria break down PAHs while abiotic degradation involves the degradation without any contribution by animals, plants or microorganisms. Abiotic degradation includes photodegradation, oxidation, hydrolysis, evaporation or absorption.

Distribution and fate in soil/sediments

Due to their relative high water solubility, the lighter and lower alkyl-PAHs are expected to have a high convection into soils and sediments. The degree of transportation

will also depend on the presence of other organic matter or fluids, for example DNAPLs. The convection of PAHs will increase in the presence of co-contaminants with a higher solubility for PAHs than water, or with a high pH. Once dissolved into a DNAPL, the movement of the DNAPL will be mainly directed by gravity.

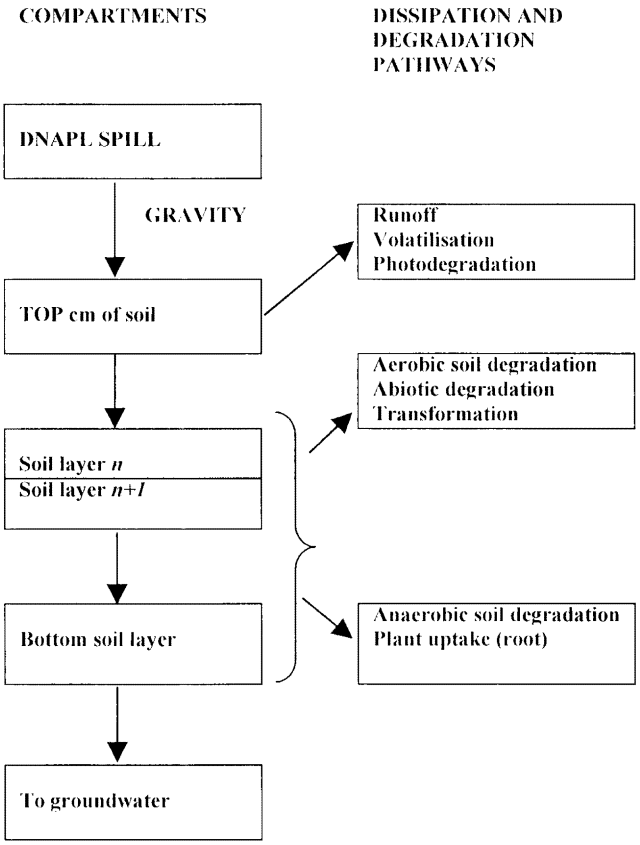

Figure 4.4: PAH environmental fate model

The heavier PAHs that are only sparingly soluble in water are expected to be more immobile, and will tend to remain on the surface, unless they move together with a DNAPL. Volatilisation from the soil surface may also occur, especially those PAHs with a vapor pressure of > 1E-10 mm Hg.

PAHs normally dissolved in DNAPLs are in a relatively stable environment and may slowly decompose with photo chemical or biological processes or dissolve in surrounding groundwater. Larger PAHs and those with a higher degree of alkylation will have a lower rate of degradation. Photo oxidation will be restricted to the top layer of the soil, as sunlight cannot penetrate the deeper soil levels.

Distribution and fate in an aquatic environment

It is evident from **Table 4.1** that the heavy PAHs are highly insoluble in water. They will, however, dissolve into groundwater in sufficient proportions to pollute the groundwater beyond limits set by the USEPA. The solubility of benzo[a]pyrene (PAH reference compound) is 20 times the allowable concentration limit given by the USEPA. This indicates that even the smallest amount of DNAPL found in soils may contaminate the surrounding groundwater above the EPA standards. Due to the fact that the DNAPL density is greater than water, it will sink deep into the earth where it will deposit on an impermeable layer of soil or rock. Once dissolved, the most common mechanism for the removal of PAHs from water is the sorption to suspended matter or sediment. The concentration of the heavy PAHs are, therefore, normally higher in sediments than in the overlaying water. Dissolved PAHs can also volatilise from surface water or decompose with photochemical reactions. They are, however, resistant towards chemical oxidation and hydrolysis.

Chapter 5

THE ANALYSIS OF COAL TAR POLLUTED GROUNDWATER SAMPLES USING LIQUID-LIQUID EXTRACTION AND GC/MS

INTRODUCTION

The solvent extraction method, using methylene chloride, which was investigated in this study, is based on the USEPA method 8270[32,33] and the modified method reported by Douglas[5]. He refined the USEPA method to meet the quality objectives required for advanced chemical fingerprinting. Chemical fingerprinting requires reliable data for the alkyl-PAH isomers with detection limits of at least 0.01 ng/cm^3 for individual PAHs or alkyl-PAH groups. The liquid extraction method was investigated in this study for its suitability to characterise coal tar pollution in water samples and for health risk based risk assessments. As discussed earlier, a detection limit of 0.01 ng/cm^3 is required for all the PAHs and alkyl-PAHs for chemical fingerprinting. For a health risk assessment the lowest guideline concentration (0.0093 ng/cm^3) is for dibenzo[a,h]anthracene, which is the most potent carcinogen. Detection limits for the other PAHs increase according to their relative potency. The following key refinements were implemented to optimise the method for chemical fingerprinting and health risk assessments:

- An Ultra Turrax high performance dispersing tool was used to enhance the extraction efficiency.
- Sample analysis was optimised for low-level target analytes with a signal-to-noise of at least 3:1.
- The same analyst was used for a batch of samples
- Special attention was given to the very low soluble 5-ringed PAH compounds. The injection technique was optimised to minimise mass discrimination and to improve the sensitivity of four- and five-ring PAH compounds
- The instrument was carefully maintained, checked for low noise levels in the ion trap and the regularly tuned for maximum resolution and sensitivity
- The target analyte list was expanded to include PAH, hetero-aromatic compounds and their alkylated homologues. Dibenzothiophenes are among the important analytes because the ratios of the sulphur compounds to non-sulphur aromatics are characteristic to specific sources
- A small volume of toluene was added to the extract prior to evaporation (pre-concentration) as keeper solvent, to keep the target analytes in solution and prevent their evaporation.
- A high level of quality assurance and quality control (described in **Chapter 3**) was implemented to improve the reliability of results
- The solvent phase was evaporated to a known volume (usually 1 cm^3) using a rotary evaporator to reduce the sample preparation time.

A list of target analytes is shown in **Table 5.1.** The sample purification and enrich-

ment schemes are shown in **Figure 5.1**. The purpose of the sample purification step was to remove polar compounds that can interfere during the GC/MS analysis, to remove moisture and to pre-concentrate the analytes.

Table 5.1: Target Polycyclic Aromatic Hydrocarbons, Quantitation Internal standards, Quantitation ions, Retention Times, Average RF

Target Analytes	Abbreviation	Rings	Primary quantification Ion (m/z)	Int. Std.	Retention Time (min)	Response Factor found
Naphthalene	N	2	128	A	9.84	1.14
C_1- Naphthalenes	C1-N	2	142	A		
C_2- Naphthalenes	C2-N	2	156	A		
C_3- Naphthalenes	C3-N	2	170	A		
C_4- Naphthalenes	C4-N	2	184	A		
Acenaphthylene	AE	3	152	B	15.55	1.49
Acenaphthene	AC	3	154	B	16.28	1.23
Biphenyl	BI	2	154	B		
Dibenzofuran	DI		168			
Fluorene	F	3	166	C	18.50	0.98
C1-Fluorenes	C1-F	3	180	C		
C2-Fluorenes	C2-F	3	194	C		
C3-Fluorenes	C3-F	3	208	C		
Phenanthrene	P	3	178	C	22.72	1.11
Anthracene	A	3	178	C	22.94	1.00
C1-Phenanthrene/anthracenes	C1-P/A	3	192	C		
C2-Phenanthrene/anthracenes	C2-P/A	3	206	C		
C3-Phenanthrene/anthracenes	C3-P/A	3	220	C		
C4-Phenanthrene/anthracenes	C4-P/A	3	234	C		
Dibenzothiophene	D	3	184	C		
C1-Dibenzothiophene	C1-D	3	198	C		
C2-Dibenzothiophene	C2-D	3	212	C		
C3-Dibenzothiophene	C3-D	3	226	C		
Fluoranthene	FL	4	202	C	28.07	1.34
Pyrene	PY	4	202	C	28.98	1.42
Benzo[a]anthracene	BA	4	228	D	34.19	1.14
Chrysene	C	4	228	D	34.30	1.56
C1-Chrysene	C1-C	4	242	D		
C2-Chrysene	C2-C	4	256	D		
C3-Chrysene	C3-C	4	270	D		
Benzo[b]fluoranthane	BFL	5	252	D	36.89	1.68
Benzo[a]pyrene	BaP	5	252	D	37.46	1.86
Benzo[ghi]perylene	BP	5	276	E	39.85	1.20
Dibenz[ah]anthracene	DA	5	278	E	39.92	1.20
Indeno[123-cd]pyrene	IP	5	276	E	40.42	1.20
Internal standards						
Naphthalene-d_8	Nd_8	2	136	**A**	9.84	1
Acenaphthene-d_{10}	Ad_{10}	3	164	**B**	16.15	1
Phenanthrene-d_{10}	Pd_{10}	3	188	**C**	22.62	1
Chrysene-d_{12}	Cd_{12}	4	240	**D**	34.09	1
Perylene -d_{12}	Pd_{12}	5	264	**E**	37.57	1

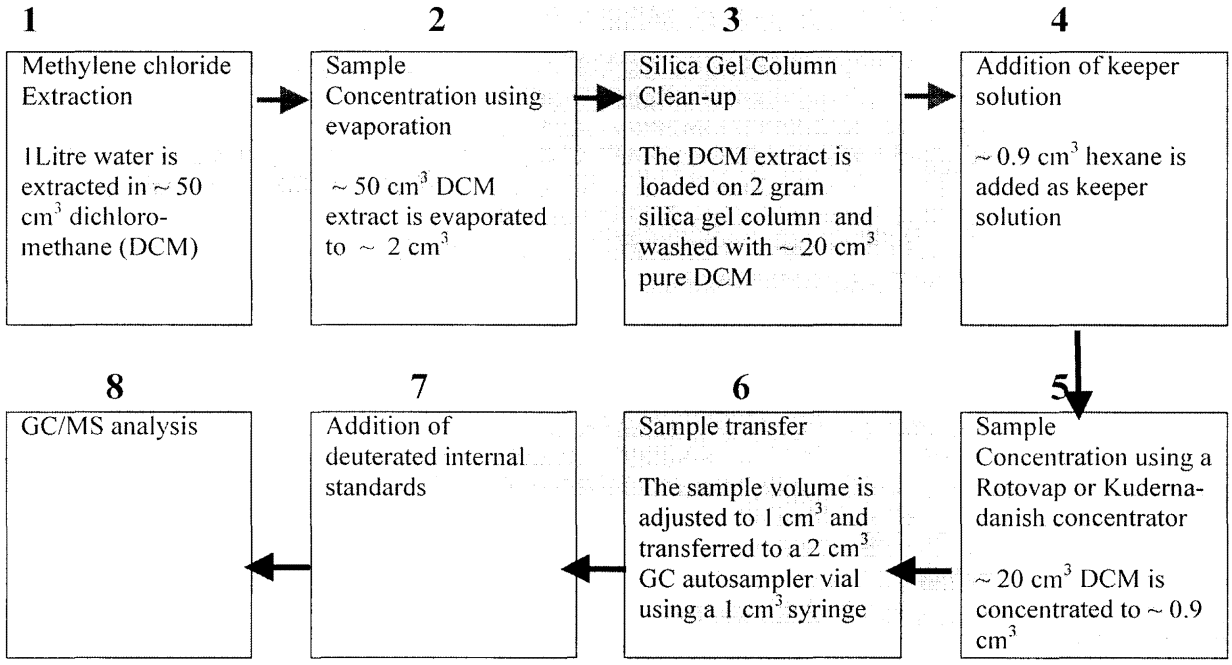

Figure 5.1: The sample purification and enrichment scheme for the analysis of groundwater samples

EXPERIMENTAL

GC-MS Analysis Conditions

The analytical conditions and QC/QA requirements that are stipulated in **Chapter 3** were used, unless otherwise indicated.

Groundwater Sample Extraction

Reagents and standards

Nanopure water was employed throughout. All solvents and other reagents used were of analytical grade. A standard mixture containing 2000 µg/cm^3 each of the 16 EPA priority PAHs, was purchased from Supelco (Sigma Aldrich, South Africa). The internal standard mixture containing deuterated PAHs was purchased from Chemservice (Anatech, South Africa), and added to all standards and samples.

Liquid-liquid Extraction Procedure

- A 1000 cm^3 volume of the water sample was transferred to a separation funnel using a measuring cylinder (this volume was changed according to the expected PAH concentration in the sample).
- A volume of 50 cm^3 dichloromethane was added to the sample followed by 30 drops of acetic acid to lower the pH and increase the extraction efficiency.
- The tip of the Ultra Turrax was inserted into the sample. The distance between the dispersion tool and the vessel bottom was not less than 10 mm and the filling level not less than 55 mm. The sample and solvent was mixed for at least 1 minute.
- The dispersing tool was removed, the funnel stoppered and the sample and solvent phases allowed to separate (usually overnight, depending on sample matrix).
- The solvent phase was drained into a 250 cm^3 round bottom flask through a glass column containing glass wool and anhydrous Na_2SO_4 stationary phase.

- The stationary phase was washed with 10 cm^3 of dichloromethane.
- The excess DCM was evaporated under a stream of air to obtain a final volume of about 2 cm^3.
- A glass column fitted with a porous disk was filled with about 2 grams of stationary phase (chromatographic quality silica gel or neutral alumina). The column dimensions was 10 mm x 300 mm. The height of the stationary phase in the column was be about 50 mm.
- The stationary phase was equilibrated with DCM and air bubbles removed by shaking.
- The concentrated extract was transferred to the top of the stationary phase in the column by using a 1 cm^3 syringe. The flow rate was between 1 and 5 cm^3/minute.
- The extract was passed through the column and the eluent collected in a clean 250 cm^3 round bottom flask. The stationary phase was washed with an additional 20 cm^3 of pure DCM. Hexane (0.9 cm^3) keeper solvent was then added to the round bottom flask.
- The DCM was evaporated using a rotary evaporator to obtain a final volume of just less than 1 cm^3.
- The hexane concentrate was withdrawn from the round bottom flask using a 1 cm^3 syringe and small quantities of toluene added to the flask until the syringe was filled to the 1 cm^3 mark.
- The syringe contents were transferred to a 2 cm^3 GC autosampler screwcap vial and sealed with a teflon-coated septum.
- The appropriate amount of internal standard was added to each standard and sample, to obtain a concentration of 20 $\mu g/cm^3$.

RESULTS AND DISCUSSION

Method Validation

The method performance characteristics were measured against the data quality objectives (DQO's) listed in **Table 3.4,** including accuracy, repeatability, linearity, sensitivity, selectivity and specificity. The analytical performance of the method was also established to verify its suitability for hazard and chemical characterisation. The overall analytical results are summarised in **Table 5.2**.

Accuracy and repeatability

The accuracy and precision was determined by analysing a spiked water sample with known concentration several times. Recoveries for individual PAHs of between 85.3 – 103.3% were found, which were well within the desired objective of 80 – 120%. The results are graphically presented in **Figure 5.2.** Relative standard deviations of better than 15% were observed between these determinations. The accuracy and precision was found to be acceptable for the analyses of 16 priority PAHs using the drinking water standards specified by the USEPA.

Calibration

Straight-line calibration curves were constructed for each PAH to validate the calibration. The curves were found to have good linearity over the range of 20 $\mu g/cm^3$ to 160 $\mu g/cm^3$, characterised by correlation coefficients of better than 0.99 for each PAH.

Method sensitivity and method specific detection limits

The minimum concentration of a substance that can be detected is governed by the signal to noise ratio obtained with a given amount, which is dependent on various factors, such as the method performance and the complexity of the sample matrix. The estimated MDLs found in the full scan mode ranged between 0.03 ng/cm^3 (naphthalene) and 0.49 ng/cm^3 (benzo[g,h,i]perylene).

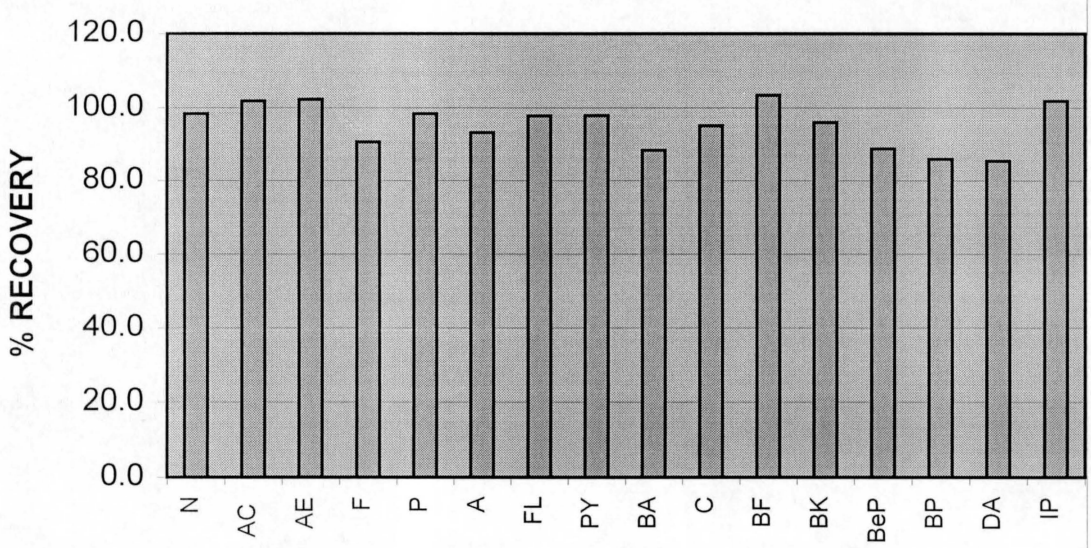

Figure 5.2: Recovery of PAHs added to water at a 40 ng/cm3 level. Results are based on 10 independent determinations.

For chemical fingerprinting purposes, the MDL of most PAHs (especially the 4- and 5-ring compounds) were found to be higher than the desired limit of 0.010 ng/cm^3. For health risk assessment purposes the detection limits for the carcinogens benzo[a]pyrene, benzo[g,h,i]-perylene, dibenz[a,h]anthracene and indeno[123-cd]perylene was found to be higher than the USEPA guideline concentration. The liquid extraction method investigated in this chapter (based on a 1000 cm^3 sample concentrated to 1 cm^3) is, therefore, not sensitive enough for chemical fingerprinting or health risk assessment purposes. Douglas[5] has, however, demonstrated that the required limits for chemical fingerprinting can be met by increasing the sample volume to 2 litres, decreasing the final volume to 0.25 cm^3 and using the mass spectrometer in the single ion monitoring mode. In the case of an ion trap (used in our laboratory) the alternative is to reduce the number of ions in the ion trap (increase the sensitivity) by using the mass spectrometer in the Single Ion Storage (SIS) mode. Acquiring data is the SIS mode is unfortunately associated with a loss of valuable mass spectral information. Full scan spectra provide a more assured identification of target compounds, allowing library search routines to be performed on non-target compounds. This enables the analyst to distinguish target compounds in complex matrices. When dealing with environmental samples, it is desirable to acquire as much information about the sample as possible. In our laboratory SIS is not used on a routine basis but only in instances where lower detection limits are required. The method used under standard conditions is, therefore, not suitable for chemical fingerprinting, without further refinements.

Method selectivity

A typical chromatogram for a procedural blank, 40 ng/cm^3 standard and for a typical groundwater sample respectively, is shown in **Figure 5.3**. The groundwater sample was taken in an area nearby a confirmed coal tar spill and selected as an example because it represents a typical sample that is analysed by our laboratory. The procedural blank shown in this figure was chosen as an example to illustrate the level of impurities that can be expected under normal laboratory conditions. A number of unidentified peaks (compounds) were observed in the chromatograms of the

procedural blank and the sample. Contamination in the procedural blank was mainly due to the glassware, acetic acid, sodium sulphate and the solvents. It can be seen from **Figure 5.3** that interfering compounds in the blank mainly occur in the early parts of the chromatogram but do not interfere with the PAHs. The interfering compounds in the sample were different from those of the blank, but did also not interfere with the PAHs.

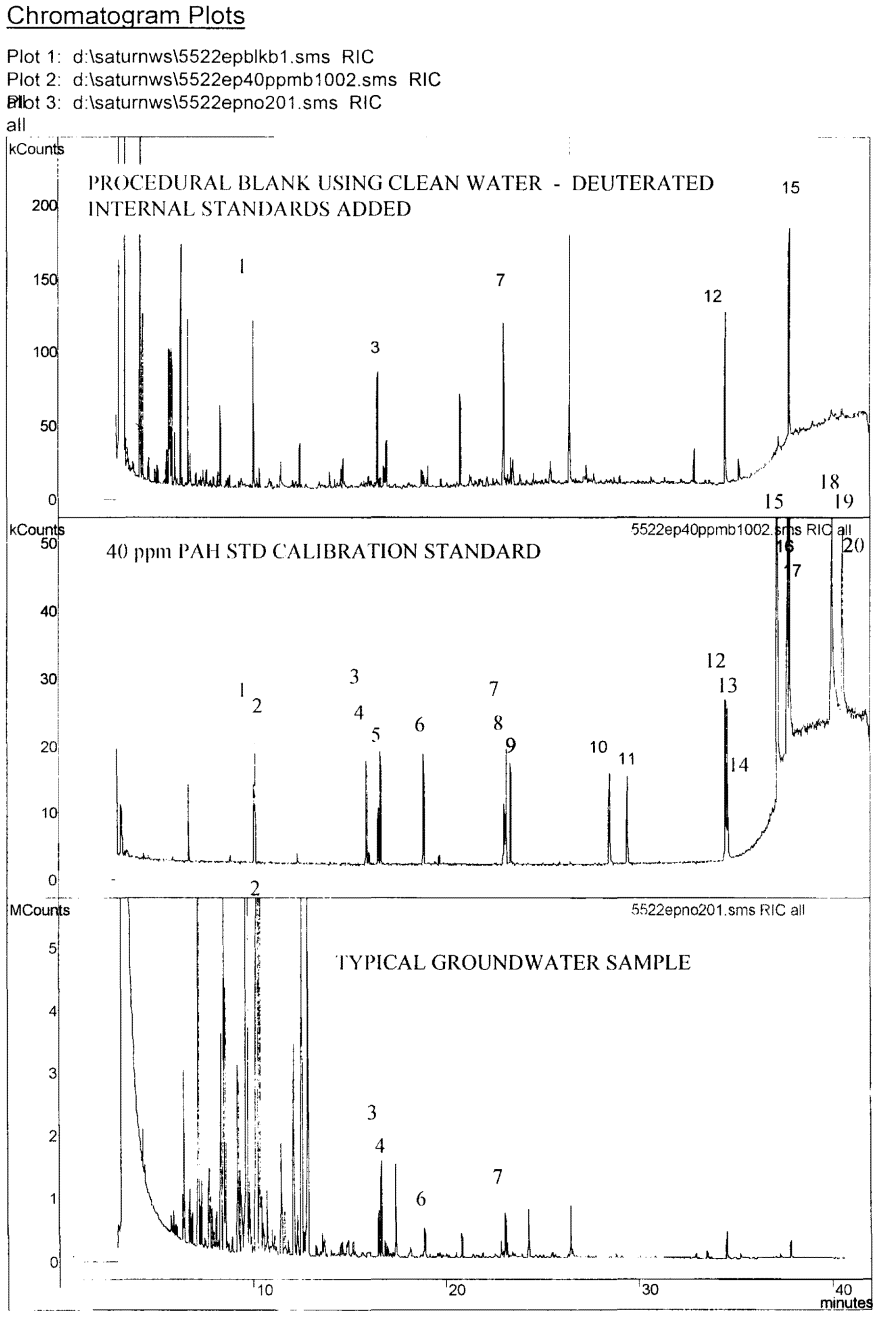

Figure 5.3: Typical total ion chromatograms of a Procedural Blank, PAH standard and a contaminated groundwater sample : (1)d10-naphthalene (2) naphthalene (3) d8-acenaphthene (4) acenaphthene (5) acenaphthylene (6) fluorene (7) d10-phenenthrene (8)phenenthrene (9) anthracene (10) fluoranthene (11) pyrene (12) d12-chrysene (13) benzo|a|anthracene (14) chrysene (15) d12-perylene (16) benzo|k|fluoranthene (17) benzo|b|fluoranthene (18) benzo|e|pyrene (19) benzo|ghi|perylene (20) dibenz|ah|anthracene (21) indeno|123-cd|pyrene

Table 5.2: Calibration and analytical results

	CALIBRATION (5 levels)		ACCURACY AND PRECISION (n = 10)			SENSITIVITY			REPRESENTATIVINESS	WATER STANDARDS
Compound	Regression Coefficients (R^2)	Standard Deviation (ng/cm^3)	Value found for a 40 ng/cm^3 spiked sample	% Recovery	%RSD for a 40 ng/cm^3 Standard (n=10)	Signal to Noise (S/N) At 40 ng/cm^3	Quant. Limit [a] ng/cm^3	Detection limit [b] ng/cm^3	Procedural Blank Values ng/cm^3	[c] USEPA Guideline ng/cm^3
Naphthalene	1.000	0.028	39.3	98.3	3.8	3484	0.11	0.03	0.77	1500
Acenaphthylene	1.000	0.067	40.7	101.8	7.6	1613	0.25	0.07	<0.10	1500
Acenaphthene	0.999	0.047	40.9	102.3	6.2	4360	0.09	0.03	0.34	2200
Fluorene	1.000	0.026	36.2	90.5	2.1	2260	0.18	0.05	0.26	1500
Phenanthrene	1.000	0.044	39.3	98.3	2.7	1394	0.29	0.09	0.80	1500
Anthracene	1.000	0.034	37.3	93.3	1.7	602	0.66	0.20	0.13	11000
Fluoranthene	1.000	0.011	39.1	97.8	1.8	4332	0.09	0.03	0.34	1500
Pyrene	0.999	0.026	39.2	98.0	2.3	4711	0.08	0.03	<0.10	0.11
Benzo[a]anthracene	1.000	0.040	35.3	88.3	13.5	1679	0.24	0.07	<0.10	0.092
Chrysene	1.000	0.021	38.0	95.0	3.2	1609	0.25	0.07	<0.10	2.09
Benzo[k]fluoranthene	0.997	0.099	41.3	103.3	15.8	1660	0.24	0.07	<0.10	0.92
Benzo[b]fluoranthene	0.990	0.035	38.4	96.0	8.8	1553	0.26	0.08	<0.10	0.092
Benzo[a]pyrene	0.997	0.077	35.5	88.8	4.0	759	0.53	0.16	<0.10	0.0092
Benzo[g,h,I]perylene	0.999	0.043	34.4	86.0	7.0	244	1.64	0.49	<0.10	0.42
Dibenz[a,h]anthracene	0.999	0.047	34.1	85.3	5.1	279	1.43	0.43	<0.10	0.0092
Indeno[1,2,3-cd]pyrene	0.996	0.077	40.7	101.8	7.1	253	1.58	0.47	<0.10	0.092

(a) - Signal to noise = 10, and based on a 1000x concentration factor
(b) - Signal to noise = 3, and based on a 1000x concentration factor
(c) - Guideline concentration of the USEPA for a health risk based a 10^{-6} noncancer hazard.

The laboratory has found that the background peaks can be limited by using ultra pure chemicals and by taking extensive care to prevent contamination. This is, however, not necessary for routine analyses, as the method was found to be selective towards PAHs with good separation between the analytes of interest and interfering compounds. The chromatographic inertness criteria were also measured against the requirements as specified in USEPA method 525. Baseline separation was achieved between anthracene and phenanthrene and between benzo[a]anthracene and chrysene, without any co-eluting or interfering compounds.

Representativeness

The pretreatment procedure added a considerable uncertainty to the overall results, as evident by the high blank values. Procedural blank values were found for naphthalene (0.77 ng/cm^3), acenaphthene (0.34 ng/cm^3), fluorene (0.26 ng/cm^3), phenanthrene (0.80 ng/cm^3), anthracene (0.13 ng/cm^3), and fluoranthene (0.34 ng/cm^3). These values were generally lower than the maximum contaminant levels allowed by the USEPA, but much higher than the levels required for reliable chemical fingerprinting (0.001 ng/cm^3). In order to reduce and control this uncertainty, the sources of errors that might occur during the pre-treatment steps (as shown in **Figure 5.1**) must be minimised. This can be accomplished by taking special measures as discussed in the previous paragraph.

Advanced Chemical Fingerprinting and Alkylated PAH Isomer identification

Advances in the use of summed alkylated homologues (e.g. C_3-dibenzothiophenes), as well as the use of relative abundances of individual isomers in such a group, have been discussed in **Chapter 2**. The extent to which individual isomers as well as summed groups can be identified in water samples using the modified USEPA method 8270 discussed in this chapter, was investigated. One of the main problems with isomer quantification associated with coal tar pollution is the low solubility of 4- and 5-ringed PAH compounds in water and the low concentrations of C_2 to C_4 alkyl-PAHs in coal tar. Coal tar has a typical pyrogenic profile where the parent is most abundant and the alkylated PAH less abundant. Generally, the higher the degree of alkylation, the lower the concentration. The concentration of alkyl-PAHs in coal tar contaminated groundwater samples is, therefore, normally found in trace level quantities, e.g. in the low pg/cm^3 range. The sensitivity of the method for alkylated PAH isomers is further complicated by the fact that the total signal for the group is distributed between several isomers. This is illustrated in a study that was made using the analysis data of the most contaminated boreholes analysed by our laboratory (sample No 11 and No 4) as indicated in **Table 5.3**. The difficulty in the detection of higher degree alkyl-PAHs is shown in these examples. The selected ion chromatograms of the C_0- to C_2-naphthalenes are shown in **Figure 5.4.** It is evident from these chromatograms that a strong signal is obtained for naphthalene and the C_1-naphthalenes down to concentrations of < 1 ng/cm^3. The detection of C_2-naphthalenes was near the detection limit, while C_3- and C_4-naphthalenes could not be detected at all. Besides the naphthalene isomers, the C_1-D and C_1-P isomers could also be detected. It is, therefore, possible to determine source ratios based on these isomers. The analyte profile histogram of a sample that was highly contaminated by coal tar is shown in **Figure 5.5** to illustrate chemical characterisation of borehole samples using PAH distributions.

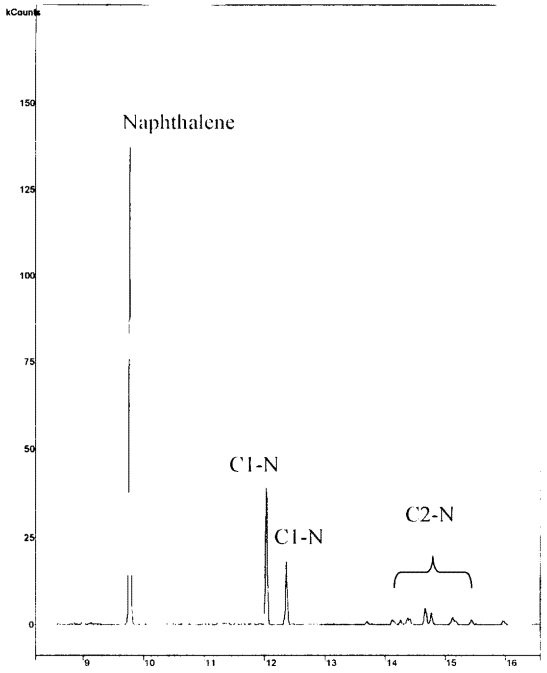

Figure 5.4 (a): Selected ion chromatogram for the naphthalenes - sample containing > 1 µg/cm3 PAHs

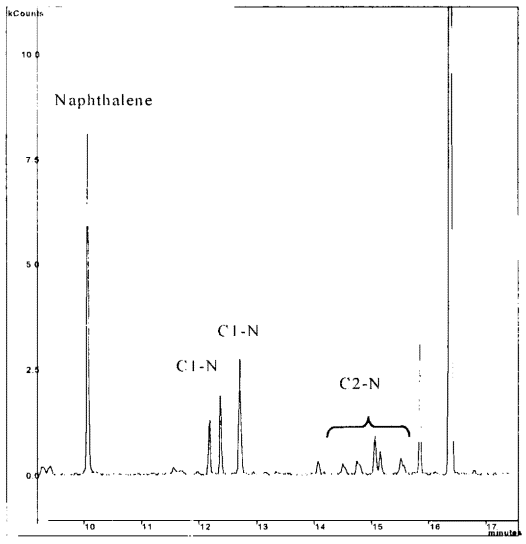

Figure 5.4 (b): Selected ion chromatogram for the naphthalenes – sample containing < 10 ng/cm3 PAHs

Due to the lack of data on 3- to 6-ring PAHs, chemical characterisation based on analyte distribution patterns (see **Chapter 2)**, is difficult. The naphthalenes dominate the profile and it is evident that very limited information can be obtained from this set of analytical data. The majority of borehole samples that were analysed in our laboratory had similar patterns and presented the same difficulty in data interpretation. The pattern is generally similar to a pyrogenic profile (ratio between naphthalene and methyl naphthalene), showing minor signs of weathering.

Specificity for alkylated PAH isomers

To demonstrate the specificity of the method the selected ion current of the phenanthrenes was compared to the profile of a reference standard. The selected ion chromatograms of the phenanthrenes are shown in **Figure 5.6.** This sample was contaminated by coal tar while the reference standard was contaminated by crude oil (CRM 103-100). The relative differences between the abundance of the alkyl-phenanthrenes are evident. These examples were chosen to demonstrate the difficulty in detecting the alkylated phenanthrenes in coal tar polluted groundwater samples, which probably only occur in levels lower than the method detection limit (< 0.085 ng/cm^3). Interfering peaks were also observed at the retention times where C1-P and C2-P elute. Similar results were found for chrysene isomers and it was concluded that the sensitivity and specificity of this method is not acceptable for determining diagnostic ratios based on alkyl-PAH isomers

The occurrence of PAHs in typical groundwater samples

The levels of PAHs normally found in water samples at industrial sites and mining operations were investigated using the solvent extraction method outlined in this chapter. The majority of samples were contaminated with trace levels of PAHs at a level of lower than 2 ng/cm^3 for individual PAHs. Contamination on industrial sites was mainly coal tar related, while contamination in mining operations was mainly diesel and lubrication oil related.

The results for the 16 priority PAHs found in several borehole samples are given in **Table 5.3**. Note the absence of the heavy PAHs (5 ringed structures) in these samples, which do not seem to occur in any of the groundwater samples at detectable levels. This is probably due to their low aqueous solubilities, high fugacities in water and partitioning back into sediments. The occurrence and concentration of these compounds also depend on the source of contamination. The relative abundance of the heavy compounds in some coal tar by-products is very low. Based on the average concentration of PAHs in all the samples, naphthalene (the most soluble PAH of the list) was found to be the most abundant contaminant, followed by acenaphthene. Fluoranthene and pyrene were also present in detectable quantities in most cases. The relative abundance of these compounds is typical of coal tar contamination, as discussed in **Chapter 2**.

Table 5.3. Results for the 16 priority PAHs from various borehole samples, expressed as ng/cm^3

	N	AC	AE	F	P	A	FL	PY	BA	C	BK	BB	BeP	DA	BP	IP
Groundwater samples from industrial sites																
No 1	818	2.6	47.2	59.2	10.2	3.74	0.25	0.09	0.00	0.00	0.00	0.0	0.00	0.00	0.00	0.00
No 2	489	2.25	72.4	38.3	8.7	0.79	0.00	0.00	0.00	0.00	0.00	0.0	0.00	0.00	0.00	0.00
No 3	1.17	0.00	0.17	0.14	0.34	0.00	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 4	3.34	0.00	0.60	0.62	1.74	0.00	0.56	0.00	0.00	0.24	0.00	0.00	0.00	0.00	0.00	0.00
No 5	2.27	0.00	0.37	0.38	1.04	0.00	0.31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 6	1.83	0.00	0.31	0.27	0.54	0.00	0.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 7	2.62	0.00	0.44	0.39	0.91	0.00	0.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.00	0.00	0.00	0.00
No 9	0.50	0.00	0.28	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.00	0.00	0.00	0.00
No 10	129	3.35	37.3	1.10	0.47	0.00	0.09	0.00	0.00	0.00	0.00	0.0	0.00	0.00	0.00	0.00
No 11	596	0.6	44.1	10.8	5.78	0.27	1.14	0.42	0.00	0.00	0.00	0.0	0.00	0.00	0.00	0.00
No 12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.00	0.00	0.00	0.00
No 13	0.53	0.02	0.00	0.09	0.48	0.00	0.13	0.04	0.06	0.06	0.00	0.0	0.00	0.00	0.00	0.00
No 14	52	0.38	17.3	2.93	13.4	3.18	7.22	5.02	1.43	1.98	0.00	0.0	0.00	0.00	0.00	0.00
Samples from mining operations																
No 15	0.00	0.00	0.00	0.0	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.00	0.00	0.00	0.00
No 16	0.95	0.00	0.00	0.00	3.21	0.00	2.35	2.42	2.17	1.20	5.30	5.67	0.00	0.00	0.00	0.00
No 17	0.26	0.00	0.00	0.00	0.54	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.00	0.00	0.00	0.00
No 18	0.00	0.00	0.00	0.45	0.40	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.00	0.00	0.00	0.00
No 19	0.00	0.00	0.00	0.79	0.56	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.00	0.00	0.00	0.00
Surface water from a sludge dam																
No 20	1.12	0.00	0.00	0.00	5.44	0.33	6.15	7.01	5.52	5.70	11.9	12.0	0.00	0.00	0.00	0.00
Averages	**99**	**0.46**	**11.0**	**5.78**	**2.71**	**0.42**	**0.94**	**0.75**	**0.45**	**0.46**	**0.86**	**0.88**	**0.0**	**0.0**	**0.0**	**0.0**

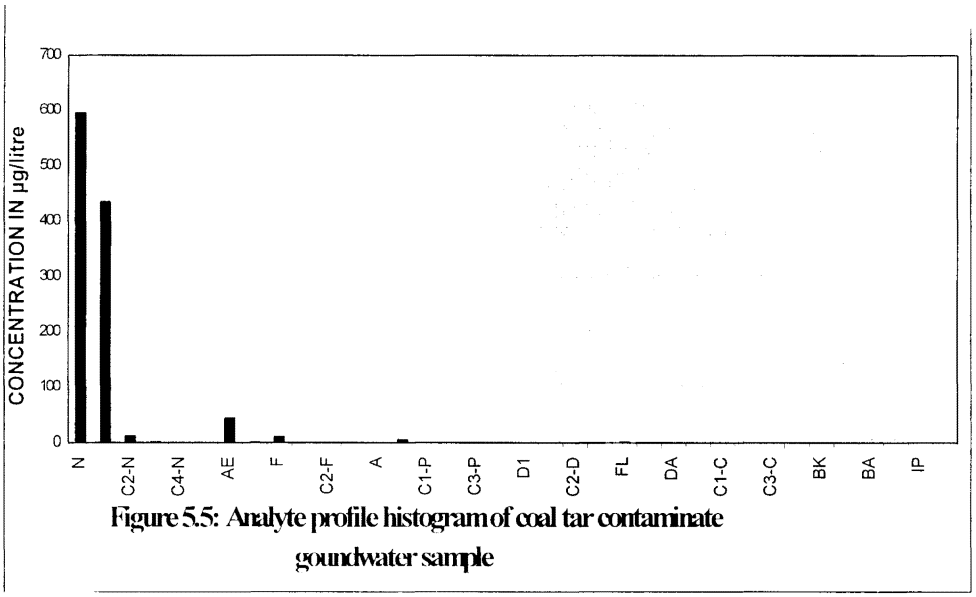

Figure 5.5: Analyte profile histogram of coal tar contaminate goundwater sample

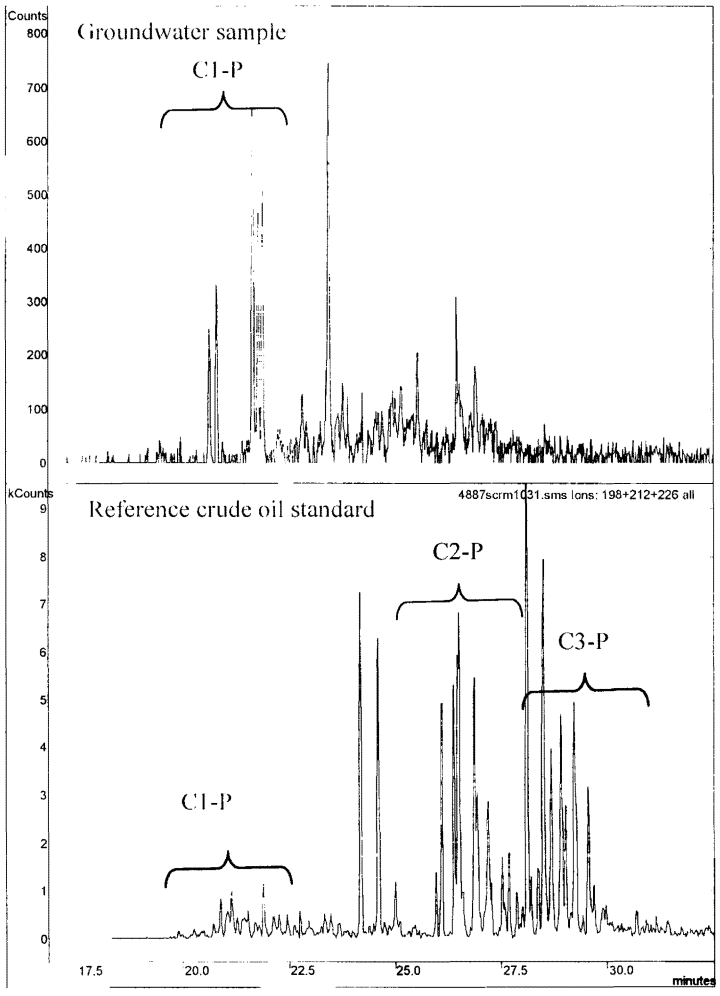

Figure 5.6: Selected ion chromatogram for the phananthrene isomers (m/z = 198, 212, 226)

Critical stages in the analysis procedure

Sampling and sample pre-treatment

The main consideration in the choice of sample container and transportation is to maintain the sample integrity and not to alter the sample composition. The most common factors affecting the stability of PAHs in water is photo-degradation, vaporisation, partitioning onto micro-particles in the water, partitioning into organic phases and adsorption onto the surface of the container. Preventing sample contact with any type of plastic or polymeric material can limit PAHs losses. Transportation and storage precautions must include cooling to below 5 °C and the exclusion of light. The addition of 0.1-1.0 % methanol will help to dissolve the PAHs.

Sample extraction

All equipment and glassware should be thoroughly cleaned before use and glassware must be treated in a muffle furnace at 450 °C to remove any traces of contamination from the glass surface. Only solvents of a high analytical purity should be used, as the extraction step is followed by an evaporation step to preconcentrate the analytes. Performing a procedural blank in parallel with samples checks for solvent purity and equipment contamination.

Sample clean-up

Adsorbents that are used for sample clean-up, such as silica gel, must be purified from contaminants by washing with pure solvent. The quality of the adsorbent is also important, as it may alter the selectivity of the clean-up step.

GC separation

Non polar columns are normally used to perform PAH separations, but it is important to use a column with the lowest bleed possible due to the sensitivity of the mass spectrometer. Columns with a high bleed will contribute to a high background and will lower the signal to noise ratio, resulting in higher detection limits. The resolving power and column bleed should, therefore, be checked on a regular basis to ensure the quality of results. Of the columns tested in our laboratory the Supelco Meridian column was found to have the lowest bleed.

MS quantification

The low-resolution ion trap mass spectrometer is considered to be less stable than a flame ionisation detector, but is essential for low detection limits and identification purposes. The optimisation and operation of the MS is crucial for reliable results. The instrument is very sensitive to carrier gas purity, leaks, moisture, contaminated injection liner and a contaminated ion trap. The moisture can be removed by baking out the ion trap for a few hours. Regular maintenance, such as the replacement of the injection liner and cleaning of the ion trap, should be performed to ensure the optimal operation of the system.

Standards

It is not so much the uncertainty of the PAH concentrations in the commercially available PAH standard mixtures that is of concern, but the storage and preparation of calibration standards. These standards are normally prepared in small volumes, resulting in larger dilution errors, and the lower concentration standards are less stable than the parent solution. A standard practice adopted in our laboratory is to prepare fresh calibration standards with every batch of analyses.

CONCLUSIONS

The accuracy and precision of the extraction method described in this chapter, using a concentration factor of 1000, was found to be acceptable compared to the data quality objectives (DQOs) listed in **Table 3.4**. The lowest quantifiable limit ranged from 0.03 ng/ cm^3 for naphthalene to 0.46 ng/cm^3 for indeno[1,2,3-cd]perylene. The quantifiable limits for the non-carcinogen PAHs were found to be a few orders of magnitude lower than the USEPA guideline concentrations, but considerably higher in he case of most of the carcinogens (see **Table 5.2**). The liquid extraction method is, therefore, not suitable for health risk assessments without further refinements and optimisation. The interpretative use of the experimental data was also found to be very limited (due to the low concentration of alkyl-PAHs in coal tar) with the conclusion that the method is not sensitive enough for this purpose. Sub pg/cm^3 detection limits are necessary to detect individual isomers in an alkyl homologue and the heavy PAHs. Only limited chemical characterisation is possible, for example the identification of petrogenic of pyrogenic profiles. The most serious disadvantage of this method was found to be the high procedural blank values obtained during standard laboratory practices. Contamination levels ranged from 0.1 to 0.8 ng/cm^3. The overall analytical performance of this method for the analysis of coal tar contaminated water samples, as measured against the set goals and objectives of this study, is shown in **Table 5.4.**

Table 5.4: Summary of analytical method performance for the analysis of coal tar contaminated water samples

Performance Criteria	Poor	Not acceptable	Acceptable	Excellent
Accuracy			x	
Repeatability			x	
Sensitivity (DL and QL) as required by USEPA		x		
Sensitivity (DL and QL) as required for Chemical Characterisation		x		
Linearity of calibration				x
Selectivity			x	
Specificity		x		
Representativiness		x		
Detectability of diagnostic ratios: D/C1-P C1-D/C1-P C2-D/C2-P C2-N/C1-P C3-N/C2-P C2-P/C2-C	 x x x	 x x x 	 	
Suitability for advanced chemical fingerpriting		x		

Chapter 6

THE USE OF SPME AND GC-MS FOR THE CHEMICAL CHARACTERISATION AND ASSESSMENT OF PAH POLLUTION IN AQUEOUS ENVIRONMENTAL SAMPLES

INTRODUCTION

The use of the Solid Phase Microextraction technique (SPME), which was introduced by Pawliszyn [1] in 1989, was investigated in this chapter for the extraction of PAHs from aqueous samples. The following aspects were investigated:

- Method detection limits and method validation
- Selectivity of SPME for PAHs
- Extraction efficiency of selected target analytes
- Depletion studies of PAHs in a complex matrix
- The suitability of the results for hazard identification and characterisation
- The suitability of the results for chemical fingerprinting

This method serves as an alternative to the modified liquid-liquid extraction technique (USEPA method 8270) reported by Boehm and co-workers[14] that was investigated in **Chapter 5**. The technique of SPME was chosen because of the advantages associated with this method of extraction, which is discussed in **Chapter 2.** The suitability of the method for the following applications was investigated

Hazard Identification

Hazard identification is based on the confirmation of the presence or absence of PAHs. The directive 80/778/EEC states a maximum contaminant level of 0.2 ng/cm^3 for the marker compounds fluoranthene, benzo-[a]pyrene, benzo[b]fluoranthene, benzo[k]-fluoranthene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene.

Chemical Fingerprinting

The determination of alkylated naphthalenes, phenanthrenes and chrysenes, as well as C_1 - C_3 dibenzothiophenes at trace levels is critical for chemical fingerprinting purposes. A detection limit of 0.01 ng/cm3 is required for individual PAHs. The detection of trace levels of alkyl substituted compounds is necessary for determining reliable diagnostic ratios[18] that can be used to differentiate between coal tar or petroleum contamination.

Health Risk Assessments

The guideline concentrations of PAHs required for health risk assessments are shown in **Table 3.1.** The guideline concentration for dibenz[a,h]-anthracene, for example, is 0.0092 ng/cm^3. Oral exposure characterisation of drinking water is calculated based on body weight, exposure duration and amount ingested (see **Table 3.1**). The importance of a sensitive and reliable analysis of PAHs was discussed earlier and the application of direct SPME-GC/MS for health risk assessments is emphasised in this study.

EXPERIMENTAL

Chemicals

Nanopure water was employed throughout. An analytical reference standard mixture of 16 priority PAHs, 2000 µg/ml each and the isotopically labelled PAH mixture, 4000

µg/cm^3 each of naphthalene-d8, phenanthrene-d10, chrysene-d12 and perylene-d12 were obtained from Ultra Scientific (Anatech, South Africa). Methylene chloride (analytical grade) was purchased from Riedel-de-Haen (Sigma Aldrich, South Africa).

GC/MS conditions

The conditions that are stipulated in **Chapter 3** were used, except for the following changes:

- The GC was operated in the splitless mode with an injector temperature of 280 °C.
- An inject liner with an internal diameter of 0.75 mm was installed to increase the efficiency of the SPME injection.

Solid Phase Microextraction

A 100µm polydimethylsiloxane fiber was obtained from Supelco (Sigma Aldrich, South Africa). For optimum repeatabilty the technique was automated using a Varian Model 8200 autosampler. Organic compounds were extracted from aqueous samples by sampling in the liquid phase, using a 1.2 cm^3 sample in 1.8 cm^3 sample vial sealed with a teflon lined septum. The fibre was immersed into the liquid and agitated by the autosampler (vibrator) for 25 minutes and then immediately inserted into the GC injector at 280°C for thermal desorption, followed by GC/MS analysis.

RESULTS AND DISCUSSION

Method validation

The objective for the SPME-GC/MS method developed in this study is to obtain reliable measurements at low concentrations in complex matrices. The summary of the analytical performance is given in **Table 6.1**. Reference materials for PAHs in environmental water samples are not currently available and the analytical performance studies were performed using laboratory prepared standards. The method was optimised at the lower concentration ranges and calibration standards were obtained by spiking ultra-pure water with a certified PAH standard mixture to obtain calibration standards with concentrations ranging from 0.2 ng/cm^3 to 8 ng/cm^3. Straight-line calibration curves were constructed and a good linearity was characterised by correlation coefficients of about 0.99.

The recovery and repeatability were determined by the addition of a known amount of PAHs (6 ng/cm^3) to ultra-pure water. The recovery obtained (analysis result using internal standards and response factors divided by added amount) for each PAH ranged from 96 to 142%. Relative standard deviations (%RSD) were better than 20% in all instances. A general trend of an increase in RSD with an increase in the size of the PAH was observed.

The detection and quantification limits stated in **Table 6.1** are estimated from the signal to noise ratios. The method was found to be the most sensitive for naphthalene, signal to noise ratio of 8961 (signal = 112985 counts, noise = 13 counts) at the 2 ng/cm^3 level, and an estimated corresponding detection limit of 0.0006 ng/cm^3. Chrysene showed the lowest signal to noise level and highest detection limit. All the PAHs exhibit detection limits and blank values well below the guideline concentrations specified by the USEPA. Blank values were obtained on ultra-pure water samples spiked with internal standards for quantification.

Table 6.1: Calibration and analytical results

	CALIBRATION (4 levels: 2 – 8 ng/cm^3)		ACCURACY AND PRECISION			SENSITIVITY			REPRESENTATIVINESS	WATER STANDARDS
Compound	Regression Coefficients (R^2)	% RSD	Ave values found for a 6 ng/cm^3 spiked sample	% Recovery	% RSD (n=10)	Signal to Noise (S/N) At 2 ng/cm^3	Quant. Limit [(a)] ng/cm^3	Detection limit [(b)] ng/cm^3	Procedural Blank Values ng/cm^3	Guideline concentrations[(c)] USEPA ng/cm^3
Naphthalene	0.9998	2.21	6.12	102	8.9	8961	0.002	0.0006	0.000	1500
Acenaphthylene	0.9993	5.21	5.95	99	3.0	6143	0.003	0.0009	0.000	1500
Acenaphthene	0.9994	3.59	5.88	98	3.5	5940	0.003	0.0009	0.000	2200
Fluorene	0.9998	1.81	6.42	107	7.0	6254	0.003	0.0009	0.000	1500
Phenanthrene	0.9997	2.31	5.99	100	1.6	1407	0.014	0.0040	0.021	1500
Anthracene	0.9995	2.48	5.78	96	3.5	1856	0.010	0.0030	0.000	11000
Fluoranthene	0.9997	1.13	6.27	105	11.3	2725	0.007	0.0020	0.015	1500
Pyrene	0.9987	3.78	6.41	107	12.5	2970	0.007	0.0020	0.012	0.11
Benzo[a]anthracene	0.9768	23.9	8.42	140	6.3	1019	0.020	0.0060	0.000	0.092
Chrysene	0.8805	41.3	8.54	142	4.1	866	0.046	0.0070	0.031	2.09
Benzo[k]fluoranthene	0.8344	54.3	7.07	118	11.8	1945	0.012	0.0030	0.000	0.92
Benzo[a]pyrene	0.8962	43.2	7.71	129	17.8	1355	0.017	0.0045	0.000	0.0092

(a) - Signal to noise = 10
(b) - Signal to noise = 3
(c) – USEPA Guideline Concentrations for a 10^{-6} cancer risk.

Some of the observed blank values were found to be higher than the detection limits, which shows that that the detection limits obtained by extrapolation in **Table 6.1** cannot be reached in practice due to background levels (chemical noise). The values were, however, relatively low and indicate minimal carry-over from the SPME fiber when analysing samples with low contamination levels. Analysis of severely contaminated samples may lead to carry-over problems.

The analytical performance of the SPME-GC/MS method (**Table 6.1**) were found to be better than the performance of the solvent extraction technique (**Table 5.2**). The linearity of the calibration curves and the precision measurements were comparable. Detection limits found with the SPME method were between 10 and 100 times lower. The SPME signal to noise ratios were found to be higher for lower concentrations, for example naphthalene: S/N_{SPME} = 8961 at 2 ng/cm^3 compared to $S/N_{EXTRACTION}$ = 3484 at 40 ng/cm^3. The improvement found is mainly due to the fact that the SPME injection is done in a splitless mode while the extract is injected with a 1:25 split ratio. The blank values obtained with SPME were also much lower than those obtained with the liquid-liquid extraction technique, which improved the uncertainty of the results. In the case of the extraction procedure trace pollutants in the solvents are also concentrated together with the analytes and contamination is much more likely due to all the glassware and equipment involved during the analysis. SPME, on the other hand, does not require sample preparation procedures, such as pre-concentration or matrix clean-up.

Selectivity for PAHs

The hydrophobic nature of PAHs suggests high distribution coefficients between the non-polar PDMS-fiber and the water matrix. The selectivity of SPME for individual PAHs is illustrated in **Figure 6.1**, which is a standard chromatogram obtained from a water sample spiked with 2 ng/cm^3 each priority PAH. Certain chromatographic inertness performance criteria as specified in USEPA method 525 are illustrated in **Figure 6.1**. Baseline separation for anthracene and phenanthrene and separation of benzo[a]anthracene and chrysene by a valley less than 25% of average peak height, were achieved without difficulty.

Efficiency of a SPME fiber extraction

The absorption of analytes into the polymeric phase is described by the conventional volume-based distribution coefficient[35]:

$$K_{dv} = \frac{M_f / V_f}{M_w / V_w} \quad \ldots.6.1$$

where M_f is the mass of analyte extracted by the fiber at equilibrium, M_w is the mass of analyte remaining in the water, V_f and V_w are the volumes of the fiber and water respectively. Another parameter, which can be used to predict SPME fiber-water partitioning behaviour, is the octanol-water partition coefficients (K_{ow}). Good agreement between K_{ow} and K_{dv}, obtained with the 100µm PDMS fiber, has been reported in the literature for low molecular analytes (such as benzene, toluene and xylenes). Yang and co-workers[36] reported negative correlation between K_{ow} and K_{dv} for analytes with higher molecular weights. Based on the experimental data they found, they concluded that K_{ow} could not be used to anticipate the K_{dv} trend in SPME for PAHs with molecular weights higher than naphthalene. They also found disagreement between K_{dv} values with different coating thickness and demonstrated that K_{dv} is not valid to describe the sorption behaviour of these analytes.

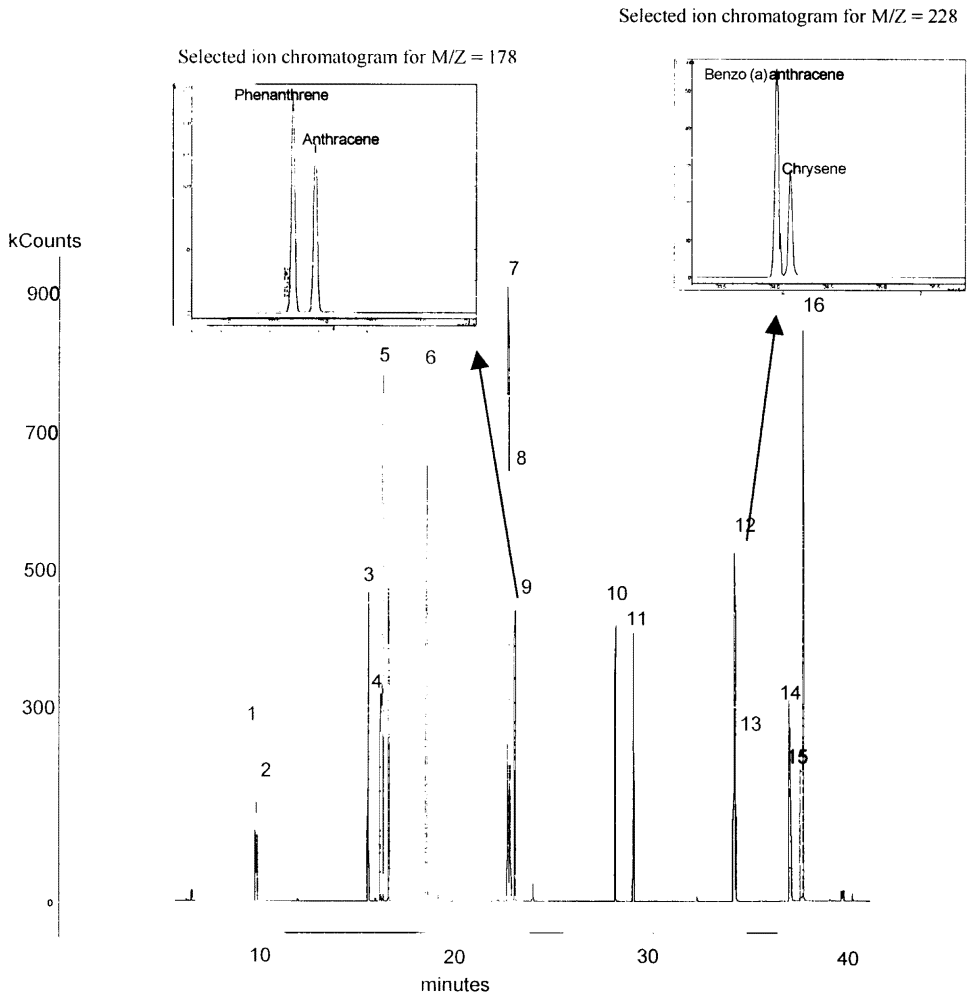

Figure 6.1: Chromatogram of 2 ng/cm^3 PAHs illustrating chromatographic and inertness performance. (1)d_8-naphthalene (2) naphthalene (3) acenaphthylene (4) d_{10}-acenaphthene (5) acenaphthene (6) fluorene (7) d_{10}-phenanthrene (9) anthracene (10) fluoranthene (11) pyrene (12) benzo[a]anthracene (13) chrysene (14) benzo[b]fluoranthene, benzo[k]fluoranthene (15) d_{12}-perylene (16) benzo[a]pyrene.

Better agreement was found when using a surface-based sorption-partitioning coefficient (K_{ds}). In this study, for simplicity, the fractional amount of analyte adsorbed onto the 100µ PDMS fiber (extraction efficiency and sensitivity) was determined experimentally. Analytes included several PAHs and their alkyl homologues. It is very useful to define the fractional amount of solute in each phase after time limited non-equilibrium extraction. The investigation was therefore not based on extractions where equilibrium has been reached.

As shown in a previous study[37], equilibrium can take as long as a few hours to days, which is not practical for a routine method. It was also shown that a proportional relationship exists between the adsorbed analyte and its initial concentration in non-equilibrium conditions. A non-equilibrium extraction time of 25 minutes was adopted for the purpose of this study, a convenient time that would allow automated extraction for the duration of the previous GC/MS run of typically 25 minutes. Extraction efficiency was then determined by

averaging four independent determinations of different concentrations ranging between 0.2 and 8 ng/cm^3. Due to limits imposed by aqueous solubilities, concentrations of chrysene, benzo[a]anthracene, benzo[k]fluoranthene and benzo[a]pyrene are limited to a maximum concentration of 2 ng/cm^3 in standards. The sample volume used throughout this study was 1.2 cm^3. The amount of analytes absorbed into the fibre was determined as follows:

(1) the sum of peak areas $\sum A_i$ for a known quantity of analyte (C^0_{aq}) was determined from two successive extraction steps, using the following equation[44]

$$\sum A_i = A_1^2/(A_1 - A_2) \quad \text{.... (6.2)}$$

(2) The amount extracted with a single extraction (C_1) was then determined using:

$$C_1 = A_1/\sum A_i \times C^0_{aq} \quad \text{.....(6.3)}$$

(3) The efficiency of a single stage extraction was then determined as the fractional amount found in the fibre phase after equilibrium, and expressed as % :

$$\%P = (C_1/C_0)\times 100 \quad \text{.....(6.4)}$$

The range of extraction efficiency found for selected PAHs and alkyl-PAHs under the conditions used in this study is shown in **Table 6.2**. It must be emphasised that the extraction efficiency (%P) values depicted in the table were obtained under the specific non-equilibrium conditions of this study. It illustrates the variation in %P that is dependent on various factors, such as the fiber condition (number of times used), absorption time, sample pH, sample matrix, sample temperature, agitation method, etc. Examining the results in Table 6.2 reveals that the average extraction efficiencies found for parent PAHs range between 20% and 65%.

TABLE 6.2: Extraction efficiency (P) of various PAHs from ultrapure water

Analyte	% P Range
Naphthalene	20 – 35
C_1-Naphthalenes	35 – 45
C_2-Naphthalenes	55 – 65
C_3-Naphthalenes	50 – 60
C_4-Naphthalenes	40 – 50
Biphenyl	45 – 55
Acenaphthylene	45 – 55
Acenaphthene	45 – 55
Fluorene	45 – 55
Dibenzofuran	45 – 55
Dibenzothiophene	30 – 40
Phenanthrene	40 – 60
Anthracene	40 – 60
Fluoranthene	40 – 60
Pyrene	40 – 60
Benzo[a]anthracene	40 – 60
Chrysene	40 – 60
Benzo[k]fluoranthene	35 – 60
Benzo[a]pyrene	35 – 60
Benzo[g,h,I]perylene	35 – 60
Dibenz[a,h]anthracene	35 – 60
Indeno[1,2.3-cd]pyrene	35 – 60

A general trend of an increase in extraction efficiency with an increase in degree of alkylation was observed. This agrees with the findings of Liu et. al.[13] that alkyl-PAHs show much higher *K* values than the parent PAHs, because PAHs with side chains are more soluble in the hydrophobic stationary phase and, hence, more completely extracted. The extraction efficiency of C_3-N and C_4-N was, however, found to be lower than that of C_2-N. This could be due to the fact that the experiment was performed in non-equilibrium conditions (relatively short adsorption time) and that the heavier compounds diffuse more slowly into the fiber.

Chemical Characterisation of pollutants by means of Multiple Extraction SPME (ME-SPME)

Chemical mixtures that leak into water leave behind a characteristic pattern, and the main purpose of estimating the concentrations of alkyl-PAHs is to match the PAH distribution pattern of a sample to that of a potential source. Modified solvent extraction techniques have been reported for this purpose[18]. Because standards for alkyl-PAHs are presently unavailable, the concentration of these compounds are normally calculated based on the total peak area of all the isomers in an alkyl homologue and using the RF of the corresponding parent PAH. Solvent extraction techniques have been used for this calculation method because similar extraction efficiencies are obtained for all PAHs. In the case of an SPME analysis the variation of extraction efficiencies with the degree of alkylation is the main reason why the relative response of alkyl-PAHs cannot be compared to the response of the corresponding parent PAH. Other factors that can contribute to these differences are changes in sample matrix and small changes in analytical conditions. The analytical error of estimating alkyl-PAH concentrations arises from the difference between the extraction efficiency of the parent PAH and alkyl-PAHs respectively.

The method of multiple extraction SPME (MESPME) was investigated to compensate for extraction efficiency differences. An aqueous sample with known naphthalene to C_3-naphthalene concentrations, containing d8-naphthalene as internal standard, was used for this purpose. The $\sum A_I$ of each alkyl homologue was consequently obtained by data from two extraction steps and **Equation 6.2.** The RF for each alkyl homologue was calculated and compared to those obtained with direct SPME that is based on a single extraction. The results are shown in **Figure 6.2**. For reasons discussed earlier, the alkyl-naphthalene RFs that were obtained with direct SPME were much higher than the RF for the corresponding parent PAH (naphthalene). The RFs found for the alkyl-naphthalenes using MESPME were, however, much closer to the expected value of 1.00. RF values of the parent PAHs can safely be used for all alkyl-PAHs provided that the MESPME method is applied. The results demonstrate the suitability of MESPME estimate PAH and alkyl-PAH concentrations even for compounds for which standards are not available.

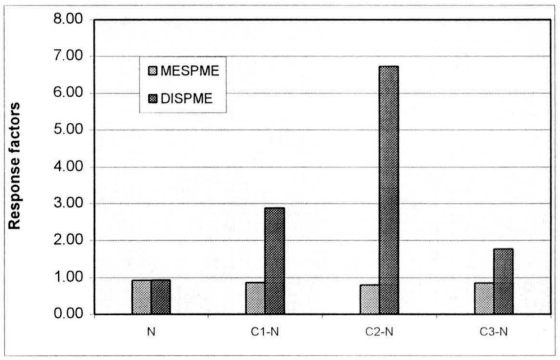

Figure 6.2: Response factors for the naphthalene homologous series using a sample of known concentrations

As discussed earlier (**Chapter 2**) the main assessment use of alkyl-PAH profiles is source identification. The results obtained with MESPME was found to be suitable to construct an analyte profile histogram to establish similarities and differences between the sample and potential sources as well as for comparison with literature profiles. The basic use is to match the profile to a typical combustion process profile (pyrogenic) or a typical crude oil/refined products profile (petrogenic)[14]. Another use is to ratio the relative abundance of the alkylated homologues of one PAH family (e.g. C_2-phenanthrene) to that of another PAH family (e.g. C_2-dibenzothiophene). These ratios are then used to distinguish between different sources. An ideal source ratio would be unique to that particular source, and if the two analytes would degrade at similar rates[38]. Weathering ratios are determined in a similar way except that two alkylated

homologues from two different PAH families are chosen that degrade at a different rate, e.g. C_3-N/C_2-P, where C_3-N will degrade faster than C_2-P.

Depletion Studies for SPME in a Complex Matrix

Aqueous environmental samples normally contain diverse and highly complex matrices in which multiphase systems exist. An example of such a system is water contaminated with a DNAPL. It was shown in a previous study[39] that less of the target analytes are adsorbed on a SPME fiber when analysing in matrices other than water, such as biological fluids, urine, milk or blood. Since SPME is an equilibrium partitioning process, a fractional amount of solute will be extracted at equilibrium or at any other period in time. This amount is linearly related to the concentration of the analyte, as long as the analysis procedure is standardised. In a typical multiphase environmental sample, the total number of moles (n) of analyte in the system can be described by **Equation 6.5**, where C_0 is the initial analyte concentration, V_{MT} is the total matrix volume, C_f and V_f is the moles of solute in the fiber, C_w V_w is the moles of solute in the water phase and $\sum C_{Mi}V_{Mi}$ is the moles of solute in the ith phase of the matrix[12].

$$n = C_0V_{MT} = C_fV_f + C_wV_w + \sum C_{Mi}V_{Mi} \quad \text{.....(6.5)}$$

The fractional amount of solute adsorbed on the fiber (p_f) at equilibrium can then be determined using the following equation:

$$P_f = C_fV_f / C_0V_{MT} \quad \text{..... (6.6)}$$

The amount of solute which can partition into the sample matrix ($\sum C_{Mi}V_{Mi}$), can have an effect on C_fV_f and, hence, on P_f. The amount of analyte adsorbed normally decreases as the matrix become more complex, i.e. an increase in the number of phases in the sample and the volume (V_{Mi}) of each phase according to **Equation 6.5**. In the steel industry, for example, a contaminated water sample can contain lipids (rolling oils), mineral oil (lubricants) and typical coal tar components (**Figure 2.2**). A previously characterised water sample found to be contaminated with coal tar and mineral oil was used to investigate the multiple extraction of naphthalene in a complex matrix. The results are shown in **Figure 6.3**, comparing the extraction profile with that of a clean water matrix. The results illustrate that in the case of the complex matrix, a portion of the analyte partitioned into the mineral oil and coal tar phase resulting in smaller extraction efficiency of the SPME fiber. The total organic concentration in this water sample was 0.01% and illustrates changes in extraction efficiency in low concentrations of organic compounds. It can, however, be accounted for by using quantitation methods such as internal standards or standard addition.

This laboratory uses deuterated internal standards and the average response factors generated from a linear 3-point calibration graph, to quantify the target parent PAHs. Alkyl-PAHs are quantified by using the technique of ME-SPME, straight baseline integration of each level of alkylation and response factors of the respective unsubstituted parent PAH. The combination of these methods significantly improves the quality and reliability of analytical data.

Improvement in signal to noise ratio using Selected Ion Storage

As illustrated in this chapter, the complexity of the sample is an issue when dealing with trace level analysis. A high level of selectivity is required for this purpose, which distinguishes analytes of interest from compounds that are co-extracted by the SPME fiber and may

possibly interfere with the analysis. In this method a degree of selectivity is achieved during each of the following analytical stages:

- SPME extraction: the selective extraction of non-polar compounds using a PDMS SPME extraction
- Gas chromatography: separation between target analytes and from interfering compounds
- Mass spectrometry: reconstruction of the gas chromatogram based on a particular mass from the mass spectrum of the anayte.

The signal to noise ratio is improved during each of these analytical stages. The technique of SIS was investigated to further improve signal to noise ratios as it removes interfering matrix ions from the ion trap leading to greater sensitivity and less spectral noise. Using the SIS mode, the universal detectivity of the MS is limited to the quantification ions of the PAHs of interest resulting in an improved signal to noise ratio, but with less qualitative information. Interfering ions are removed in the SIS mode leading to greater sensitivity. The results are shown in **Figure 6.4** where the chromatograms for a typical environmental sample is shown comparing the result of a sample analysed with (1) Solvent extraction and GC/MS (2) SPME extraction and full scan MS and (3) SPME-GC/MS in the SIS mode. The improvement in the signal to noise ratio is illustrated in this figure. The sample used in this study was contaminated with various aromatic compounds from an unknown source and that contained naphthalene, C_1-naphthalenes and C_2-naphthalenes. In the case of the solvent extraction, quantification of the C_2-naphthalenes was difficult due to the small signal and high noise interference from the other aromatic compounds. The SPME extraction was found to be more specific towards the PAHs, leading to less interference and a higher signal to noise ratio. Also notice the increase in sensitivity with increasing alkylation, comparing example two and three with example one. In the case of the solvent and SPME extraction with full-scan MS the relative intensities of the isomers were also subjected to matrix interference. The SIS mode demonstrated superior specificity for the detection of individual alkyl-PAH isomers in water samples with complex matrices.

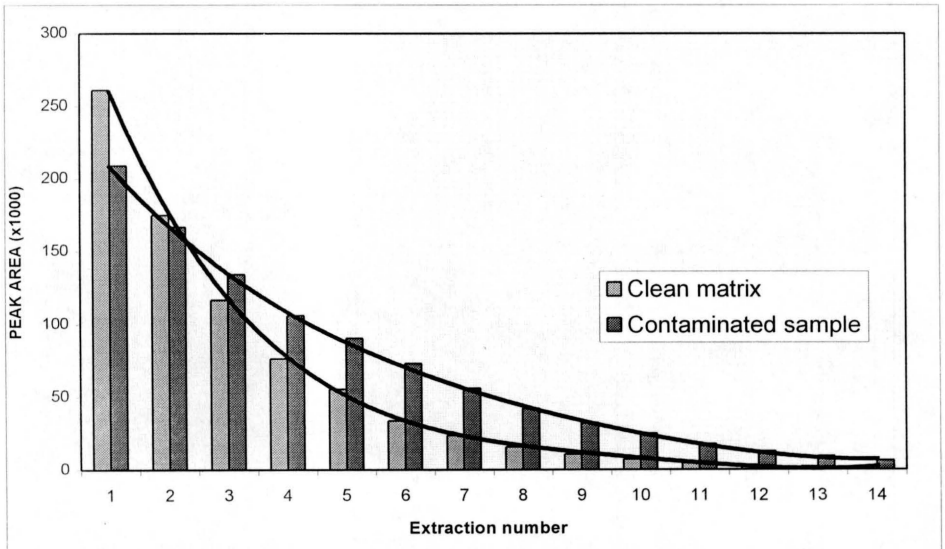

Figure 6.3: MESPME-extraction of naphthalene from (1) a clean matrix and (2) a contaminated sample

The occurrence of PAHs in contaminated groundwater

Groundwater samples that were obtained from industrial sites were analysed with the technique of SPME in the SIS mode. The results for the 16 priority PAHs are given in **Table 6.3.** The general trend of the results obtained with a SPME analysis were similar to those obtained with the extraction method (see **Table 5.3**) namely the absence of heavy PAHs (5 ringed structures). Naphthalene was also found to be the most abundant contaminant (probably due to its high solubility in water), followed by acenaphthene, fluoranthene and pyrene. As mentioned earlier the relative abundance of these compounds are typical of coal tar contamination. The overall selectivity and sensitivity were found to be better with the SPME method.

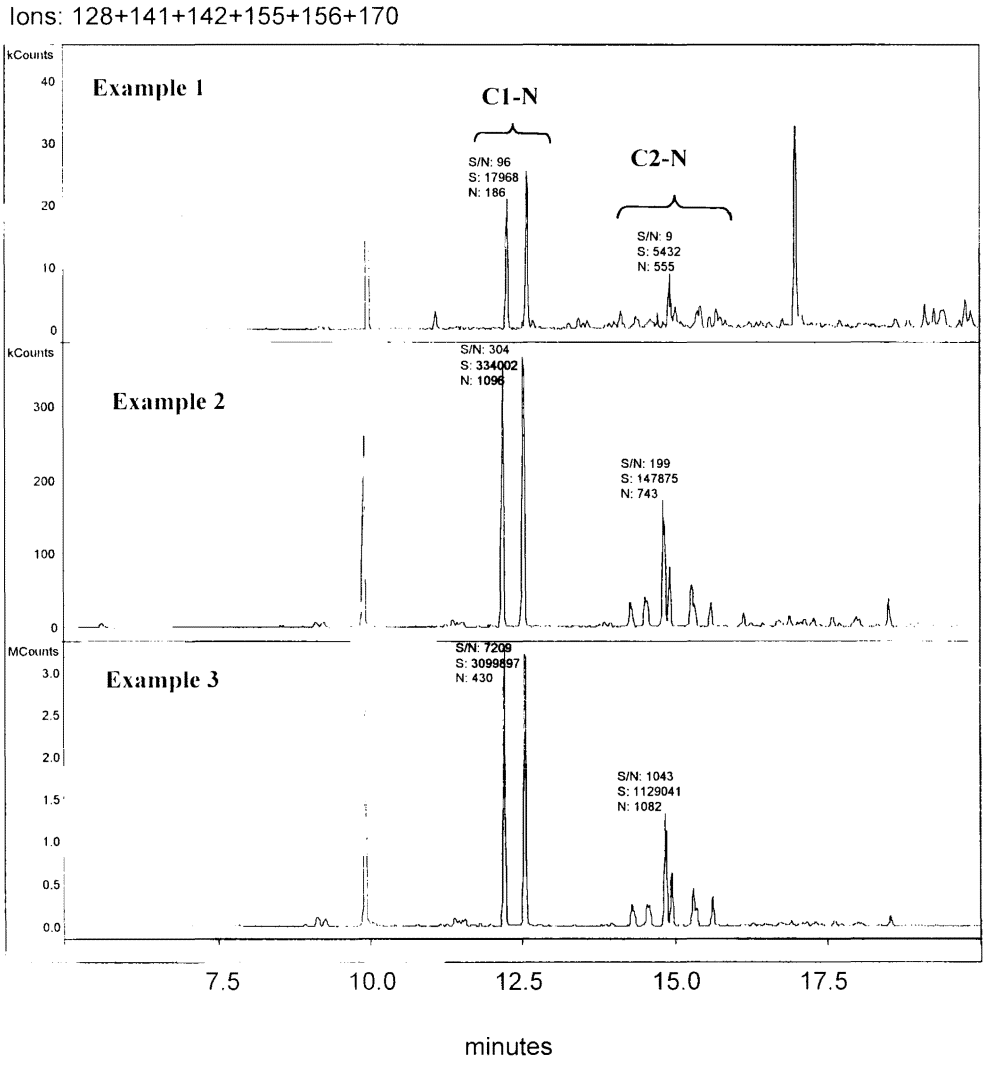

Figure 6.4: Reconstructed ion chromatograms of naphthalene, C_1-naphthalenes and C_2-naphthalenes in contaminated water sample showing signal to noise ratios. (1) Solvent extraction and full-scan MS mode (2) SPME extraction and full-scan MS mode (3) SPME extraction and SIS MS mode. (sum of ions: 128+141+142+155+156+170)

CONCLUSIONS

The technique of SPME-GC/MS was found to be a sensitive, selective, reliable and efficient method for the determination of PAHs in aqueous environmental samples. As a screening method it would be very useful, for example, during phase 3 of an Advanced Chemical Fingerprinting Project (see Figure 2.13). To a limited extent, the method can also be used for chemical fingerprinting. The main advantage of the method was, however, its sensitivity towards the carcinogenic PAHs, where detection limits were found to be lower than the health-risk based guideline concentrations for PAHs in water specified by the USEPA. Other advantages over a liquid extraction were:

- As a result of the simple pre-treatment procedure, the uncertainty of the overall results was reduced.
- SPME was applied at non-equilibrium conditions with resulting shorter analysis times.
- The method requires much smaller samples, which is better suited for the handling and transportation of large batches of samples.
- The elimination of solvent extraction techniques and automation of the extraction process together reduce analytical costs and turnover times and avoid disposal of toxic solvents.
- The method provides expedited site characterisation because it omits tedious sample preparation procedures and only uses a small sample.

Table 6.3. Results for the 16 priority PAHs from various borehole samples, expressed as ng/cm^3

	N	AC	AE	F	P	A	FL	PY	BA	C	BK	BB	BeP	DA	BP	IP
Groundwater samples from industrial sites																
No 1	0.00	0.00	0.09	0.10	1.85	0.21	3.80	2.64	0.01	0.01	1.00	0.00	0.00	0.00	0.00	0.00
No 2	0.09	0.00	0.13	0.10	0.91	0.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 3	0.30	0.00	0.28	0.00	2.54	0.48	2.19	2.11	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
No 4	0.00	0.00	0.24	0.00	4.78	0.91	11.8	9.00	0.10	0.10	0.00	0.00	0.00	0.00	0.00	0.00
No 5	0.00	0.00	0.00	0.03	4.20	0.46	13.1	9.36	0.22	0.22	0.00	0.00	0.00	0.00	0.00	0.00
No 6	7.55	0.00	2.42	0.46	29.2	3.79	12.6	7.94	0.22	0.22	0.00	0.00	0.00	0.00	0.00	0.00
No 7	3.44	0.00	0.00	0.00	0.00	0.00	0.14	0.19	0.11	0.23	0.00	0.00	0.00	0.00	0.00	0.00
No 8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 9	9.26	0.00	0.16	0.26	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 11	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.06	0.00	0.27	0.00	0.00	0.00	0.00	0.00	0.00
No 12	0.00	0.00	0.24	0.68	11.5	0.00	12.7	9.59	0.82	1.83	0.00	0.00	0.00	0.00	0.00	0.00
No 13	0.00	0.00	0.64	1.20	11.3	0.00	6.59	4.87	0.50	1.19	0.00	0.00	0.00	0.00	0.00	0.00
No 14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 15	363	0.65	17.8	16.3	5.74	1.48	1.49	1.18	0..00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 16	329	0.73	17.6	7.02	12.8	0.83	3.28	1.70	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 17	1.46	0.00	0.26	0.18	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 18	1.36	0.00	0.23	0.17	0.42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 19	0.00	0.00	0.23	0.17	0.47	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 20	0.05	0.00	0.25	0.16	0.44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Surface water samples from an industrial site																
No 21	0.13	0.18	9.63	0.00	0.22	0.23	0.04	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 22	60.1	2.96	5.28	2.80	3.30	0.45	0.44	0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Averages	**35.8**	**0.07**	**2.03**	**1.34**	**4.33**	**0.42**	**3.40**	**2.43**	**0.10**	**0.20**	**0.05**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**

The method was optimised in lower concentration range, namely 2 – 8 ng/cm^3. A range of performance characteristics that were measured indicated a fair overall degree of precision and trueness and the method was found to be adequate for the objective of the measurement. The accuracy and precision of the method was demonstrated by working under strict QA and QC rules and using spiked samples. The extraction efficiency of parent PAHs ranged between 30 and 66% and was found to be dependant on various conditions, such as fiber condition, adsorption time, sample pH, sample matrix, sample temperature, agitation method etc. Most of these conditions are under the control of the analyst, except the sample matrix. The ability of the method to be relatively insensitive towards any change in the conditions (robustness), was improved by using the technique of multiple extraction SPME. Matrix effects were further reduced using the mass spectrometer in the Selected Ion Storage mode. The method has good linearity in the low concentration range investigated and has the sensitivity required for hazard identification and health risk assessments. A detection limit of 0.0045 ng/cm^3 was found for dibenz[a,h]anthtracene, which is lower than the guideline concentration of 0.0093 ng/cm^3 required by the USEPA. The method is also suitable for chemical fingerprinting because a detection limit of 0.01 ng/cm^3 can be reached for all the individual PAHs. The overall analytical performance of this method, as measured against the set goals and objectives of this study, is shown in **Table 6.4**.

Table 6.4: Summary of SPME-GC/MS analytical method performance

Performance Criteria	Poor	Not acceptable	Acceptable	Excellent
Accuracy			x	
Repeatability			x	
Sensitivity (DL and QL) as required by USEPA				x
Sensitivity (DL and QL) as required for Chemical Characterisation				x
Linearity of calibration			x	
Selectivity				x
Specificity				x
Representativiness			x	
Detectability of diagnostic ratios in coal tar polluted samples: D/C1-P C1-D/C1-P C2-D/C2-P C2-N/C1-P C3-N/C2-P C2-P/C2-C	 x x x		 x x x 	
Suitability for advanced chemical fingerprinting			x	

Chapter 7

THE DETERMINATION OF PAHS IN SOIL SAMPLES USING PRESSURISED LIQUID EXTRACTION AND GC/MS

INTRODUCTION

The extraction, matrix clean-up and pre-concentration of PAHs from the soil samples are important sample preparation steps, which are necessary before the extract can be submitted for a quantitative analysis using GC/MS. A critical requirement for the extraction method used is to have good recovery of analytes. Noordkamp and co-workers[40] investigated and compared various methods for the extraction of PAHs from sludge and sediments, namely microwave-, ultrasonic-, various solvents- and Soxhlet extraction. Other techniques such as Supercritical Fluid Extraction[41] and Pressurised Liquid Extraction[42] have also been reported. The relatively new Pressurised Liquid Extraction (PLE) technique for the extraction of PAHs from soil and sludge samples that was discussed in **Chapter 2**, was investigated. The technique is also referred to as Accelerated Solvent Extraction (ASE). The main advantage of this extraction method above the others is automation and that the extraction process is more efficient at the elevated temperature and pressure. The GC/MS method used for the quantitative analysis of PAHs was based on the EPA method 8270. Modifications that were made to improve the overall results of the method included the redefining of the target analytes and internal standards, varying the sample mass according to expected contaminant levels (see **Table 7.1**), quantification of alkyl-PAH homologues and addition of a "keeper" solvent before evaporation. The results of this method were investigated for its applicability to the analysis of PAH contaminated soil samples and suitability for chemical fingerprinting. The sample purification and enrichment scheme is shown in **Figure 7.1.**

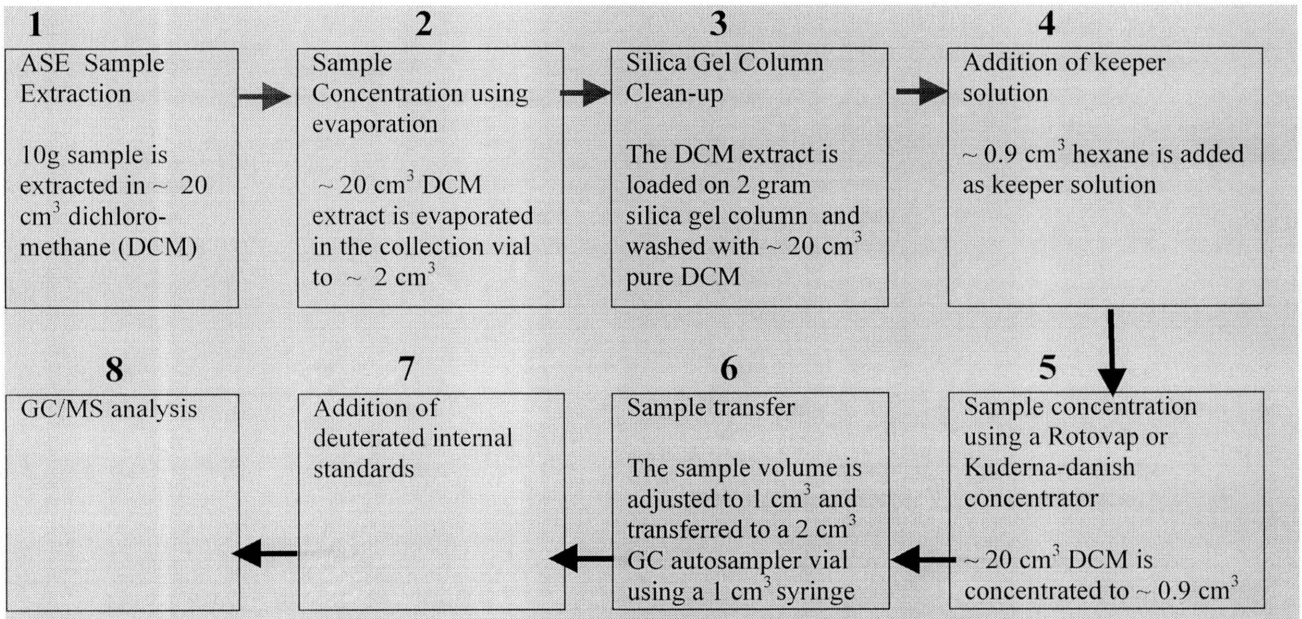

Figure 7.1: The sample purification and enrichment scheme for the analysis of soil samples

EXPERIMENTAL

Soil standards

Certified soil standard (SRS 100-103) was obtained from Resource Technology Corp. (Industrial Analytical).

Sampling and the preparation procedure for soil samples

Samples were dried before filling into the extraction cell. Samples that contained water (greater than 10%) were mixed in equal proportions with anhydrous sodium sulphate. Gummy, fibrous, or oily materials not amenable to grinding were cut, shredded, or otherwise separated to allow for mixing or maximum exposure of the sample surfaces for extraction. A cellulose disk was placed at the outlet end of the extraction cell. Approximately 0.1 - 30g (see **Table 7.1**) of each sample was weighed into a 11-cm^3 extraction cell or approximately 3 grams into a 32- cm^3 extraction cell (M_1). The extraction cells were placed into the autosampler tray and the collection tray loaded with the appropriate number (up to 24) of 40 cm^3, pre-cleaned, capped vials with septa.

ASE 200 Conditions

System pressure:	14 MPa (2000psi)
Oven Temperature:	100 °C
Sample size:	0.1 - 10 grams
Oven Heat-up time:	5 minutes
Static time:	5 minutes
Solvent:	Dichloromethane
Flush volume:	60% of extraction cell volume
Nitrogen purge:	1 MPa (150 psi) for 60 seconds

Preparation of extracts for GC/MS analysis

- The extraction vial was opened and the excess DCM extract obtained from the ASE evaporated under a stream of air to obtain a final volume of about 2 cm^3.
- A glass column fitted with a porous disk was filled with about 2 grams of stationary phase (chromatographic quality silica gel or neutral alumina). The column dimensions was 10 mm x 300 mm. The height of the stationary phase in the column was be about 50 mm.
- The stationary phase was equilibrated with DCM and air bubbles removed by shaking.
- The concentrated extract was transferred to the top of the stationary phase in the column by using a 1 cm^3 syringe. The flow rate was between 1 and 5 cm^3/minute.
- The extract was passed through the column and the eluent collected in a clean 250 cm^3 round bottom flask. The stationary phase was washed with an additional 20 cm^3 of pure DCM. Hexane (0.9 cm^3) keeper solvent was then added to the round bottom flask.
- The DCM was evaporated using a rotary evaporator to obtain a final volume of just less than 1 cm^3.
- The hexane concentrate was withdrawn from the round bottom flask using a 1 cm^3 syringe and small quantities of toluene added to the flask until the syringe was filled to the 1 cm^3 mark.
- The syringe contents were transferred to a 2 cm^3 GC autosampler screwcap vial and sealed with a teflon-coated septum.
- The appropriate amount of internal standard was added to each standard and sample, to obtain a concentration of 20 $\mu g/cm^3$.

Conditions, calibration procedure, quality control and quantitative analysis

Extracts obtained in the above way were analysed by GC/MS using the gas chromatographic and mass spectrometer conditions as described in **Chapter 3**. A 2µl aliquot of the sample was injected into the GC, equipped with a high resolution J&W DB-5 fused-silica column.

Table 7.1: Sample mass and final volume for the determination of PAHs in soil samples

Expected PAH concentration in the soil (mg/kg)	Mass in grams (M_1)	Dilution volume in cm^3 (V_1)
< 1	30g	0.25
1 – 10	10g	1
10 – 100	10g	10
100 – 500	10g	50
500 –1000	5g	50
1000 – 5000	1g	50
5000 – 10000	0.5	50
>10000	0.1	50

The temperature program of the GC oven is based on the conditions of EPA method 8270, which were developed to achieve near baseline separation of the 16 priority PAHs. The same list of target analytes, quantitation ions and internal standards, as discussed in **Chapter 5** (**Table 5.1**) were used. Before sample analysis, a five point initial calibration based on 16 parent PAHs was established, demonstrating the linear range of the analysis. Check standards were analysed with every ten samples to validate the integrity of the initial calibration. The method of internal standards, using peak areas and relative response factors (RF) generated from the linear initial calibration, was used to quantify parent PAHs. Peaks of alkyl-PAH homologues were manually integrated and their concentrations determined using the selected ion current of the primary ion (m/z), and the RF of the respective unsubstituted parent PAH compound. That is, in the absence of standards for the alkyl-PAHs, equal response is assumed between the primary ions of these compounds and the corresponding parent PAHs.

RESULTS AND DISCUSSION

Method Validation

This investigation mainly deals with the determination of PAHs in industrial soils and sediments, which have been polluted by coal tar, mineral oil, lubricating oil or similar PAH sources. Some of the PAHs, particularly the 4- to 6-ring structures, are relatively resistant to degradation, and can be used for source identification. Accurate analytical data for PAHs is required, as the toxicity of certain PAHs (see **Table 3.1**) is a concern. Maximum concentration levels are normally specified the sum of the 16 USEPA priority PAHs. The Dutch soil standard specifies a maximum total concentration of 40 mg/kg.

The interpretative objective of this method was to detect PAHs originating from anthropogenic sources relative to the background. Samples collected from unpolluted areas were analysed to determine typical background levels. The chemical data obtained from selected areas were analysed to determine the typical contaminant levels and the method sensitivity for the specific alkyl-PAH isomers that are normally used for ratio calculations. The selection criteria for the integration and reporting of each alkylated isomer were based primarily on retention time, pattern recognition relative to the soil CRM, and on the presence of selected confirmation ions. Non-zero results for each PAH were reported when the concentration is above the practical quantification limit (see **Table 7.3**). The presence of petroleum hydrocarbons (n-alkanes) in samples were also investigated to determine the contribution of petrogenic sources to the overall pollution and the

influence thereof on the PAH determinations, such as peak overlap. The performance characteristics of the method were measured against the data quality objectives that are listed in **Table 3.3**. Only the method detection limits (MDLs) of parent PAH compounds were determined, but the MDLs for isomer groups, such as C_2-naphthalenes, would generally be higher than the MDL for parent compounds, because the instrument response for each series is spread over multiple peaks. To optimise the sensitivity, data were collected only when the signal-to-noise ratio was greater than 3:1. The selectivity of the method was evaluated for its ability to detect trace levels of PAHs in complex matrixes.

Recovery and repeatability

The recoveries of PAHs from a soil matrix using PLE were determined using a certified SRS-103 soil standard with a PAH content over a wide concentration range, namely 10 – 1500 mg/kg. For this determination, a 2 gram sample was concentrated to 20 cm^3, i.e. a dilution factor of 10. The recoveries obtained are shown in **Table 7.2**.

Table 7.2: Recovery of PAHs from contaminated soil Calibration and analytical results

Compound	Recovery SRS-103 (mg/kg)	Certified Value (mg/kg)	Recovery SRS-103 as %
Naphthalene	36.4	34.8	105
Acenaphthylene	18.4	16.5	112
Acenaphthene	633	627	101
Fluorene	356	443	80
Phenanthrene	2087	1925	108
Anthracene	541	431	126
Fluoranthene	1475	1425	104
Pyrene	1237	1075	115
Benzo[a]anthracene	273	264	103
Chrysene	335	316	106
Benzo[k,b]fluoranthene	160	182	88
Benzo[a]pyrene	69	96	72
Benzo[g,h,i]perylene	29	14.2	204
Indeno[1,2,3-cd]pyrene	20	25	80

The average percentage recoveries of all PAHs were required to fall between 80 and 120%. The recoveries compared well with the certified values and except for anthracene (126%) and benzo[g,h,i]-perylene (204%). It must, however, be kept in mind that the extraction was optimised for the high concentration phenanthrene, fluorene and pyrene (dilution factor of 10) with a resulting low concentration in solution for the 5- and 6-ring compounds. They were measured at the lower end of the calibration curve with expected high %RSDs.

The average repeatability for a mid-range verification standard (40 mg/kg) was determined by using the average of twelve independent results. The RSDs ranged between 6.1% (naphthalene) and 26.8% (benzo[a]anthracene) that were all lower than the data quality objective of 30%. The highest RSDs were obtained for the 5- and 6-ring compounds. The repeatability was found to be suitable for its intended use.

Calibration

A straight-line calibration curve was constructed for each PAH to validate the linearity of the calibration over the range of 20 $\mu g/cm^3$ to 160 $\mu g/cm^3$. The values are summarised in **Table 7.3.** The 2- and 3- ring compounds showed good linearity in almost all cases and were characterised by correlation coefficients of better than 0.99. The laboratory found that fluctuations in response factors were mainly caused by injection discrimination. The GC inject speed, inlet pressure and split ratio were found to have a large influence on mass discrimination. The RSDs of the relative response factors were monitored over the longer period and showed a %RSD of smaller than 30% over the linear range of the calibration, which conforms to the data quality objectives in **Table 3.3**.

Table 7.3: Calibration and analytical results

		5-level CALIBRATION			ACCURACY AND PRECISION OF VERIFICATION STANDARD			SENSITIVITY			REPRESEN-TATIVINESS (n=19)
Compound	Internal Std	Average RF	Average Regression Coefficients (R^2)	Average %RSD	Value found for a 40 ng/cm^3 spiked sample	% Recovery	%RSD for a 40 ng/cm^3 Standard (n=10)	Signal to Noise (S/N) At 40 ng/cm^3	Quant. Limit [(a)] mg/kg	Detection limit [(b)] mg/kg	Procedural Blank Values mg/kg
Naphthalene	A	0.98	0.998	6.4	40.0	100	6.1	3484	0.004	0.001	0.000
Acenaphthylene	B	1.58	0.996	4.9	39.5	99	7.7	1613	0.008	0.002	0.000
Acenaphthene	B	1.20	0.996	6.1	38.9	97	8.2	4360	0.004	0.001	0.000
Fluorene	C	0.64	0.993	8.5	39.6	99	16.3	2260	0.008	0.002	0.000
Phenanthrene	C	0.95	0.995	8.8	40.3	101	11.0	1394	0.010	0.003	0.093
Anthracene	C	0.85	0.979	15.2	40.4	101	14.2	602	0.022	0.007	0.016
Fluoranthene	C	1.50	0.999	3.2	37.4	94	16.3	4332	0.003	0.001	0.015
Pyrene	C	1.71	0.999	3.8	36.4	91	16.1	4711	0.003	0.001	0.014
Benzo[a]anthracene	D	2.71	0.991	22.0	36.4	91	26.8	1679	0.008	0.002	0.012
Chrysene	D	2.84	0.990	13.7	37.2	93	25.6	1609	0.008	0.002	0.023
Benzo[k]fluoranthene	D	3.42	0.992	11.1	35.0	88	23.2	1660	0.008	0.002	0.000
Benzo[a]pyrene	D	3.15	0.990	15.0	40.3	101	25.2	759	0.017	0.006	0.000
Benzo[g,h,I]perylene	E	2.82	0.999	0.3	42.9	107	24.4	244	0.054	0.016	0.019
Dibenz[a,h]anthracene	E	3.06	0.996	9.4	38.6	97	26.4	279	0.054	0.016	0.000
Indeno[1,2,3-cd]pyrene	E	2.86	0.996	5.9	41.4	104	20.0	253	0.054	0.016	0.000

(a) - Signal to noise = 10, and based on a 30x concentration factor
(b) - Signal to noise = 3, and based on a 30x concentration factor
(c) - Maximum concentration level, US Environmental Protection Agency.

Internal standards: A = Naphthalene–d8 B = Acenaphthene-d10 C = Phenanthrene-d10 D = Chrysene-d12 E = Perylene-d12

Method Detection limits

Estimated MDLs are based on a sample mass of 30 grams and a final volume of 1 cm^3, i.e. a concentration factor of 30. Under these conditions individual parent PAHs can be determined with the lowest quantifiable limit ranging from 0.004 mg/kg for naphthalene and 0.054 mg/kg for the 6-ring compounds. These practical quantification limits are well below the regulatory requirement of a total of 40 mg/kg, as specified in the Dutch soil standards. The MDLs ranged from 0.001 to 0.016 mg/kg, which was lower than the 0.066 mg/kg specified by the USEPA for individual PAHs and in most cases, lower than the 0.010 mg/kg required for chemical fingerprinting studies. The ASE-GC/MS method was found to be suitable for the application to hazard and advanced chemical fingerprinting.

Representativeness

The average PAH content of procedural blanks was obtained from values that were acquired over a period of one year. These values ranged between 0.000 and 0.093 mg/kg, which were all within the limit of 10 x MDL, except for phenanthrene, which was 31 x MDL.

Selectivity

A typical chromatogram for a PAH contaminated soil sample (SRM-103-100) is shown in **Figure 7.2**. This sample was chosen because it contains large quantities of a full range of pollutants and because this sample was contaminated by a petrogenic source, presenting large quantities of alkyl-PAHs and aliphatic hydrocarbons. Excellent separation is achieved between the large variety of contaminants and the separation between phenanthrene (8) and anthracene (9) is shown in the figure. This example illustrates the selectivity of the method to separate the target analytes from co-extracted compounds.

Specificity for alkyl substituted isomers

A high degree of specificity is required to be able to differentiate among various isomers, which is used to calculate source or weathering ratios. The selected ion chromatograms of isomers that are normally used for this purpose (naphthalenes, phenanthrenes and dibenzothiophenes) are shown in **Figures 7.3, 7.4 and 7.5**. The figure shows data obtained for two samples, namely the crude oil contaminated reference standard SRM 103-100 and a typical coal tar contaminated soil sample. The results in **Figures 7.3 – 7.5** illustrates the following:

- most isomers are well separated from co-extracted compounds and each other which allow the analyst to differentiate among most isomers
- the sensitivity of alkyl substituted isomers decrease with an increase in the degree of alkylation due to the pyrogenic profile of coal tar contaminated samples.

In the case of this specific coal tar contaminated sample the C_2-substituted isomer peak intensities were characterised by a very low signal to noise ratio. In samples with a low degree of contamination C_2-P, C_1-D and C_2-D isomers peaks could not be detected at all. The conclusion is that the calculation of reliable source and weathering ratios, e.g. C_2-P/C_2-D and C3-N/C2-P respectively, are only possible in samples with a high degree of contamination.

The analyses of typical soil and sediment samples

Various soil and sediment samples obtained from different industrial areas were analysed for this purpose using PLE and GC/MS analysis. Sediment samples were obtained in a wastewater channel flowing from an industrial site. The site history of the sampling points revealed that coal tar spills occurred at these sites over the last few years and were

contaminated with PAHs. The drill-core samples were collected at intervals of one meter, i.e. (a) is taken 1 meter below the surface, (b) is taken 2 meters below the surface etc. The results for the 16 priority PAHs found in these samples are given in **Table 7.4**. The concentrations of individual PAHs found in the samples varied from 0.05 to 396 mg/kg. Different trends were observed for the three different boreholes, No 1 - 3. In the case of Sample No 1 contamination was mainly present in the top layer of the soil, with a gradual decrease in PAH concentration deeper down. The trend in borehole No 2 was exactly the opposite, namely a relative low concentration of PAHs on the surface, with an increase in PAH concentration with an increase of depth. In bore hole No 3 there was first an increase and then a decrease in PAH concentrations with an increase of depth. PAHs were also found in certain sediment samples. The concentration of PAHs in the sediment samples was relatively low and the heavy PAHs were found to be more abundant. The results are in agreement with the theory that heavy PAHs have a high fugacity in water and will tend to partition onto sediments.

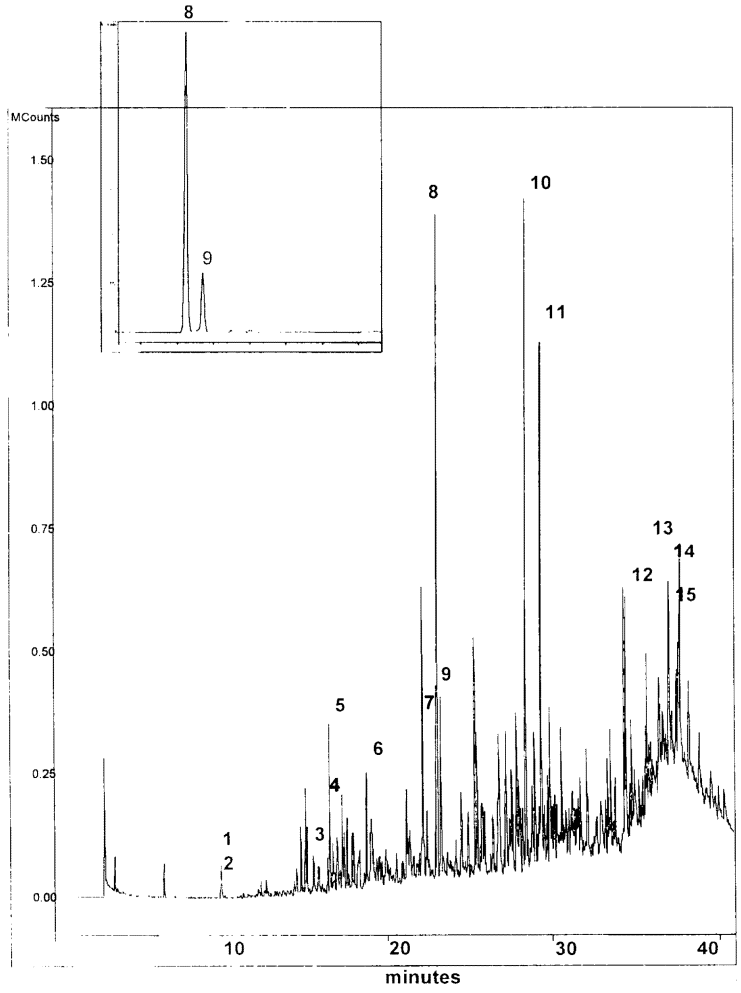

Figure 7.2: Total ion chromatogram of a contaminated soil extract – SRM 103-100: : (1)d10-naphthalene (2) naphthalene (3) d8-acenaphthene (4) acenaphthene (5) acenaphthylene (6) fluorene (7) d10-phenenthrene (8)phenenthrene (9) anthracene (10) fluoranthene (11) pyrene (12) d12-chrysene (13) chrysene (14) d12-perylene (15) benzo[a]pyrene. Selected ion current (m/z = 178) for phenanthrene and anthracene shown in the window at the top to illustrate the spesificity.

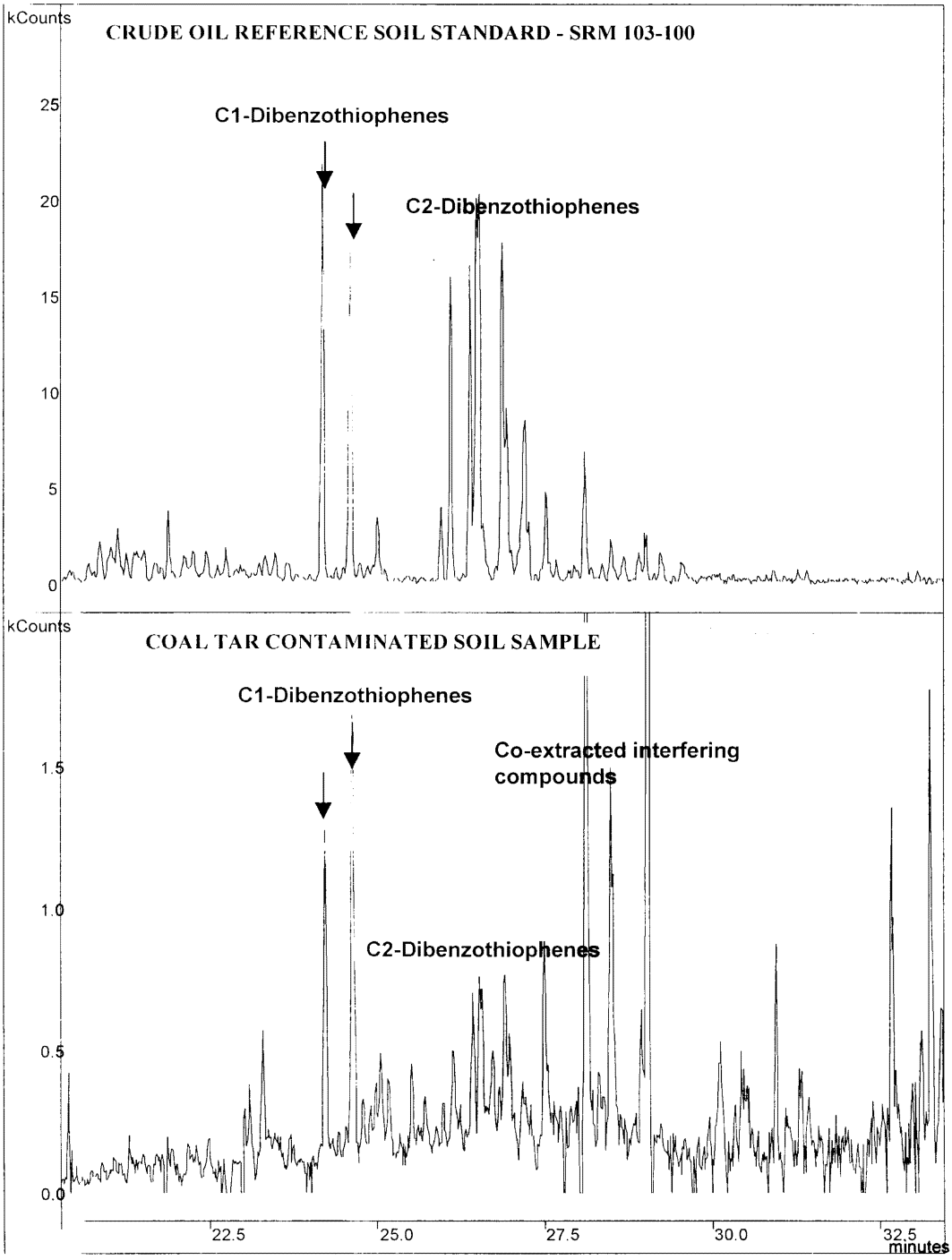

Figure 7.3
: Selected Ion Current plots for alkyl substituted dibenzothiophene isomers

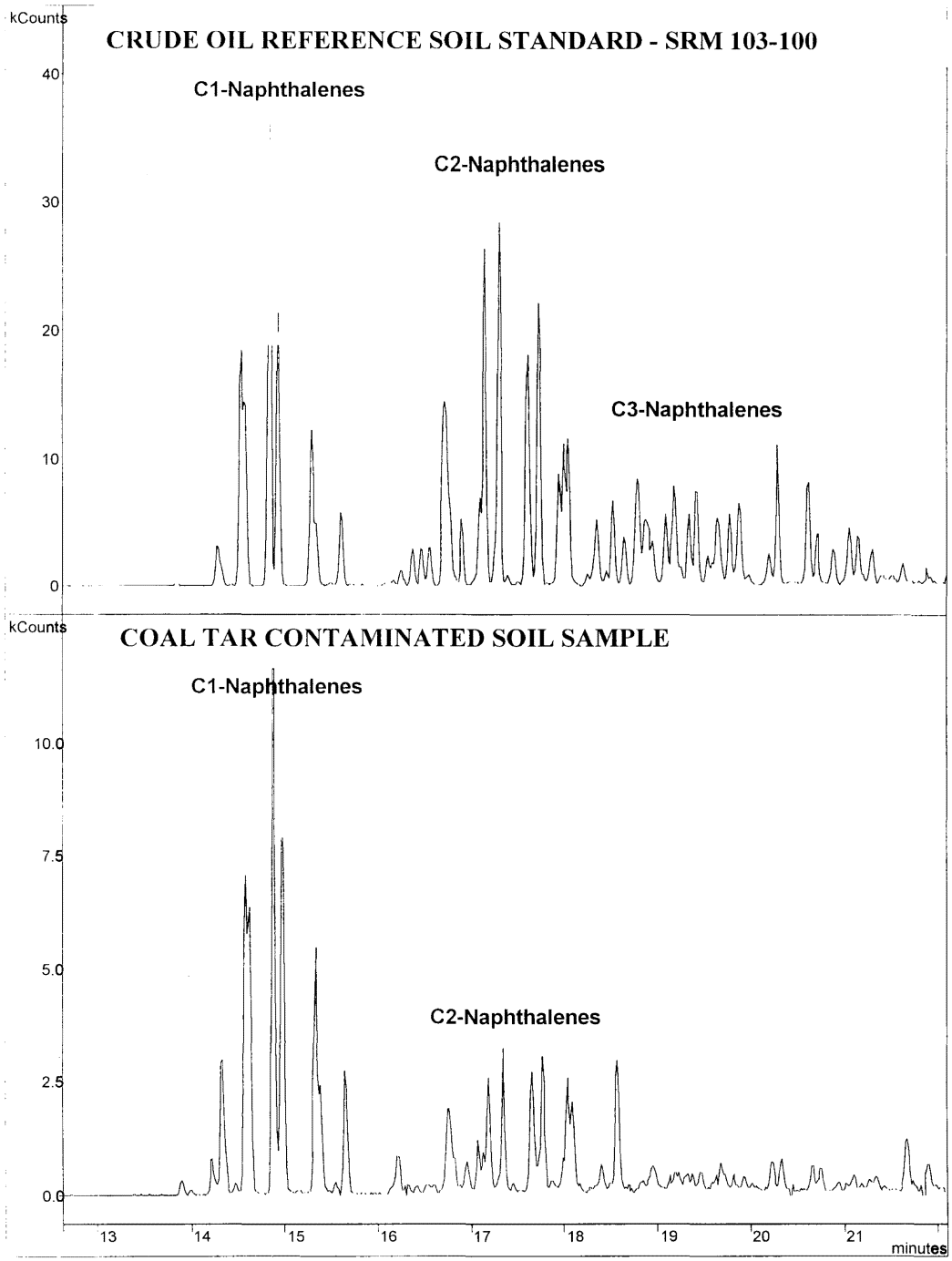

Figure 7.4: Selected ion current plots for the alkyl substituted naphthalene isomers

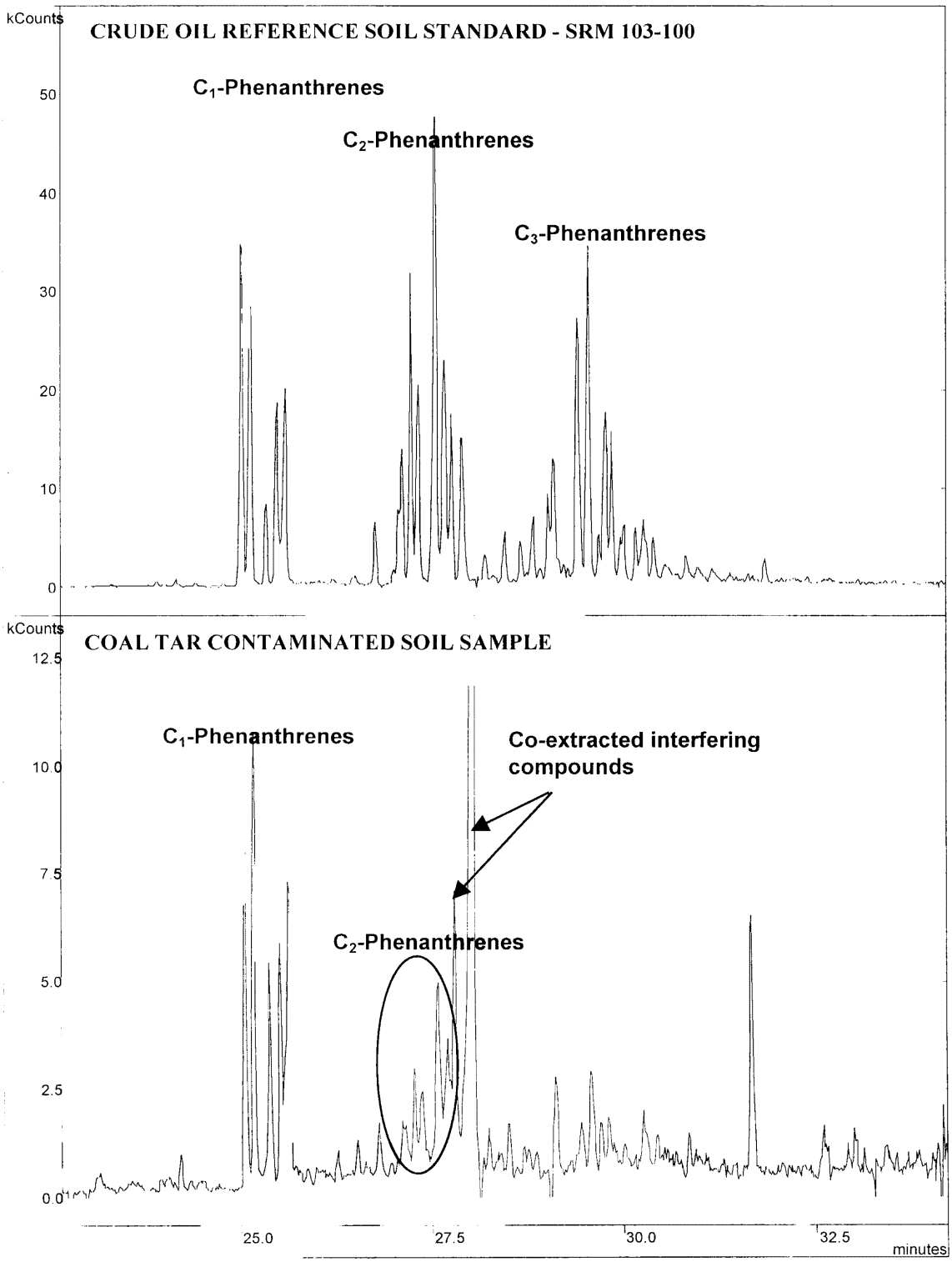

Figure 7.5: Selected Ion Current plots for alkyl substituted phenanthrene isomers

As coal tar is the suspected source of contamination, a relatively high abundance of FL and PY were found. The results for soil samples that were collected in an unpolluted area but close to an industrial site, indicate that background levels of PAHs in the area are generally < 0.08 mg/kg. These values are low enough to allow the detection and characterisation of coal tar pollution.

Critical stages in the analysis procedure

Sampling and sample pretreatment

The most critical factors affecting the stability of PAHs in soils is vaporization and photo-degradation. Transportation and storage precautions must include cooling to below 5 °C and light must be exclude to avoid photo-degradation.

Sample purification and enrichment

It is critical to remove the polar organic substances from the DCM extract to limit matrix interference and ensure high quality results

Sample extraction

As contamination is always a factor in trace analysis, the extraction cells and glassware should be thoroughly cleaned before use and glassware must be treated in a muffle furnace at 450 °C to remove any traces of contamination from the glass surface. Only solvents of a high analytical purity should be used, as the extraction step is followed by an evaporation step. The solvent purity and equipment contamination was checked by performing a procedural blank in parallel with samples.

Sample clean-up

Adsorbents that are used for sample clean-up, such as silica gel, must be purified from contaminants by washing with pure solvent. The quality of the adsorbent is also important, as it may alter the selectivity of the clean-up step.

Standards

The storage of certified reference soil standards is critical. These standards must be stored in a refrigerator below 5 °C to prevent evaporation.

CONCLUSIONS

The PLE extraction method followed by GC/MS was validated during this investigation and found to be suitable for the determination of PAHs in soil samples in µg/kg to mg/kg range. The detection limits of the method were well below the soil standards specified by the USEPA. Based on the detection limits, selectivity and specificity, the method was also found to be suitable for advanced chemical fingerprinting. In most of the soil samples that were investigated during this study it was possible to distinguish between petrogenic and pyrogenic profiles, even at low levels of contamination (< 1 mg/kg). The detection of isomers of C_2- to C_4-alkyl-PAHs was, however, very limited due to the low abundance of these compounds found in the coal tar polluted soil samples. Due to a lack of data for the higher degree of alkyl-PAHs in slightly contaminated samples, reliable source and weathering ratios could not be determined.

For advanced chemical fingerprinting, where lower detection limits are required, the method detection limits can be improved by:

- increasing the sample size to 30 grams
- reducing the final volume to 250 µl
- acquiring the MS spectra in the SIS mode.

Implementing these changes will decrease the detection limit quoted in **Table 7.2** by a factor of between 200 and 600, but with the disadvantage of also increasing the spectral noise.

Table 7.4. Results for the 16 priority PAHs from various borehole samples, expressed as mg/kg

		N	AC	AE	F	P	A	FL	PY	BA	C	BK	BeP	BP	IP
INDUSTRIAL SOIL SAMPLES															
	Depth														
No 1(a)	1 m	3.69	114	87	39.5	726	149	768	641	--	353	181	256	234	188
No 1(b)	2 m	1.20	9.2	24.2	8.1	180	23.5	121	93	--	52	72	41	30	24
No 1(c)	3 m	0.61	0.60	1.07	0.87	10.9	0.64	6.07	4.09	2.06	1.89	2.42	1.54	0.00	0.00
No 1(d)	4 m	0.00	0.00	0.00	0.00	1.44	0.00	1.00	0.78	0.00	0.00	0.00	0.00	0.00	0.00
No 1(e)	5 m	0.00	0.00	0.00	0.00	0.83	0.00	0.78	0.69	0.00	0.00	0.00	0.00	0.00	0.00
No 1(f)	6 m	0.00	0.00	0.00	0.00	0.61	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 2(a)	1 m	1.91	2.44	0.78	0.00	4.30	1.22	5.84	4.88	2.56	2.78	6.00	3.94	3.47	3.01
No 2(b)	2 m	2.90	9.20	1.28	0.00	9.51	4.94	27.5	24.7	6.81	16.5	19.7	9.10	6.60	5.20
No 2(c)	4 m	2.90	10.9	4.93	0.00	46.7	9.00	43.8	33.0	18.9	19.8	7.33	11.4	8.70	7.20
No 2(d)	5 m	23.0	5.43	46.4	10.9	193	31.6	62.6	37.5	7.73	8.06	5.60	3.99	2.56	2.24
No 2(e)	6 m	56.2	4.21	72.2	45.0	164	30.5	37.6	21.1	2.30	3.34	2.75	1.64	1.63	1.48
No 3(a)	1 m	2.29	6.04	0.97	0.00	14.6	3.49	25.8	20.6	11.2	13.4	18.5	12.0	9.62	7.75
No 3(b)	2 m	4.17	7.10	1.33	0.00	8.65	0.00	14.1	11.5	6.95	8.36	9.81	9.42	5.73	5.13
No 3(c)	3 m	1.35	3.80	0.44	0.00	5.51	0.00	8.08	6.68	3.71	4.75	8.67	3.87	0.00	3.07
No 3(d)	4 m	4.80	7.18	2.37	0.00	8.71	2.60	14.7	12.6	7.80	9.70	14.3	9.99	8.51	6.70
No 3(e)	5 m	4.30	29.9	2.32	0.00	27.1	14.8	86.1	71.7	44.0	51.0	57.8	44.1	31.3	22.2
No 3(f)	6 m	7.20	62.8	23.8	8.55	91.8	42.8	225	195	91.4	101	97.6	66.2	42.8	31.0
No 3(g)	7 m	5.73	84.8	63.5	0.00	181	74.2	352	293	109	113	110	64.3	58.4	40.0
No 3(h)	8 m	11.9	84.6	79.1	0.00	250	85.6	396	329	130	130	41.4	71.0	59.6	42.5
No 3(i)	9 m	6.30	36.8	28.8	8.30	117	34.4	156	121	56.8	62.5	67.3	45.2	28.7	21.0
No 3(j)	10 m	8.30	37.8	24.1	0.00	114	33.2	158	126	57.9	65.3	24.4	43.9	30.9	21.5
No 3(k)	11 m	6.50	15.0	9.08	4.03	41.7	11.5	63.3	50.3	26.2	29.5	35.6	21.6	14.7	10.8
No 3(l)	12 m	4.11	17.1	14.6	5.97	52.9	16.1	87.2	66.3	27.6	31.1	32.3	21.0	15.4	11.0
SEDIMENT SAMPLES															
No 4(a)		0.00	0.07	0.05	0.00	0.00	0.00	1.67	0.77	0.93	1.00	1.81	2.00	0.00	0.00
No 4(b)		0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.19	0.15	0.00	0.00
No 4(c)		0.00	0.17	0.19	0.00	1.15	0.00	4.76	3.26	1.27	2.98	4.50	5.65	0.00	0.00
No 4(d)		1.49	0.54	0.96	0.32	4.89	1.42	14.6	11.5	9.12	9.80	12.9	17.1	0.00	0.00
No 4(e)		2.44	0.56	2.78	2.30	22.5	5.98	52.4	39.2	21.2	22.5	30.1	3.85	0.00	0.00
No 4(f)		0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.04	0.00	0.00	0.00	0.00	0.00	0.00
No 4(g)		0.74	0.00	0.00	0.00	0.00	0.12	1.57	0.91	0.14	0.13	0.18	0.10	0.00	0.00
SAMPLES FROM UNPOLLUTED AREAS															
No 5(a)		0.02	0.00	0.08	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 5(b)		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 5(c)		0.02	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 5(d)		0.01	0.00	0.00	0.00	0.00	0.01	0.03	0.03	0.00	0.00	0.00	0.00	0.00	0.00
No 5(e)		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 5(f)		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 5(g)		0.03	0.00	0.00	0.00	0.03	0.00	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00
No 5(h)		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 7.5: Summary of ASE-GC/MS analytical method performance

Performance Criteria	Poor	Not acceptable	Acceptable	Excellent
Accuracy			x	
Repeatability			x	
Sensitivity (DL and QL) as required by USEPA				x
Sensitivity (DL and QL) as required for Advanced chemical fingerprinting		x (for slightly contaminated samples)	x	
Linearity of calibration			x	
Selectivity			x	
Specificity			x	
Representativiness			x	
Detectability of diagnostic ratios in coal tar polluted samples: D/C1-P C1-D/C1-P C2-D/C2-P C2-N/C1-P C3-N/C2-P C2-P/C2-C		 x	 x x x x x	
Suitability for Chemical and Hazard Characterisation			x	

Chapter 8

THE ANALYSIS OF COAL TAR POLLUTION IN INDUSTRIAL SOILS USING SOLID PHASE MICROEXTRACTION AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY

INTRODUCTION

Extraction of organic compounds from soil samples

In literature, the term 'screening' is referred to a fast semi-quantitative method to determine if contaminants are present above a pre-set concentration threshold. Before a screening analysis can be performed, it is first necessary to extract the organic compounds from the soil matrix. The traditional and the more efficient Pressurised Liquid Extraction techniques are discussed in **Chapter 7**. These techniques are useful for accurately determining trace level concentrations of pollutants, but its application for routine screening is inhibited with the difficulty of automation, time consuming procedures and long analysis turnover times. The performance of these extraction methods may also change on account of the nature of the soil being extracted, since the complexity of the matrix and the presence of large amounts of many pollutants may alter the performance of previously successful procedures. Traditional extraction techniques have the additional disadvantage of requiring large amounts of solvent while changes in environmental regulations place increasingly severe restrictions on solvent use in laboratories world wide. In the work reported here the extraction of organic compounds from a contaminated soil sample, using headspace extraction with a polymer coated silica fibre (SPME) and followed by GC-MS, was investigated. The main objectives were to design an uncomplicated and efficient method with the following requirements:

- selectivity towards target PAH analytes, ranging from at least two to four ring structures and including heterocyclic compounds
- sensitivity towards environmentally important hydrocarbons for pollution assessment purposes and determination of environmental risks.
- alkyl-PAHs to be included in the target analyte list to determine toxicological effects, as some alkylated constituents are more toxic than the parent PAH
- suitability of data for chemical fingerprinting purposes
- avoidance of special sample preparation, other than grinding, drying and homogenising
- solvent free extraction
- possibility of automation
- elimination of the matrix interference as the presence of a complex environmental matrix very often causes severe analytical problems.

Optimisation of headspace extraction parameters

The objective was to optimise selective extraction conditions for the determination of PAHs of environmental interest, namely those with sufficiently high aqueous solubilities and vapor pressures to partition

into water reserves and the atmosphere. Optimum headspace parameters were investigated and reported in previous papers[10,39], and is beyond the scope of this study. It was necessary to optimise the method at non-equilibrium conditions to keep sample analysis to a reasonable time.

Hyphenated MS determination of PAHs

As shown earlier, GC/MS is a very sensitive, selective and useful analysis technique for the determination of non-polar or low-polar compounds that are thermally stable. It is the most widely used hyphenated technique for the characterization of organic pollutants, because it gives useful spectral information with detection levels of a few picograms. It incorporates the separation power of GC with the MS capability to selectively detect ions from a given mass spectrum. The use of this technique in conjunction with headspace SPME results in a simple procedure to perform fast multi-component analysis of soils and sediments with a fair degree of accuracy, precision, selectivity and sensitivity along with the possibility of automation. The MS detector can also provide reconstructed single ion chromatograms, which offers the possibility of performing extremely good separation of analytes in complex matrices followed by detailed identification of the separated compounds from the full mass spectra.

The requirements for fingerprinting and interpretative methods

Although the technique was primarily assessed as a screening tool, the usefulness of PAH data for fingerprinting purposes was also investigated. As discussed in **Chapter 2,** data on alkyl-PAHs and dibenzothiophenes are necessary for this purpose. The object, therefore, was to establish if the requirements could be achieved to distinguish between sources of hydrocarbons in the environment.

EXPERIMENTAL

Reagents and Materials

Experiments were carried out using USEPA certified PAH contaminated soil samples, CRM-103-100, CRM-104-100 and CRM-105-100, obtained from Resource Technology Corporation. A standard mixture containing 2000 ppm each of the 16 EPA priority PAHs, was purchased from Supelco (Sigma Aldrich, South Africa).

HSSPME Extraction Procedure

A 100µm-polydimethylsiloxane fiber was obtained from Supelco (Sigma Aldrich, South Africa) and used to extract soil samples by headspace. A 0.1g soil sample was transferred into a 1.8 cm^3 sample vial that was sealed with a Teflon-lined septum. At least two hours was allowed for thermal equilibrium to be reached throughout the soil and headspace. The fibre was exposed for 40 minutes to the headspace without making contact with the soil and then immediately inserted into the GC injector for thermal desorption and GC/MS analyses. Attention was given to the following parameters, and the chosen conditions were used to verify analytical performance:

Fiber selection

A 100-µm PDMS fibre was chosen because it showed the highest extraction efficiency and, therefore, lowest detection limit in a previous investigation [43]. Detection limits of at least 1 mg/kg were desired in this study.

Sample and headspace volumes

As indicated by Zhang and Pawliszyn[10] SPME is mainly an equilibrium analytical

method, and in the case of headspace sampling the amount of analytes absorbed by the liquid polymeric coating is related to the overall equilibrium of analytes in a three phase system, namely sample, air and polymer phase. They expressed it as:

$$n_{hs/spme} = \frac{K_1.K_2.V_p.V_s.C_0}{(K_1.K_2.V_p)+(K_2.V_{HS}.)+V_S} \quad \ldots\ldots 8.1$$

where K_1 is the partition coefficient of the analyte between the sample and gas phases and K_2 the equilibrium constant of the analyte between gas and polymer phase. V_p, V_S and V_{HS} are the polymer fiber, sample and headspace volumes, respectively. C_0 is the concentration of the analyte in the sample. They indicated that the K_2 value and the volume ratios between the fiber and headspace and headspace and sample would affect the amount of analyte absorbed from the headspace. In the case of this study the fibre volume is fixed (Vp = 0.000621 cm^3) and a headspace volume (V_{HS}) of 1.2 cm^3 was chosen, resulting in a large volume ratio of 1932. The volume ratio is, however, only within limited control of the analyst. A standard 1.8 cm^3 glass vial was used in this study. The concentration of analytes will be homogeneous within each of the three phases once equilibrium has been reached. The time to reach equilibrium is governed by K_2, the fibre-headspace distribution constant. In practice the equilibrium time is considered as the time at which the mass adsorbed by the fibre has reached 90% of its final total mass. Although the principle behind SPME is an equilibrium partitioning process, it is not necessary to wait until full equilibrium is reached. As long as the extraction time is standardised, reproducible and sufficiently sensitive analysis is possible. For optimum repeatability it is, however, necessary to choose an equilibrium time in the region where small changes will not have a dramatic effect on detector response. Zhang[10] also showed that extraction times can be reduced by sampling analytes indirectly from the headspace above the sample instead of sampling directly from the aqueous solution, because the diffusion of analytes in the vapor phase is four orders of magnitude higher than in the aqueous phase. Since the chromatographic run time is 45 minutes (including cool down time), an exposure time of 40 minutes was adopted in our study.

Temperature

It is known that by increasing the temperature of the sample, the vapor pressure of the analyte is increased, and partition equilibrium between the sample and headspace will be reached more quickly. A higher temperature was, however, not considered for the purpose of this investigation, as it complicates automation.

Accelerated Solvent Extraction

Extraction experiments were performed with an ASE-200 system (Dionex, CA, USA) and using the procedure outlined in Chapter 7. A certified reference soil sample, CRM-103-100, PAH contaminated soil, USEPA certified, was extracted using the procedure as described in **Chapter** 7. A 1 gram air dried and finely ground sample was placed in a 11 cm^3 stainless steel extraction vessel. The sample was the extracted for 10 minutes at 100 °C, at pressure of 2000 psi in the extraction apparatus, using 1:1 acetone:methylene chloride. The extractions were carried out in two cycles and a flush volume of 60% of the extraction cell volume was also used. The extracted analytes were purged from the cell for 90 s using pressurised nitrogen (150 psi). The extract was then concentrated to a final volume of 10 cm^3, of which 1 µl was injected into the

GC/MS. Alkyl-PAH concentrations were determined by a manual integration of peaks in the selected ion mass chromatogram.

Amount of analytes adsorbed into the fiber in the headspace of a water sample

The extraction efficiencies of PAHs and alkyl-PAHs were calculated by determining the amount of each analyte adsorbed into the fiber in the headspace of a water sample. Due to the lack of soil standards with known alkyl PAHs concentrations, a spiked water sample with known PAH and alkyl-PAH concentrations was used for this purpose. Because the partition coefficient (K_1, **equation 8.1**) of an analyte between water and the gas phase differs from the K_1 of the analyte between soil and the gas phase, the results were used as an indication only. To determine the extraction efficiency of the fiber the GC response was calibrated by injecting a 40 ng (1µl of 40 µg/cm^3) PAH standard. The GC/MS response for some parent PAHs were determined with liquid injections of a 40 µg/cm^3 each PAH standard solution. Equal amounts of 40 ng/cm^3 PAHs were spiked into a water matrix, of which a sample size of 0.6 cm^3 (24 ng) was then analysed using the headspace technique. The headspace volume was 1.2 cm^3. The amount of analytes absorbed into the fibre was determined from their GC/MS response.

Analytical performance

The series of PAH contaminated soil standards, with certified parent PAH concentrations, were used to determine analytical performance parameters. The study was limited to PAHs with certified concentrations. The study was further limited to the range of concentrations in the standards. Calibration curves for selected PAHs were constructed from peak areas, obtained from different analyte concentration in the three soil standards and the linearity illustrated.

RESULTS AND DISCUSSION

Amount of analytes absorbed into the fiber at the chosen experimental conditions

The GC/MS response for some parent PAHs were determined with liquid injections of a 40 µg/cm^3 each PAH standard solution. Equal amounts of 40 ng/cm^3 PAHs were spiked into a water matrix, of which a sample size of 0.6 cm^3 (24 ng) was then extracted using the headspace technique. The headspace volume was 1.2 cm^3. The amount of analytes absorbed into the fibre was determined from their GC/MS response. The efficiency of a single stage extraction was determined as the fractional amount found in the fibre phase after equilibrium, and expressed as % :

$$\%P = (C_2/C_0)x100 \qquad \text{.....8.2}$$

where C_2 and C_0 are the mass of solute in the fibre and initial mass in the sample respectively. The results are given in **Table 8.1.** The time-limited extraction efficiency follows the trend of lower efficiency with lower vapor pressures. Analytes, which could be extracted from the headspace, are naphthalene through pyrene with extraction efficiencies of 12.8 % and 1.3 % respectively. Compounds with a vapor pressure lower than 2.4 x 10^{-10} (pyrene) could not be detected.

Analytical performance

A series of PAH contaminated soil standards, with certified parent PAH concentrations, were used to determine analytical performance parameters. The study was limited to PAHs with certified concentrations.

TABLE 8.1 : Extraction efficiency of PAHs using the headspace technique

COMPOUND	RINGS IN STRUCTURE	Quantitation ion (m/z)	Confirmatory ion (m/z)	Amount absorbed (ng) (C_o = 24 ng)	Extraction Efficiency (%)
Naphthalene (N)	2	128	127	3.07	12.80
C_1-naphthalenes (C1-N)	2	142	141	3.47	14.50
C_2-naphthalenes (C2-N)	2	156	141	1.93	8.05
C_3-naphthalenes (C3-N)	2	170	155	1.12	4.67
C_4-naphthalenes (C4-N)	2	184	169	0.42	1.77
Biphenyl (B1)	2	154	152	2.50	10.40
Acenaphthylene (AC)	3	152	153	2.42	10.10
Acenaphthene (AE)	3	154	153	2.27	9.50
Dibenzofuran (D1)	3	168	169	1.92	8.00
Fluorene (F)	3	180	165	1.43	6.00
C_1-fluorene (C1-F)	3	180	165	0.62	2.62
C_2-fluorene (C2-F)	3	194	179	0.12	0.51
C_3-fluorene (C3-F)	3	208	193	0.05	0.19
Phenanthrene (P)	3	178	176	0.91	3.80
Anthracene (A)	3	178	176	0.88	3.70
C_1-phen/anthracene (C1-P)	3	192	191	0.28	1.16
C_2-phen/anthracene (C2-P)	3	206	191	0.06	0.25
C_3-phen/anthracene (C3-P)	3	220	205	0.04	0.15
Dibenzothiophene (D)	3	184	152	0.95	3.96
C_1-dibenzothiophene (C1-D)	3	198	184	0.12	0.49
C_2-dibenzothiophene (C2-D)	3	212	197	0.09	0.38
C_3-dibenzothiophene (C3-D)	3	226	211	0.05	0.22
Fluoranthene (FL)	4	202	101	0.36	1.50
Pyrene (PY)	4	202	101	0.30	1.30
Chrysene (C)	4	228	226	n.d.	----
Benzo(a)anthracene	4	228	226	n.d.	----
Benzo(k)fluoranthene (BK)	5	252	253	n.d.	----
Benzo(a)pyrene	5	252	253	n.d.	----
Dibenz(a,h)anthracene (DA)	5	228	226	n.d.	----
Benzo(g,h,l)perylene (BP)	6	276	277	n.d.	----
Indeno(1,2,3)perylene (IP)	6	276	277	n.d.	----

n.d. = not detected.

The study was further limited to the range of concentrations found in the standards. Calibration curves were constructed from peak areas, obtained from different analyte concentration in the three soil standards and the linearity illustrated. The results including linearity, precision and detection limits are presented in **Table 8.2**. All the PAHs tested exhibited good linearity and precision and regression coefficients of better than 0.99 were found in most cases, except for anthracene (0.985) and pyrene (0.982). The precision test was performed contaminated soil CRM-105-100.The precisions found are shown as % RSD, together with the concentration levels at which the values were obtained. A precision of smaller as 10% RSD was found in all çases. The precision values are based on variations in the area counts of the signal, and not referenced to an internal standard. The certified soil standard with the lowest concentration (CRM-103-100) was used to determine the detection limit.

TABLE 8.2 : Calibration Results for Headspace SPME of PAH Contaminated Soils

Compound	Concentration Range (mg/kg)	Regression Coefficients - R^2	Precision as % RSD [a] (n=6)	Lowest standard tested	
				mg/kg	S/N
Naphthalene	1 - 35	0.9957	2.78 (15.7)	0.77	128
2-Methylnaphthalene	1 - 60	0.9960	4.52 (60.4)	< 1	12
Dibenzofuran	1 - 306	0.9972	8.28 (306)	0.66	28
Acenaphthylene	1 - 17	0.9910	4.94 (16.7)	1.21	21
Acenaphthene	1 - 640	0.9988	5.51 (640)	0.77	12
Fluorene	1 - 443	1.0000	7.84 (368)	0.65	12
Phenanthrene	6 - 1924	0.9997	8.49 (1153)	5.79	53
Anthracene	1 - 431	0.9849	6.74 (431)	1.44	5
Fluoranthene	25 – 1425	0.9947	6.80 (1410)	24.6	84
Pyrene	15 – 1075	0.9820	7.33 (1075)	15.0	46

[a] - concentration as mg/kg in brackets

Results for the lowest concentration analysed are used for this purpose and ranged from 0.77 mg/kg levels for naphthalene to about 25 mg/kg for fluoranthene with the analyte sensitivity reflecting its vapor pressure. The sensitivity decreases from naphthalene to phenanthrene due to a decrease in vapor pressure, which governs the amount of PAH absorbed into the SPME fiber in the time-limited exposure studies. In this work, quantification of analyte concentrations is based on the method of external standard, but accuracy and precision can be improved by using deuterated internal standards.

Source discrimination based on relative PAH abundance

Using the results from CRM-103-100, analyte profile histograms were constructed for the C_0- to C_4-PAHs obtained by both Headspace Solid Phase Microextraction (HSSPME) and Accelerated Solvent Extraction (ASE). The results are shown in **Figure 8.1**, where the plots are normalised to the parent PAHs. The results found in the case of ASE show that the parent PAHs of each of the series N, F, P and D are least abundant, which match more closely to a characteristic petrogenic, than to a pyrogenic profile. In the case of HSSPME a different profile was found that could lead to misinterpretation. The poor agreement between the profile of the alkyl homologue series is due to the sharp decrease in extraction efficiencies for an increase in ring size and in an alkyl-homologue:

parent (C_0)>C_1>C_2>C_3>C_4.

The decrease in extraction efficiencies is also related to the decrease vapor pressures (see **Table 4.1**) and that the results were obtained in non-equilibrium conditions. It is evident that alkyl-PAHs cannot accurately be quantified with the SPME headspace technique, using manual integration techniques of the isomer series and using the parent PAH response factors (RF's). The possibility exists to make adjustments according to extraction efficiencies, but it will add another variable to the results that will increase the analytical variance. Due to differences in extraction efficiencies within an alkyl homologue series, headspace SPME is, therefore, not a very efficient method for establishing chemical matches based on the

profile of the alkyl homologues series. Conventional extraction methods, such as the ASE technique investigated in **Chapter 7**, do prove to be a better analysis technique for this purpose. Limited distinguishing features can be obtained from the parent PAHs, for example, a dominant abundance of pyrene and fluoranthene can indicate coal tar contamination while the decrease in abundance of the two and three ringed PAHs can indicate weathering.

Relative amounts of alkyl-phenanthrenes, - dibenzothiophenes and -chrysenes.

Although alkyl-PAHs cannot be determined accurately with HSSPME, the relative abundances between these groups of analytes can be used to differentiate between different crude oils, petroleums and refined petroleums.

Source ratios

The source ratio of C_2-D/C_2-P in CRM-105-100 was investigated in this study because of the stability, resistance to weathering and source specific nature of these isomers. These compounds also have similar chromatographic retention times, vapor pressures, extraction efficiencies and low analytical variance because it can self-normalise to minor GC and MS conditions. The selected analyte ratio was found to be 0.99 on the BNA contaminated soil, CRM 105-100, using the HSSPME technique. This value was slightly higher than the ratio of 0.62, found on the same sample using the ASE technique. This is due to the difference in extraction efficiencies between C_2-D (0.38%) and C_2-P (0.25%), which in turn is due to slight vapor pressure differences. The relative standard deviation of the selected analyte ratio was calculated and found to be 5.0 % (n=6). The results are graphically presented in **Figure 8.2**. This method demonstrates low analytical variance and is therefore suitable for the determination of source ratios. The successful application of source ratio analysis using HSSPME must include an

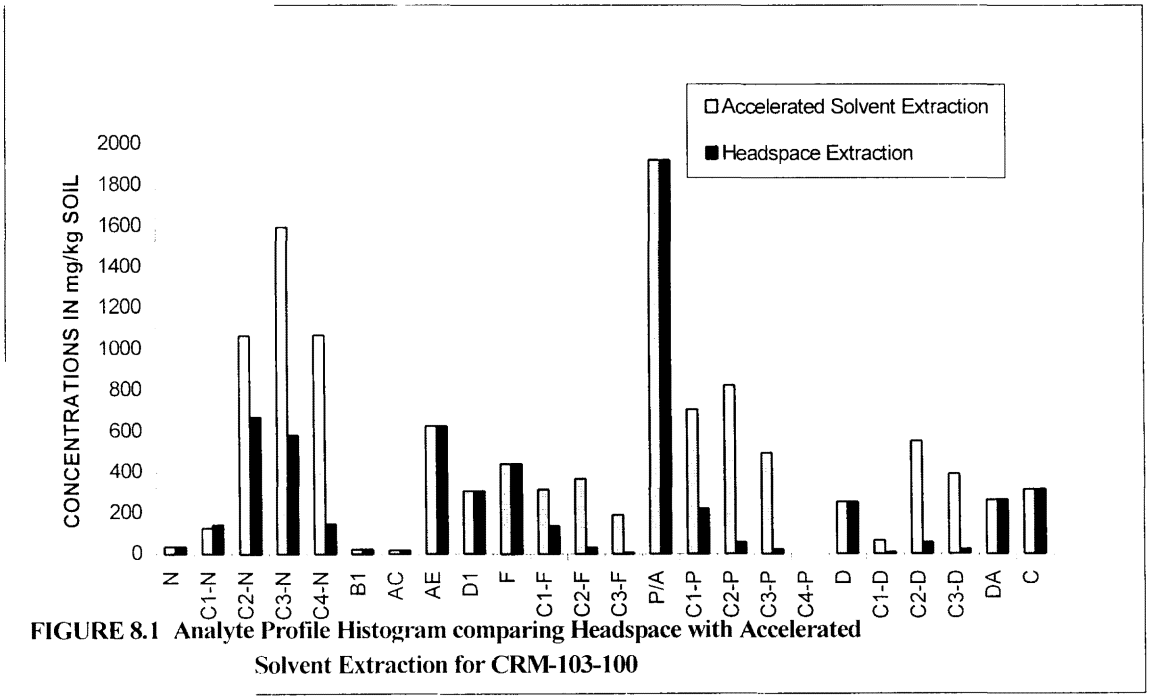

FIGURE 8.1 Analyte Profile Histogram comparing Headspace with Accelerated Solvent Extraction for CRM-103-100

initial investigation to establish the differences and similarities between source ratios in potential sources. To further limit the analytical variance, it is advisable to use the same instrument, set of instrumental parameters, analyst and manual peak integration procedure throughout the study. This is especially important in the case of the scan segments and tune factors of the ion trap MS. For best results the primary and secondary ions must be assigned to the same scan segment. In the case of this study a mass range of 100-250 was chosen in segment no 2, in order to include the primary and secondary ion masses for C_2-P (191+206) and C_2-D (212+197) in one segment.

Weathering ratios

Although the determination of weathering ratios using HSSPME is not impossible, it is associated with a lot more difficulty than in the case of source ratios. The reason for this is that the compounds which are normally used to determine weathering ratios, such as C_3-N/C_2-P, have different chemical and physical properties, such as chromatographic retention times, vapor pressures, extraction efficiencies and, therefore, a high analytical variance. A large difference also exists between values obtained between the two methods of extraction, for example, ratios of 1.29 and 11.95 were found for C_3-N/C_2-P using ASE and HSSPME respectively. When choosing PAHs with a large difference in vapor pressures, the resulting differences in extraction efficiencies are mainly responsible for the high ratios. In the above example, the efficiencies were 4.67% for C_3-N and 0.25% for C_2-P.

Individual isomer distributions

The technique was found to be suitable for the fingerprinting of the isomers in a certain alkyl homologue. Good analytical precision was found because only small physical-chemical differences, such as vapor pressure, exist between the different isomers. An example of the fingerprint for CRM-105-100, which contains large proportions of C_2- phenanthrenes, is shown in **Figure 8.3**.

As evident from this example, the fingerprint obtained with headspace SPME compares very well with the fingerprint obtained with Accelerated Solvent Extraction. The relative distribution of individual isomers in different sources can be very subtle, but as indicated by Boehm[17], they do present further opportunities for fingerprinting similar hydrocarbon sources.

Hyphenated MS determination of PAHs

Figure 8.4 shows a comparison between a total ion chromatogram (TIC) and the selected ion chromatogram of a slightly contaminated soil sample. Excellent signal to noise ratios are demonstrated in the single ion mode for relatively small concentrations. Using this technique it is possible to obtain a fast screening analysis of priority PAHs in contaminated soils. An example of a badly contaminated soil sample is shown in **Figure 8.5**. A range of alkylated naphthalenes is shown in the single ion chromatogram. This example is chosen to illustrate that identification and quantitation can be done in a complex matrix. In samples where background interference persists, a advanced MS technique such as selected ion storage (SIS) can be used to further improve results. This technique has the capability to capture groups of analyte ions (that can still be library searched) while removing interfering ions leading to greater sensitivity.

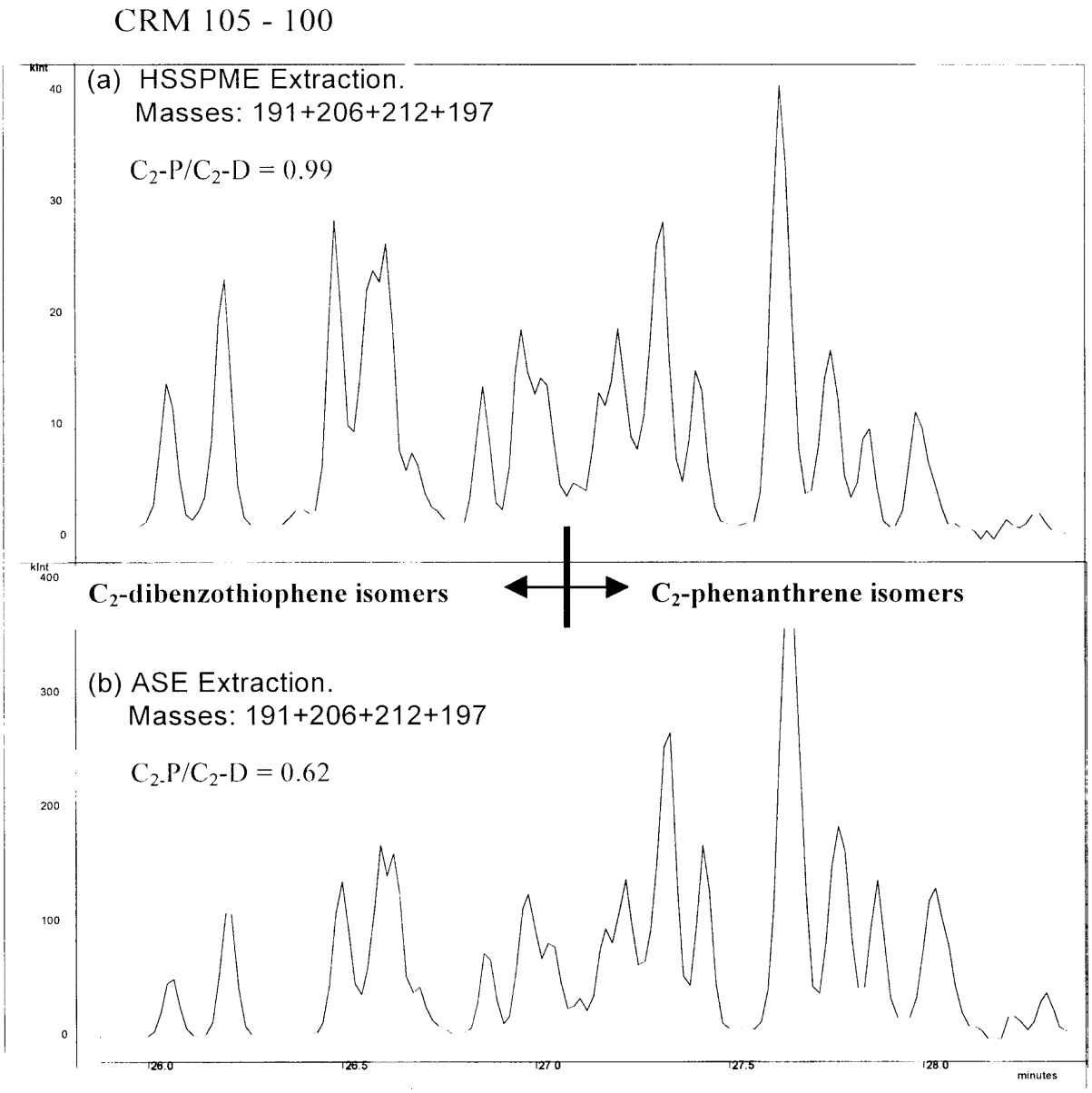

FIGURE 8.2: Selected ion mass chromatograms for C_2-phenanthrenes and C_2-dibenzothiophenes, comparing the relative isomer ratios using (a) HSSPME and (b) ASE

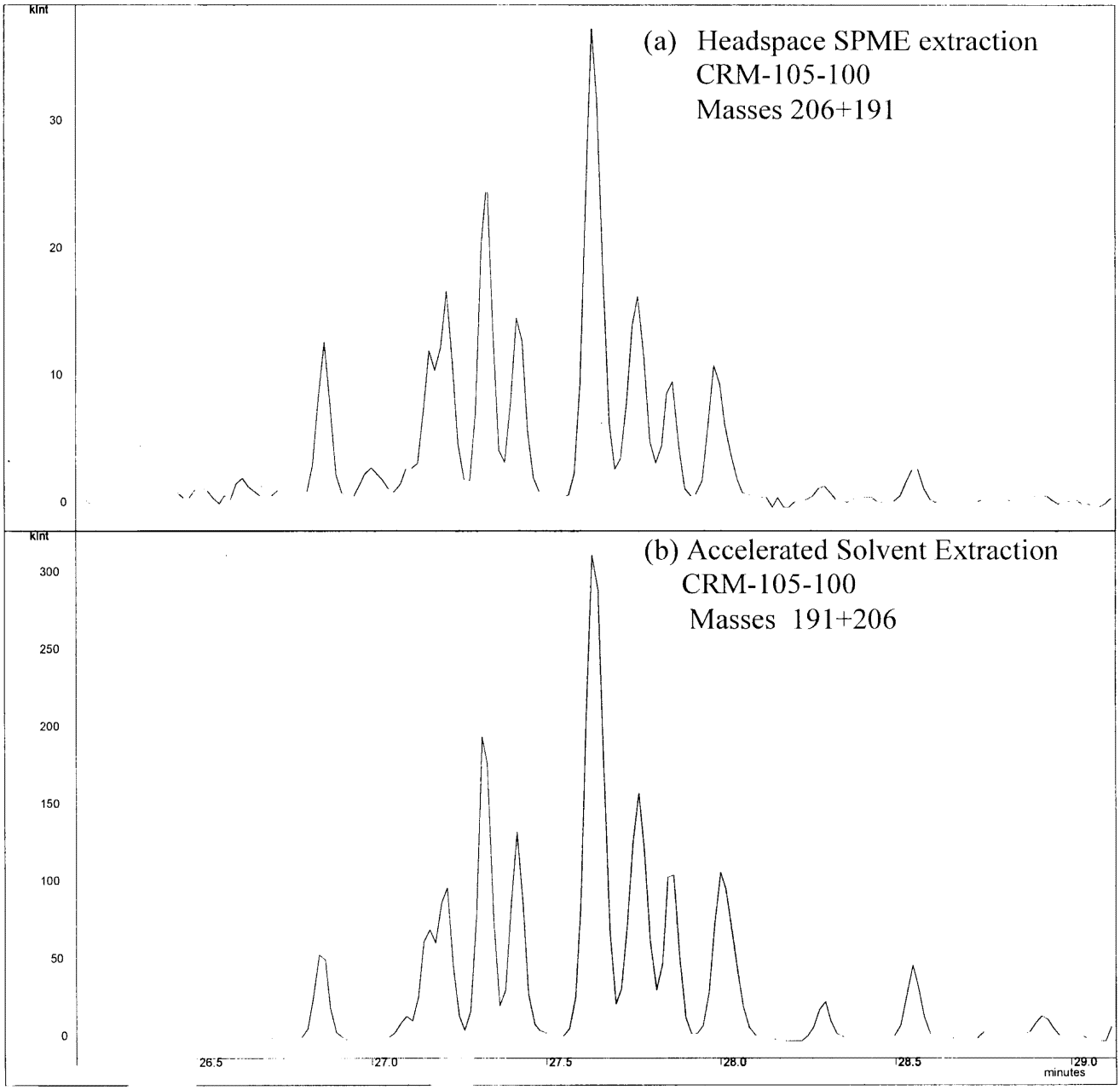

FIGURE 8.3: Selected ion mass chromatograms for C_2-phenanthrenes of (a) headspace SPME (b) Accelerated Solvent Extraction

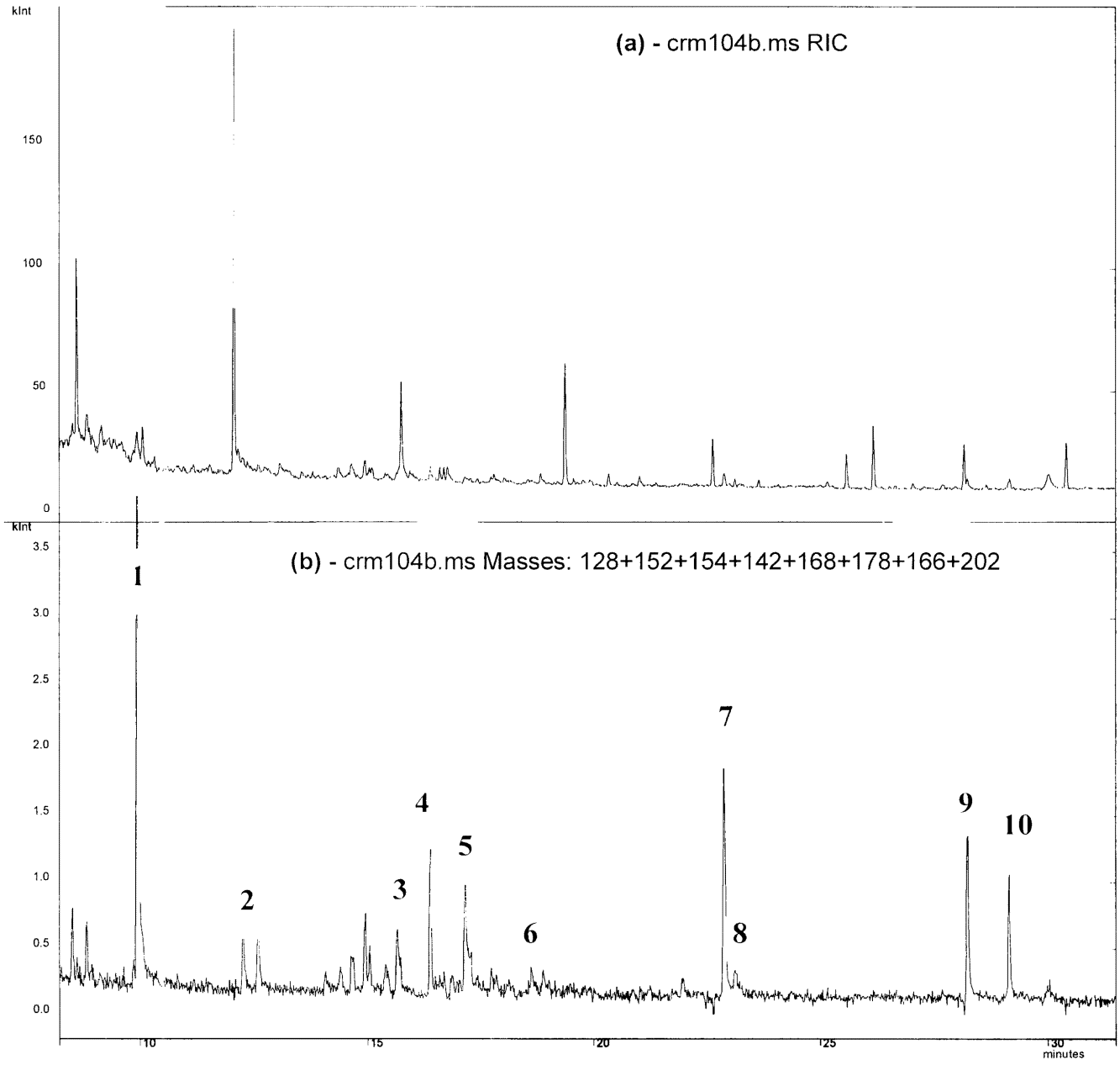

FIGURE 8.4 : Chromatogram of CRM-104-100. Sample selected to illustrate detection limits **(a)** - Reconstructed Total Ion Current **(b)** – Selected ion current of (1) naphthalene (2) 2-methyl naphthalene (3) acenaphthylene (4) acenaphthene (5) dibenzofuran (6) fluorene (7) phenenthrene (8) anthracene (9) fluoranthene and (10) pyrene

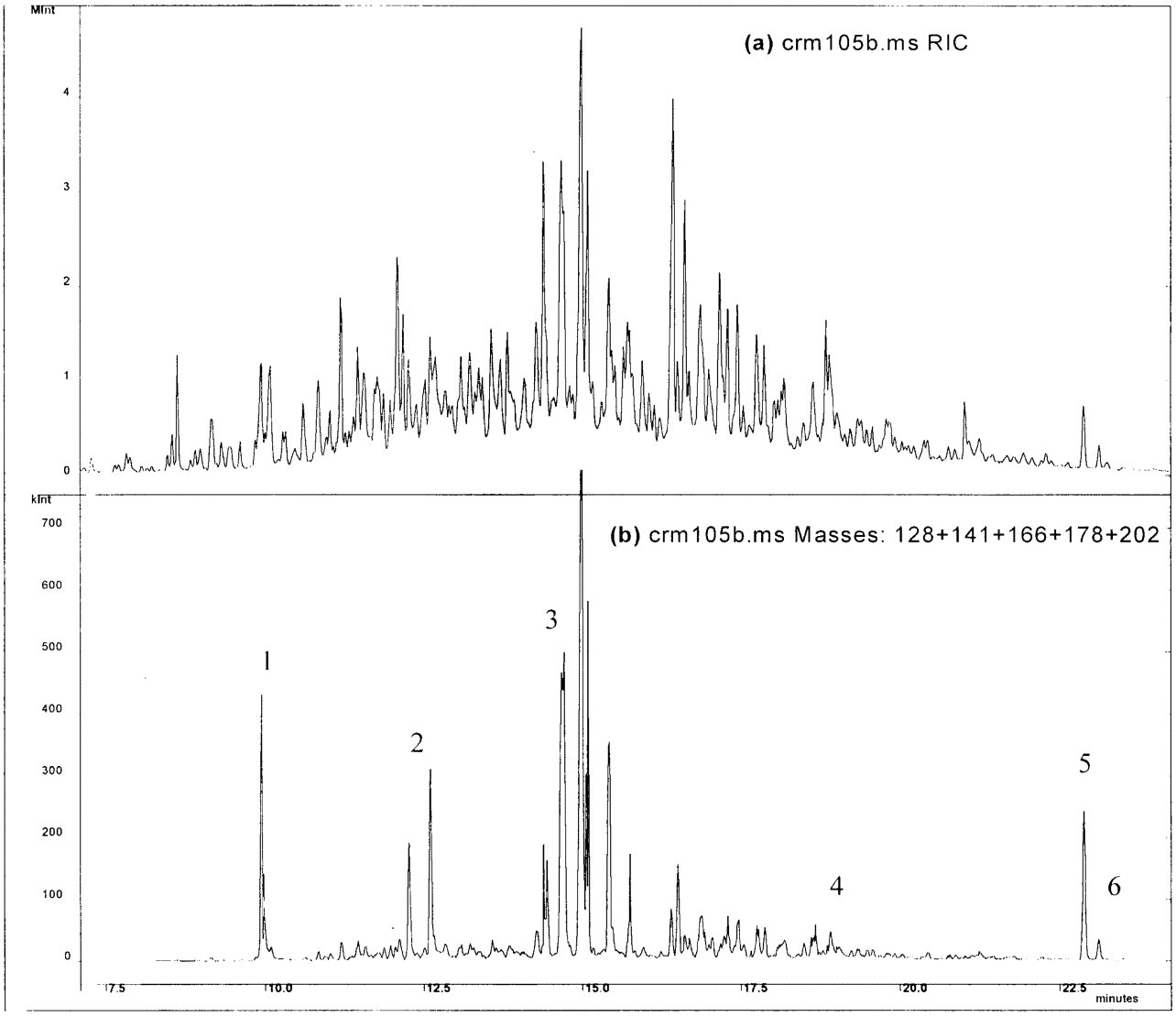

FIGURE 8.5 : Chromatograms of Crm-105-100. Sample selected to illustrate the identification of data in a complex matrix. **(a)** - Reconstructed Total Ion Current **(b)** – Selected ion current of (1) naphthalene (2) C_1-naphthalenes (3) C_2-naphthalenes (4) fluorene (5) phenenthrene (6) anthracene

CONCLUSIONS

Headspace SPME is found to be a fast, efficient and sensitive technique for confirmation of PAHs of up to four ring structures. By sampling in the headspace, sampling problems related to complex matrices can be avoided and sampling in the headspace prevents oxygen or moisture from getting into the GC column. This simple means of extraction has the advantage that it does not require any special sample preparation, other than grinding, drying and homogenising. Fast analysis turnaround times can be achieved resulting in lower analysis costs and providing scientifically sound information. Information on the presence and concentration of environmentally important PAHs can be obtained in the full scan mode. The accuracy of quantitation can further be improved with the use of deuterated internal standards and advanced methods such as MS-MS or single ion storage. The possibility of automation is a major advantage when coping with large sample quantities. Referring to **Figure 2.13**, the advantage associated with this technique is its efficiency for use during a Phase 1 site assessment. A more invasive technique, such as Pressurised Liquid Extraction and GC/MS (**Chapter 7**) is required for a high quality fingerprinting analysis or to determine the severity and extent of the contamination.

The technique as a screening method is suitable for:

- *The tiered approach* - the screening method is used to identify samples that must be analysed with a more detailed routine technique (see Phase 3 of **Figure 2.13**). If estimates with the SPME method indicate a potential for environmental impact, risk assessment is carried to a higher tier, where more precise concentration estimates are used.
- *The adaptive approach* - to use the information obtained by the screening technique for the design of future sampling or analyses.

As a tool for chemical fingerprinting, this technique supplies valuable information on PAHs, alkyl-PAHs, heterocyclic compounds and isomer ratios that have a wide interpretative use. The method will allow the determination of relative amounts of parent PAHs, alkylated phenanthrenes, -dibenzothiophenes and -chrysenes, source ratios between selected homologues, and individual isomer distributions. Weathering ratios can be determined to a limited extent.

The technique is, however, not suitable to discriminate between sources, based on relative abundance of alkyl-PAHs and the use of a characteristic analyte profile histogram. Low vapor pressures of the PAHs are the main reason why trace level concentrations of pollutants cannot be detected. The sensitivity decreases very sharply with an increase in the size of the PAH (number of rings) and valuable information is lost on the heavy PAHs. It has been shown in **Chapter 2** that a build-up in heavy PAHs is observed in degraded samples. This method would, therefore, not be suitable (too insensitive) for the analysis of degraded samples or atmospheric deposition.

Table 8.3: Summary of SPME-GC/MS analytical method performance

Performance Criteria	Poor	Not acceptable	Acceptable	Excellent
Accuracy	-	-	-	-
Repeatability			x	
Sensitivity (DL and QL) as required by USEPA		x (for heavy PAHs)	x (for some PAHs)	
Sensitivity (DL and QL) as required for Advanced chemical fingerprinting	X			
Linearity of calibration			x	
Selectivity				x
Specificity				x
Representativiness			x	
Detectability of diagnostic ratios in coal tar polluted samples: D/C1-P C1-D/C1-P C2-D/C2-P C2-N/C1-P C3-N/C2-P C2-P/C2-C	 x x x x	 x x x 		
Suitability for Chemical and Hazard Characterisation		x		

Chapter 9

SOURCE IDENTIFICATION AND THE DEVELOPMENT OF DIAGNOSTIC RATIOS

INTRODUCTION

Groundwater is a source of potable water for many households and communities. Its possible contamination by DNAPL releases into soils has become a serious environmental problem in areas adjacent to industrial sites. The development of techniques that can determine the pollution source is motivated in part by the cleanup costs, legal fees, and fines incurred by the polluter.

The potential of using GC/MS data for tracing underground DNAPLs to suspected sources is recognised by many workers in the field of hazardous waste management. The discriminatory power, sensitivity, selectivity and specificity of GC/MS were also illustrated in the previous chapters. Selective extraction techniques for spill identification have been developed in this study and the advantages of SPME as an alternative extraction method, were shown. The results (target analyte data listed in **Table 2.1**) obtained by these various methods were used to develop interpretative methods, which can be used to trace contamination in the environment to its source. The analyses of data were based on the following principles:

- Each source has a unique chemical composition
- Each source has a unique analyte distribution pattern
- Information from the GC/MS spectra can be encoded in such a way to be resistant o chemical noise
- Source ratios can be developed that stay constant during weathering changes and are relatively insensitive to changes in the overall GC profile
- Ratios can be developed that will constantly change during weathering and serve as weathering indicators

DETECTION AND OCCURANCE OF PAH ISOMERS IN TYPICAL SAMPLES

The detection and identification of data obtained with GC/MS was investigated with the following objectives:

- To develop diagnostic ratios that can be determined with good accuracy. Typical source ratios are C_1-D/C_1-P, C_2-D/C_2-P and C_3-P/C_3-D. Typical weathering ratios are C_2-N/C_1-P, C_3-N/C_2-P and C_2-P/C_2-C.
- To establish typical PAH distribution patterns in soils and sediments (compare with petrogenic and pyrogenic profiles).
- To investigate the evidence of weathering in typical soil samples

The occurrence of alkyl-PAH isomers in soil samples

The ASE-GC/MS method described in **Chapter 7** was found to be suitable for the application of advanced chemical fingerprinting. The HSSPME-GC/MS was not found suitable for this purpose. The results of alkyl substituted isomers in typical soil samples, obtained with the ASE-GC/MS method, are shown in **Figures 9.1 – 9.4**.

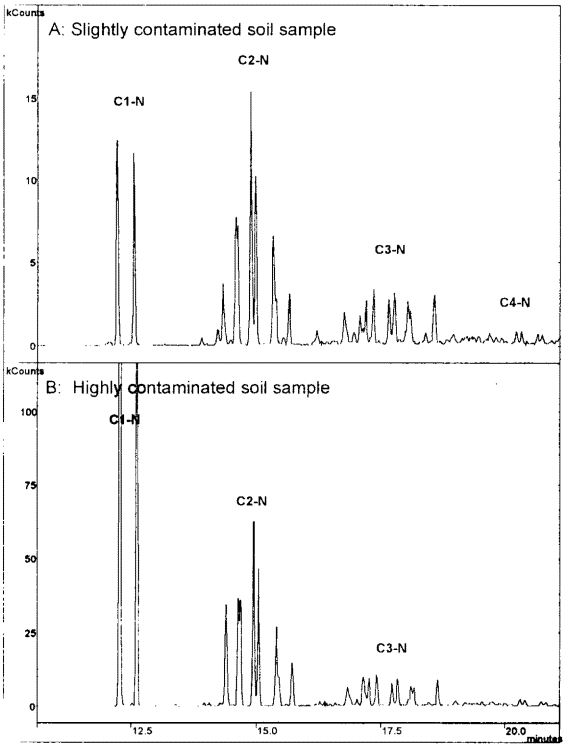

Figure 9.1: Selected ion chromatograms for the naphthalene isomers in soil

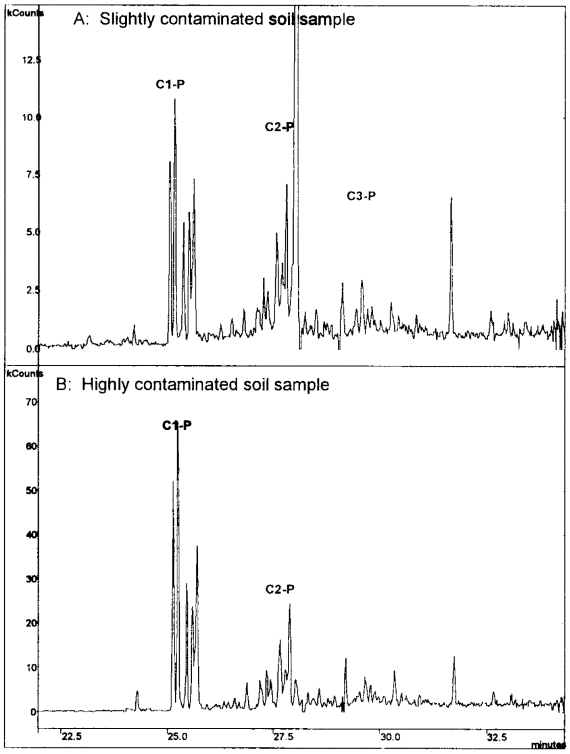

Figure 9.2: Selected ion chromatogram for the phenanthrene isomers in soil

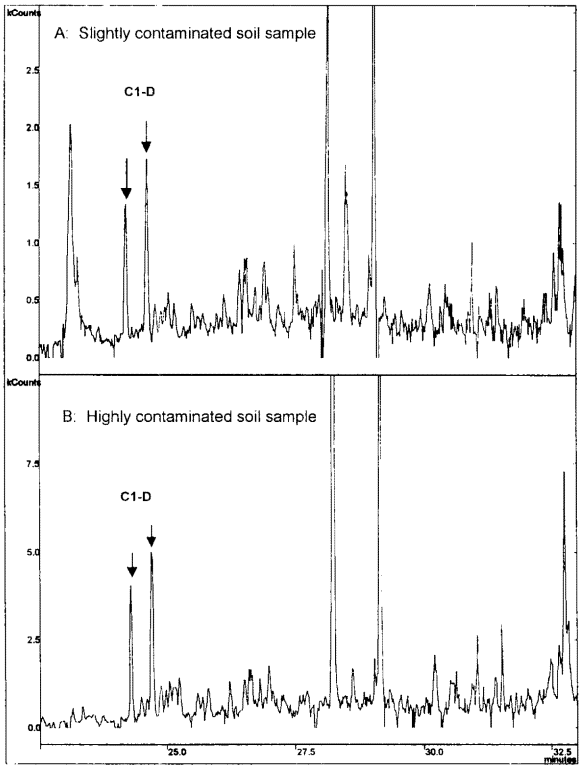

Figure 9.3: Selected ion chromatogram for the dibenzothiophene isomers in soil

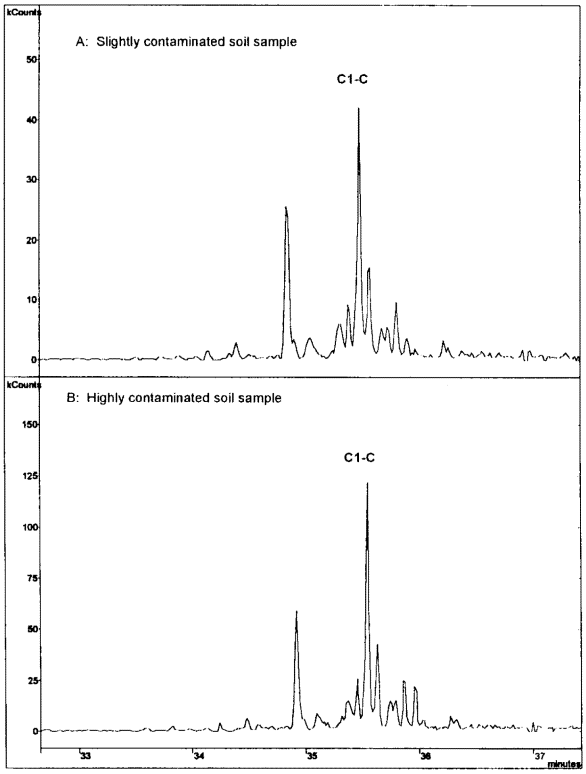

Figure 9.4: Selected ion chromatogram for the C1-chrysene isomers in soil

These results illustrate the sensitivity of the method and abundance of naphthalene, phenanthrene, dibenzothiophene and chrysene isomers. In each case the data of two samples, namely (A) a slightly contaminated sample and with a total PAH concentration of < 3.3 mg/kg and (B) a highly contaminated sample with a total PAH content of > 1550 mg/kg, are shown. The objective was to develop ratios that can be used down to low levels of contamination. As expected from a pyrogenic profile the isomer abundance decrease in the order:

$C_1 > C_2 > C_3 > C_4$.

The following isomers were found in detectable quantities:

C_1-N, C_2-N, C_3-N, C_1-P, C_2-P, C_1-D and C_1-C.

The following isomers could not be detected:

C_3-P, C_2-D, C_3-D, C2-C and C_3-C.

Although C_2-P peaks could be detected, considerable interfering peaks from co-extracted compounds were observed in the chromatogram.

The occurrence of alkyl-PAH isomers in groundwater samples collected at or nearby a steelmaking industry

It was concluded in **Chapter 5** that the sensitivity of the solvent extraction method was not good enough for the detection of isomers in alkyl homologues. The SPME-GC/MS method described in **Chapter 6** was found to be the preferred method for the analysis of PAHs in water samples, due to low detection limits that the method can achieve. The occurrence of PAHs and alkyl-PAH isomers in a total of 581 groundwater samples, which were collected on-site and in a radius of about ten kilometers from three different iron and steelmaking plants, were investigated. These samples were analysed for PAHs in our laboratory over a period of two years, using the technique of SPME-GC/MS. The chromatograms of alkyl-PAHs that are typically found in groundwater samples are shown in **Figures 9.5 – 9.6.**

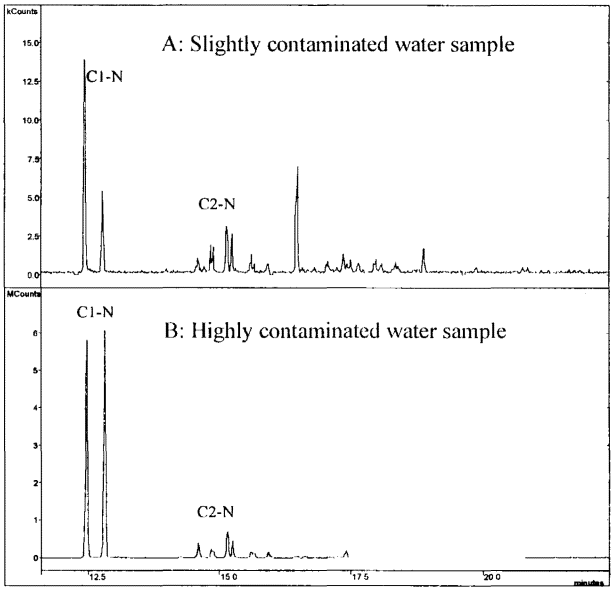

Figure 9.5: Selected ion current of naphthalene isomers (m/z = 142+156+170) in water

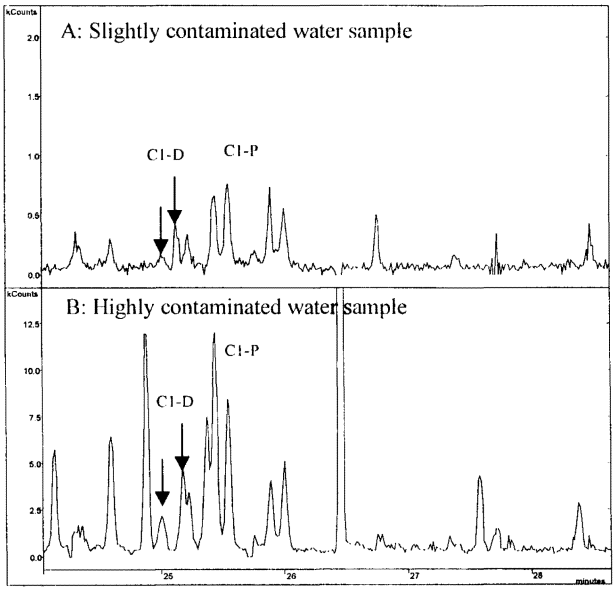

Figure 9.6: Selected ion current for C1-dibenzothiophene and C1-phenanthrene isomers in water. (m/z = 192+198)

The extent of PAH contamination in these sample were divided into 3 groups, namely highly contaminated, slightly contaminated and not detected. The number of samples that were found in each group, relative to the total number of samples, are shown in **Figure 9.7**.

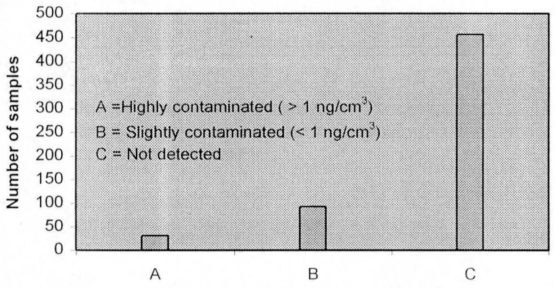

Figure 9.7: Occurance of PAHs in contaminated groundwater

The occurrence and distribution of PAHs in each group can be summarised as follows:

GROUP A: The naphthalenes were the most abundant PAHs. The PAH distribution pattern in these samples does not resemble the composition of coal tar, but rather resembles the solubility profile of PAHs. This is illustrated in Figures 9.8 (a) – (c) and shows that the occurrence of PAHs in severe coal tar contaminated water samples is mainly influenced by the PAH solubilities. The figures compares (a) the PAH distribution pattern of a typical sample, (b) the PAH solubility profile and (c) a typical coal tar profile. Only trace levels of fluoranthene and pyrene (0.004 ng/cm^3) were found in this group of samples and the C1-phenanthrenes and C1-dibenzothiophenes occurred at levels close to the detection limit (0.001 ng/cm^3). The other four- or five-ringed PAHs could not be detected at all. Similar profiles were obtained for most of the samples that were classed as severely contaminated. Other chemical properties, degree of weathering and the concentration of PAHs in the source(s) of contamination can influence PAH concentrations to a lesser degree.

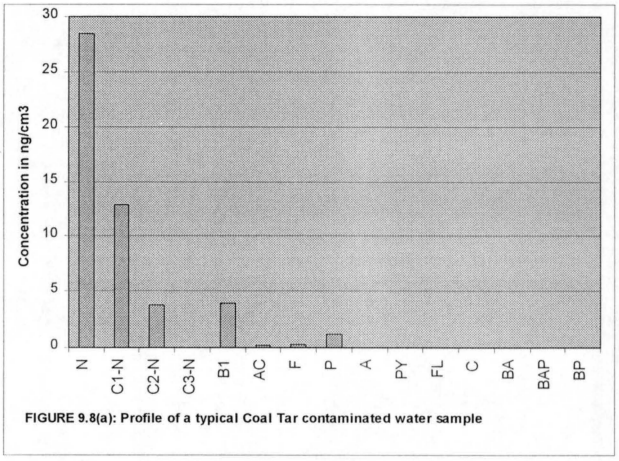

FIGURE 9.8(a): Profile of a typical Coal Tar contaminated water sample

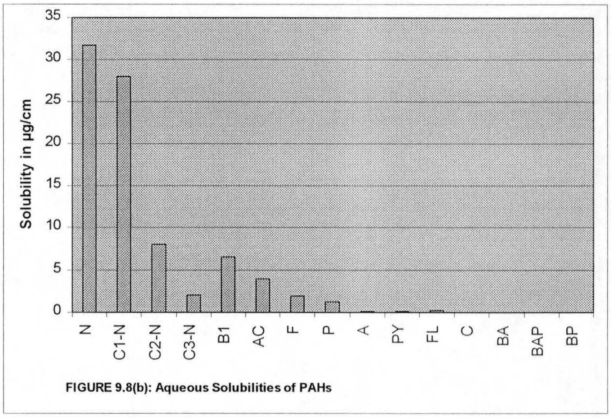

FIGURE 9.8(b): Aqueous Solubilities of PAHs

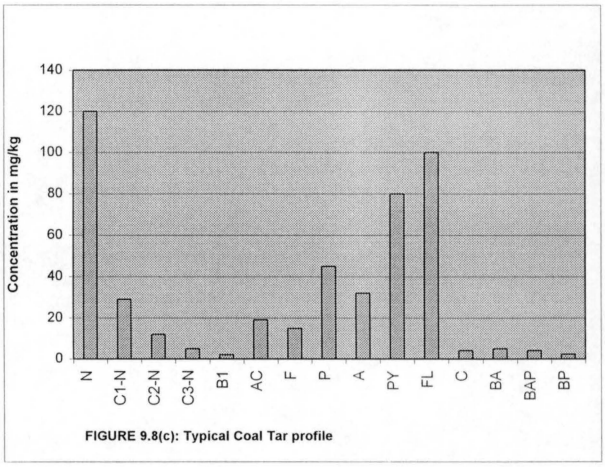

FIGURE 9.8(c): Typical Coal Tar profile

GROUP B: For the slightly contaminated samples the relative concentration of the three and four ring PAHs were much higher in comparison to the naphthalenes. Although the PAH concentrations in some samples were at trace level concentrations, C1-dibenzothiophene could still be detected. Except for fluoranthene and pyrene, the other four and five ring PAHs could not be detected.

The overall detection of PAHs in group A and B can be summarised as follows:

Detectable isomers: **C_1-N, C_2-N, C_1-D, C_1-P**
Isomers not detected: **C_3-N, C_2-D, C_2-P, C_1-C**

The detection of alkyl substituted PAH isomers in water samples were, therefore, limited due to their low abundance in coal tar and low solubilities. Detection limits of alkyl PAHs are also lower than those for parent PAHs because the total peak area of an alkyl homologue is spread over several isomer peaks. The C_1-D and C_1-P isomers could be detected in most slightly contaminated samples and very little interference from other co-extracted compounds were observed. The occurrence of these isomers generally increased with the degree of contamination, but interference from co-extracted compounds also increased. The isomers of C_1-P and C_1-D were chosen as candidates to determine source ratios because they could be detected in most coal tar contaminated water samples and have very similar chemical and physical properties. The disadvantage of this choice is that they are both compounds with a low degree of alkylation and would probably weather very quickly. The advantage is that they are ideal because of their similarity in chemical and physical properties and would dissolve to the same extent in groundwater, degrade or decompose at similar rates, partition onto the SPME fiber with similar efficiencies and behave similarly during the GC/MS analysis. Results of two typical water samples were used to illustrate the abundance of the C1-P and C1-D isomers, namely (a) a mineral oil, and (b) a coal tar contaminated water sample. These results are shown in **Figure 9.9**, where the difference in the C1-D/C1-P ratio of the two sources is evident.

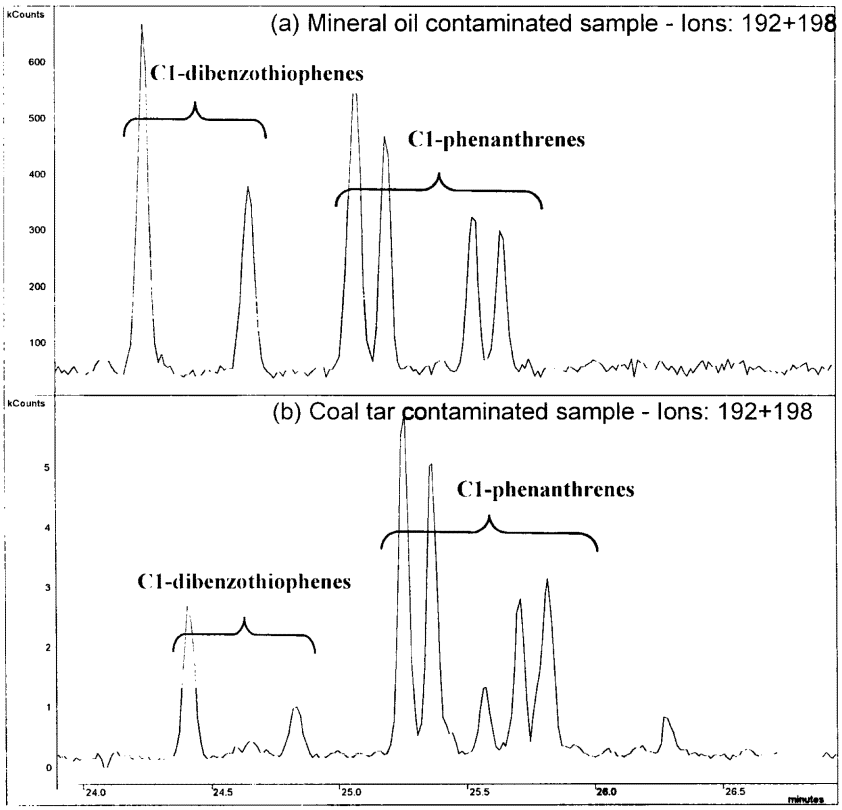

Figure 9.9: Selected ion current plots for phenanthrene and dibenzothiophene isomers in contaminated water samples

THE DEVELOPMENT OF DIAGNOSTIC RATIOS

Following the preceding studies regarding the occurrence and detection of PAH isomers is typical samples, the next step is to select appropriate diagnostic ratios (**see Phase 3 of Figure 2.13**). The principles for the selection of ideal source ratios was discussed in **Chapter 2,** for example those that have similar chemical and physical properties, i.e. the ratio stay constant during weathering and changes in the GC conditions. As shown in **Chapter 2**, the ratios of C_2- and C_3-phenanthrenes and the C_2- and C_3-dibenzothiophenes are examples of those that are considered as constant and reliable ratios. Weathering ratios are normally developed to include very sensitive, sensitive and less-sensitive ratios. In the case of a very sensitive ratio, e.g. C_2-N/C_1-P, the concentration of these isomers may degrade below their detection limits during the early stages of degradation. A less sensitive ratio, such as C_2-P/C_2-C, will be more reliable and will change at a slow rate. The selection of a specific group of isomers to be used for ratio calculations depends on a few factors, namely:

- chromatographic noise in that part of the chromatogram
- interference (peak overlap) from co-extracted compounds
- sensitivity of the analytical method
- abundance of the isomers group in the sample
- stability and rate of degradation

The determination of diagnostic ratios in water samples

As discussed earlier, recent advances[34] in chemical fingerprinting have focussed on the use the total peak area (that is the sum of all the isomer peaks in an alkyl homologue) in deriving diagnostic ratios. Various problems were, however, encountered by our laboratory using this method of quantifying the alkyl homologues in water samples. The complexity of the chromatograms is one of the concerns, which is due to the low analyte concentrations and high background levels. Certain single isomer peaks were, for example hard to distinguish in heavily contaminated samples. Another complication is that all the isomer peaks are not baseline separated. The detection of the C_1-D and C_1-P isomers was further complicated by the low signal to noise ratios that were obtained in most cases as well as interfering peaks of co-extracted compound. An example of co-extracted interfering peaks is shown in **Figure 9.10**. The peak overlap of interfering compound with the isomer peaks and poor resolution is evident from this example. This resulted in errors during the estimation of alkyl homologue concentrations and inaccurate source or weathering ratios. However, an alternative approach to hydrocarbon fingerprinting is to determine the peak area of a single isomer in an alkyl homologue, which is then multiplied by a factor to obtain the total peak area of that specific isomer group. The specific single isomer peaks that were selected for this study are shown in **Figure 9.11.** These isomers have been carefully selected based on a thorough investigation into the retention times at which interfering peaks normally elute in typical samples received by our laboratory. The selected peaks were those that had a strong signal, well isolated from other isomer peaks and where minimum interference (peak overlap with interfering compounds) could be observed. The multiplication factor used to convert single peak areas to the isomer group area was determined by averaging data that were acquired over a period of about one year. The average factors found were 3.7 for C_2-N, 2.7 for C_1-P and 2.3 for C_1-D. Diagnostic ratios, based on the method described above, were determined on selected water

samples. The ratios C_2-N/C_1-P and C_1-P/C_1-D were used as weathering and source ratios respectively. These results are shown in **Table 9.1**. As previously mentioned, the dibenzothiophene isomer is very useful for source ratio calculations because its concentration reflects the sulphur content of the source and this varies widely between different oils and coal tar. The results in **Table 9.1** include water samples that were contaminated by refined oil products (samples 1 – 4) and samples mainly contaminated by coal tar (samples 5 - 30). Although the C_1-D/ C_1-P ratio is not very resistant toward weathering, these isomers could be detected in most contaminated samples down to very low levels. In the case of samples number 19 and 20 the high source ratios found were probably due to an analytical error at the low isomer concentrations. Due to their very similar chemical and physical properties, they were found to be self-normalized to changes in GC conditions resulting in ratios with a low analytical variance. The C_2-N isomers degrade at a faster rate than the other isomers and the C_2-N/C_1-P ratio are useful to determine the degree of weathering. Using the data shown in **Table 9.1**, a plot was constructed for source ratio versus weathering ratio to illustrate that double ratio plots could be used as a means of resolving multiple sources as well as differences in the extent of degradation from a single source. This plot is shown in **Figure 9.12,** which demonstrates the usefulness of the source ratio over a wide range of weathering and biodegradation for the different sources. The strategy for the successful application of these source ratios to hydrocarbon assessment studies must, however, include an initial study to determine the ratios of potential sources.

Table 9.1: Alkyl PAH concentration in groundwater samples and calculated ratios

Sample Number	C_2-N Concentration (ng/cm^3)	C_1-D Concentration (ng/cm^3)	C_1-P Concentration (ng/cm^3)	C_1-D/C_1-P Source Ratio	C_2-N/C_1-P Weathering Ratio
1.	326	21.7	23.59	0.92	13.82
2.	18.1	2.85	1.80	1.05	10.07
3.	314	3.37	3.28	1.03	95.91
4.	24.3	4.55	4.78	0.95	5.08
5.	0.04	0.01	0.02	0.34	1.80
6.	3.41	0.05	0.17	0.29	19.59
7.	2.14	0.25	0.71	0.35	3.00
8.	2.18	0.06	0.18	0.31	11.80
9.	0.16	0.01	0.06	0.13	2.70
10.	3.41	0.05	0.20	0.25	16.7
11.	3.41	0.05	0.17	0.29	19.6
12.	2.18	0.01	0.03	0.20	65.8
13.	2.18	0.01	0.03	0.25	77.9
14.	5.80	0.04	0.22	0.17	25.8
15.	50.0	0.87	11.28	0.08	4.40
16.	1.96	0.03	0.23	0.11	8.60
17.	0.04	0.01	0.08	0.08	0.50
18.	7.00	0.05	0.46	0.10	15.30
19.	0.01	0.01	0.00	4.65	3.80
20.	0.02	0.02	0.00	4.90	6.30
21.	1.75	1.37	1.35	1.01	1.30
22.	0.05	0.00	0.01	0.11	4.70
23.	239	2.07	30.1	0.07	7.90
24.	48.8	0.28	1.97	0.14	24.8
25.	0.04	0.01	0.04	0.21	1.10
26.	0.26	0.01	0.04	0.16	6.90
27.	0.21	0.01	0.10	0.09	2.00
28.	1019	11.7	124.6	0.09	8.20
29.	1.03	0.01	0.08	0.11	12.20
30.	0.02	0.01	0.05	0.14	0.40

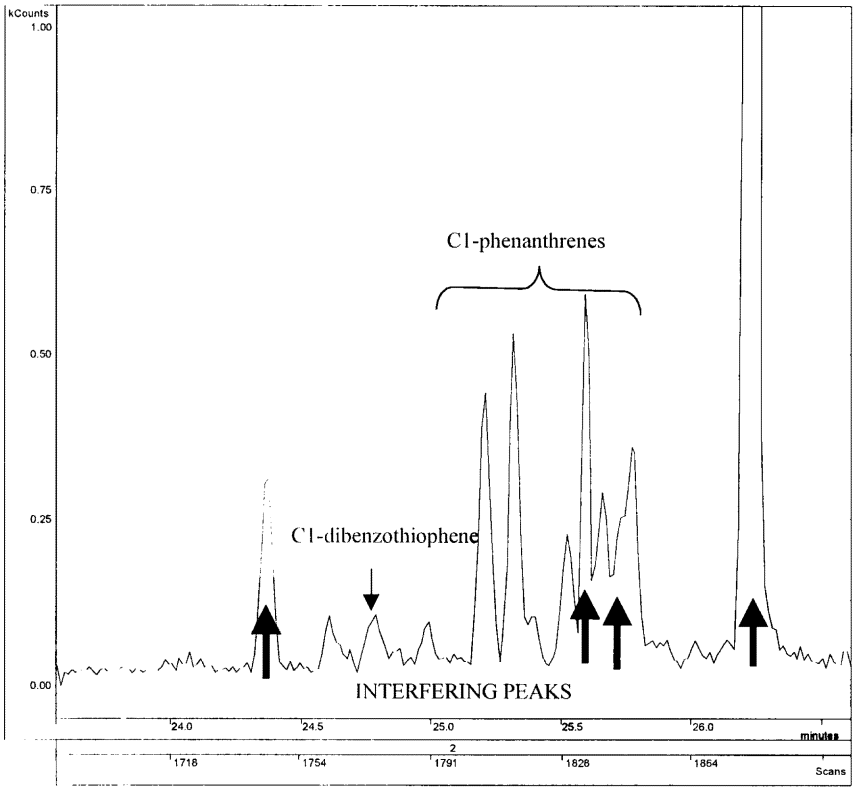

Figure 9.10: Selected ion chromatogram for the C_1-D and C_1-P isomers showing interferences

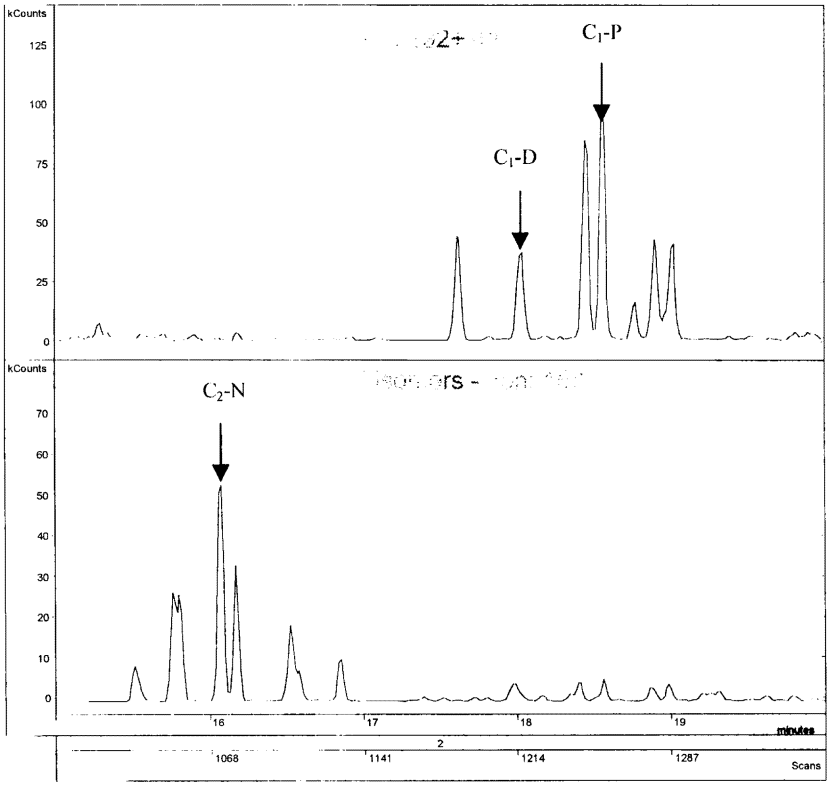

Figure 9.11: Selected ion chromatograms of PAH isomers, sowing peaks that were selected for determining diagnostic ratios

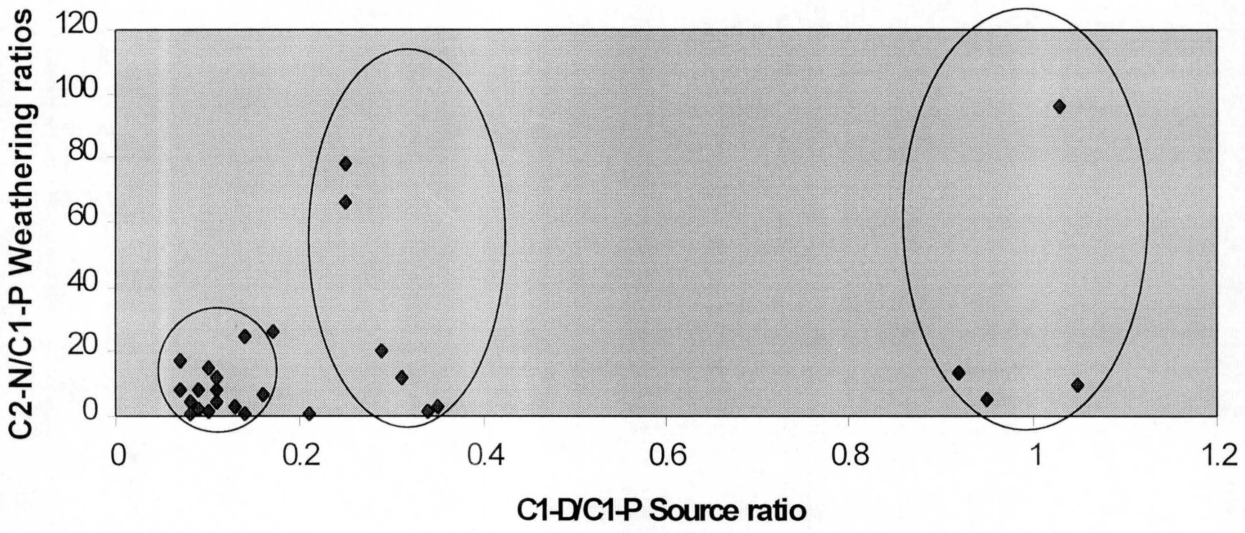

Figure 9.12: Double ratio plots of alkyl PAHs in water sample

The determination of diagnostic ratios in soil samples

Similarly to water samples, the complexity of the chromatograms of soil samples was one of the concerns during the development of diagnostic ratios. Certain single isomer peaks are for example hard to distinguish in heavily contaminated samples, especially at low levels. Examples of co-extracted interfering peaks can be seen **Figures 9.2**, **9.3** and **9.6**. The peak overlap of interfering compound with the isomer peaks and poor resolution is evident from these examples. The specific single isomer peaks that were selected for soils in this study are shown in **Figure 9.13**.

Another concern in the selection of suitable isomers was the rate of degradation. It was shown in **Chapter 2** that the rate of PAH degradation in the environment decreases with ring size, within a homologous series and with an increase in alkylation. As also indicated earlier, ideal isomers such as C_2-D, C_2-P and C_2-C were, unfortunately, either not detected in the coal tar contaminated soil samples or were present at concentrations below the reporting limits. A useful isomer that could be detected in most samples was C1-dibenzothiophene. The the C_1-D/ C_1-P ratio was , therefore, the most reliable source ratio that was found in this study, although not the most stable and resistant toward weathering. In the case of weathering ratios, C_2-N/C_1-P was found to be the most suitable ratio. The C_2-N isomers were, unfortunately, not very stable during the study and in some samples it already degraded below the method detection limit. This is evident from the results of the oil-contaminated samples (4a- 4g), which had very low concentrations of alkylated naphthalenes due to an advanced degree of weathering. The results for soil samples using the single isomer peak method, which was discussed earlier, are shown in **Table 9.2**. The results include soils which were contaminated by coal tar (samples 3a – 3 l) and soils contaminated by mineral/lubricating oil (4a – 4g).

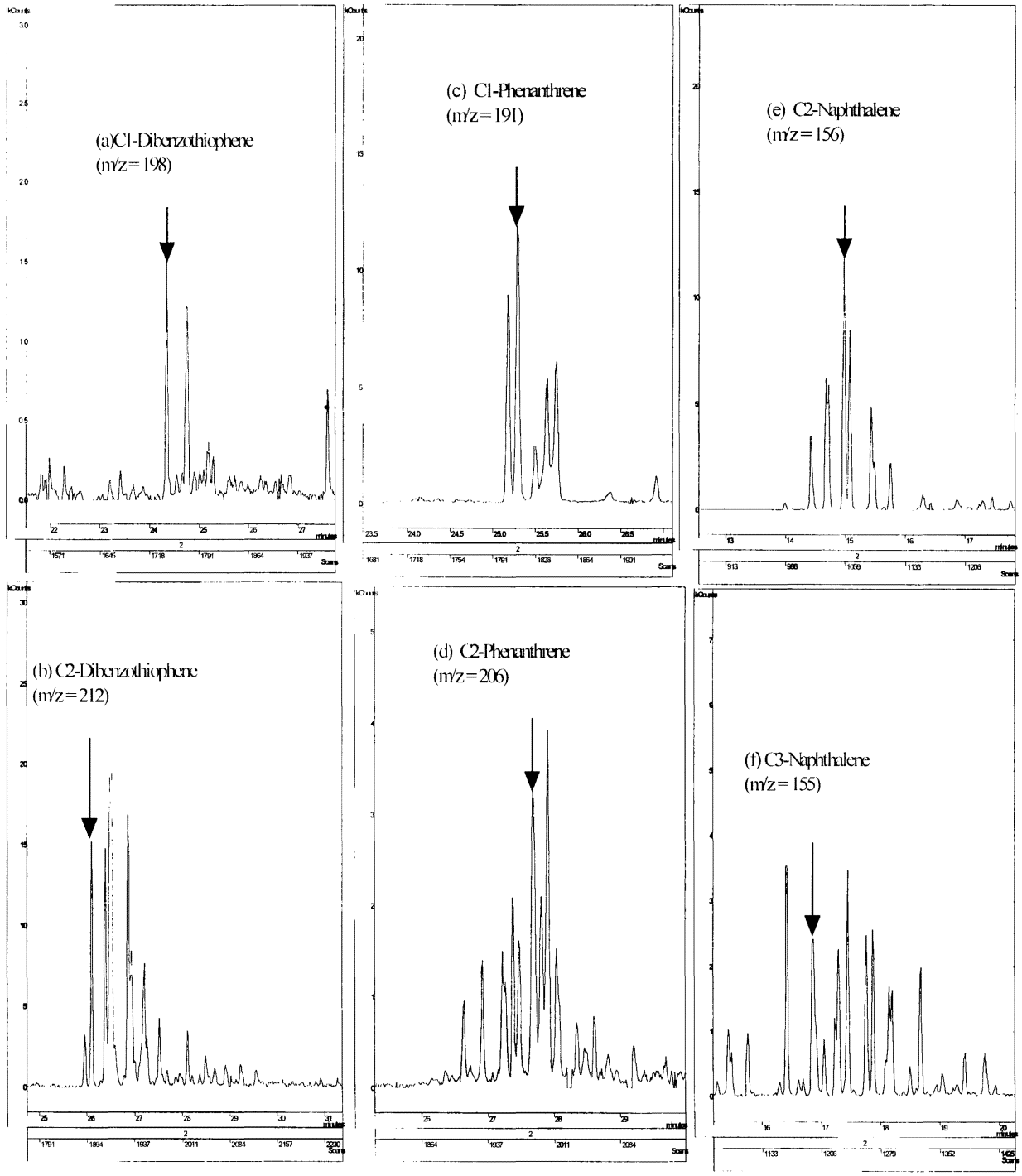

Figure 9.13: Selected ion chromatograms of PAH isomers in soil samples, showing peaks that were selected for diagnostic ratios

Table 9.2: Diagnostic ratios of selected soil samples

	Source Ratios		Weathering Ratios	
	Less Stable	Stable	Very sensitive	Less sensitive
	D/C1-P	**C1-D/C1-P**	**C2-N/C1-P**	**C3-N/C2-P**
No 1(a)	1.5	0.09	1.00	1.00
No 1(b)	2.22	0.81	1.06	1.32
No 1(c)	2.46	0.22	1.22	1.38
No 1(d)	-	-	-	-
No 1(e)	-	-	-	-
No 1(f)	-	-	-	-
No 2(a)	1.50	0.13	3.06	0.45
No 2(b)	1.04	0.14	1.06	0.45
No 2(c)	2.09	0.11	1.75	1.25
No 2(d)	2.32	0.19	3.83	2.46
No 2(e)	2.35	0.16	4.67	4.02
No 3(a)	1.07	0.18	0.97	0.38
No 3(b)	1.03	0.22	1.93	0.33
No 3(c)	1.15	0.21	1.04	0.38
No 3(d)	1.19	0.22	2.82	0.49
No 3(e)	0.61	0.18	0.43	0.20
No 3(f)	1.02	0.18	1.01	0.44
No 3(g)	1.19	0.16	1.42	0.82
No 3(h)	1.49	0.22	1.93	0.62
No 3(i)	1.99	0.24	2.25	0.63
No 3(j)	1.74	0.22	1.85	0.61
No 3(k)	1.50	0.18	1.84	0.96
No 3(l)	1.41	0.22	2.12	0.47
No 4(a)		0.48	0.04	0.16
No 4(b)		0.45	0.02	0.04
No 4(c)		0.46	0.08	0.21
No 4(d)		0.54	0.04	0.19
No 4(e)		0.52	0.16	0.05
No 4(f)		0.44	0.23	0.16
No 4(g)		0.54	0.31	1.04

The results shown in **Table 9.2** are also presented graphically is **Figure 9.14**. An average C_1-D/C_1-P source ratio of 0.20 was determined for coal tar contaminated soil, which was significantly lower than the average ratio of 0.49 that was found for the oil contaminated soils. The findings agree with the theoretical expectation as a higher ratio is expected in samples contaminated by lubricating/mineral oil sources because of their higher sulphur content. Weathering was evident by the relative increase of heavy PAHs that was observed in most cases. It was also observed in the disappearing of concentrations within the naphthalene homologue: C_0-N < C_1-N < C_2-N < C_3-N. Weathering could be due to bacterial degradation or dissolution in ground- or rainwater or a combination of both. The weathering ratios for the C_2-N/C_1-P isomers had a large variation between samples, which is probably due to the sensitive nature of this specific ratio. More constant ratios were found for the C_3-N/C_2-P isomers.

A plot was constructed for source ratio versus weathering ratio to illustrate that double ratio plots can be used as a means of resolving multiple sources as well as differences in the extent of degradation from a single source. This plot is shown in **Figure 9.15,** and similar to **Figure 9.12** demonstrates the usefulness of the source ratio over a wide range of weathering and biodegradation for the two sources. The strategy for the successful application of these source ratios to hydrocarbon assessment studies must include an initial study to determine the ratios of potential sources.

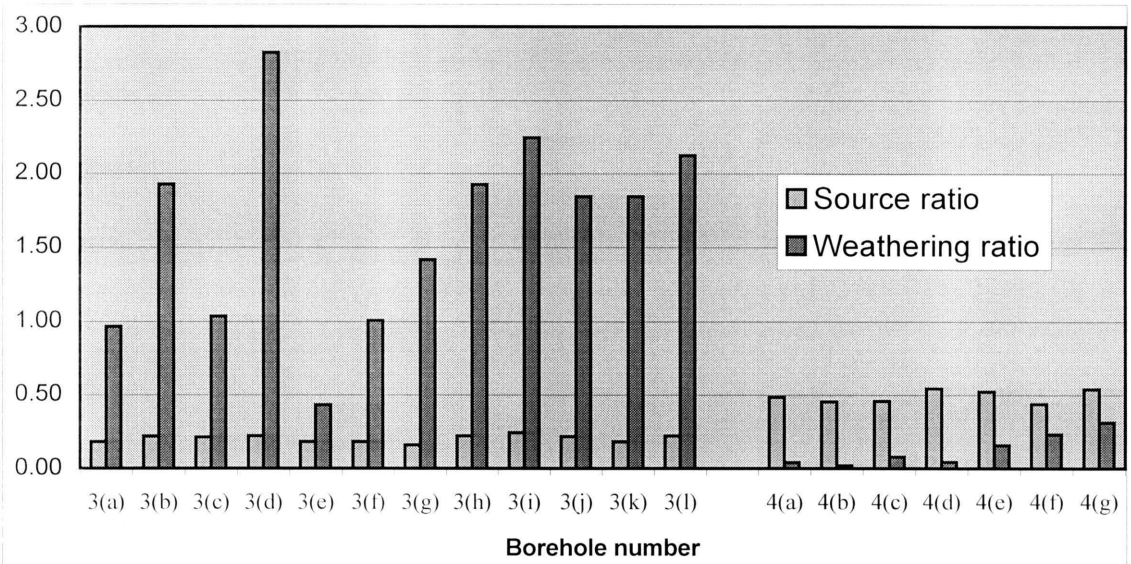

Figure 9.14: Source and weathering ratios of soil samples

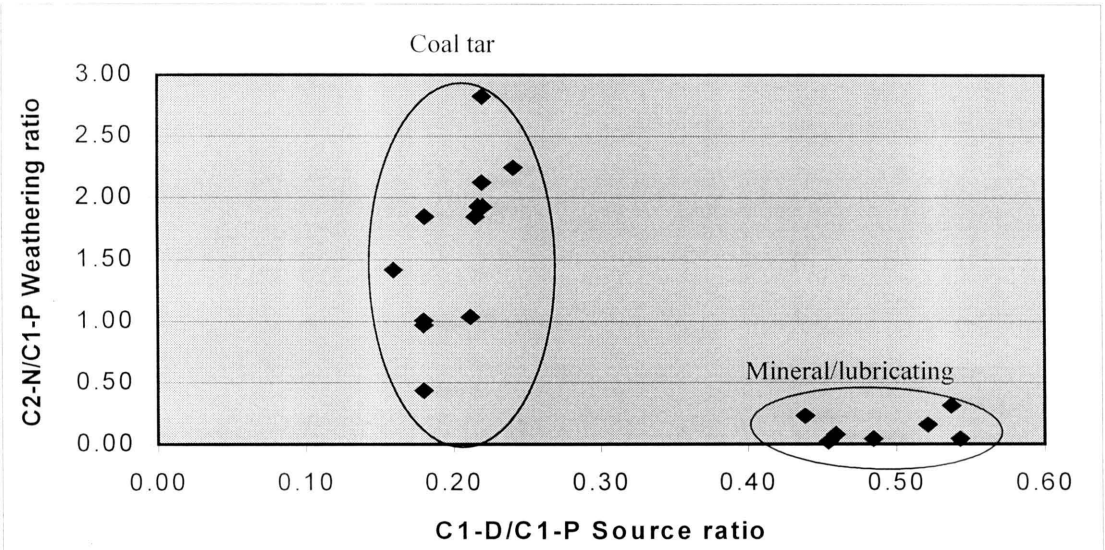

Figure 9.15: Double ratio plots for soil samples

Other analyte ratios, such as C_2-D/C_2-P, might be useful in the case of petrogenic sources. The determination of ratios in water samples was complicated by the low abundance of alkyl-PAHs in samples that are contaminated by pyrogenic sources. The concentration of parent PAHs in water samples routinely analysed by our laboratory, is normally < 10 ng/cm^3 and often < 1 ng/cm^3. Only a few samples contained PAHs in concentrations of > 10 ng/cm^3 and these were from surface water in an industrial area. The C_1-D/C_1-P source ratios that could be determined for selected water samples are shown in **Table 9.3**.

Table 9.3: Source ratios of selected water samples

	SOURCE RATIOS
	C1-D/C1-P
Coal tar contaminated samples	
No 1	0.35
No 2	0.36
No 3	0.13
No 4	0.20
No 5	0.25
No 6	0.40
No 7	0.36
No 8	0.17
No 9	0.22
No 10	0.27
No 11	0.35
No 12	0.16
No 13	0.15
No 14	0.34
No 15	0.23
No 16	0.29
No 17	0.39
Surface water samples	
No 18	0.28
No 19	0.13
No 20	0.20
No 21	0.65

Most measurements were found to be very close to the detection limit with a very low signal to noise ratio. The results are, therefore, not expected to be very accurate. This was also evident from the high analytical variance between results. The fact that the samples were influenced by multiple sources (pyrogenic and petrogenic) could also be a reason for the variance. A source ratio of between 0.15 and 0.25 was observed for some of the samples, which is similar to the source ratio found on the contaminated soil samples. Only one surface sample had a high source ratio of 0.65 (petrogenic source) and the others were in-between. The conclusion was made that the determination of C_1-D/C_1-P source ratios in groundwater samples is useful, but is limited to samples containing these isomers in concentration of > 0.07 ng/cm^3 (based on the MDL of phenanthrene with SPME-GC/MS and the number of C_1-P isomer peaks).

ANALYTE DISTRIBUTION PATTERNS IN SOILS

Fingerprinting of hydrocarbons is made possible by the variety of individual compounds found in hydrocarbon sources and in the great variability in the relative abundances of these compounds among different sources. The main objective is to distinguish combustion related sources (coal tar) from petroleum using fundamental differences in the distribution of PAHs according to the number of aromatic rings and the degree of alkylation.

Weathering can also alter these patterns as illustrated in **Figure 9.16**. Results for the drill core soil samples analysed in **Chapter 7**, using the ASE-GC/MS method, were used to illustrate the change in profile with weathering. With an increase in the depth of the sample, an increase was observed in the relative concentration of the naphthalene homologous series and a decrease in the relative concentration of the 5-ring compounds.

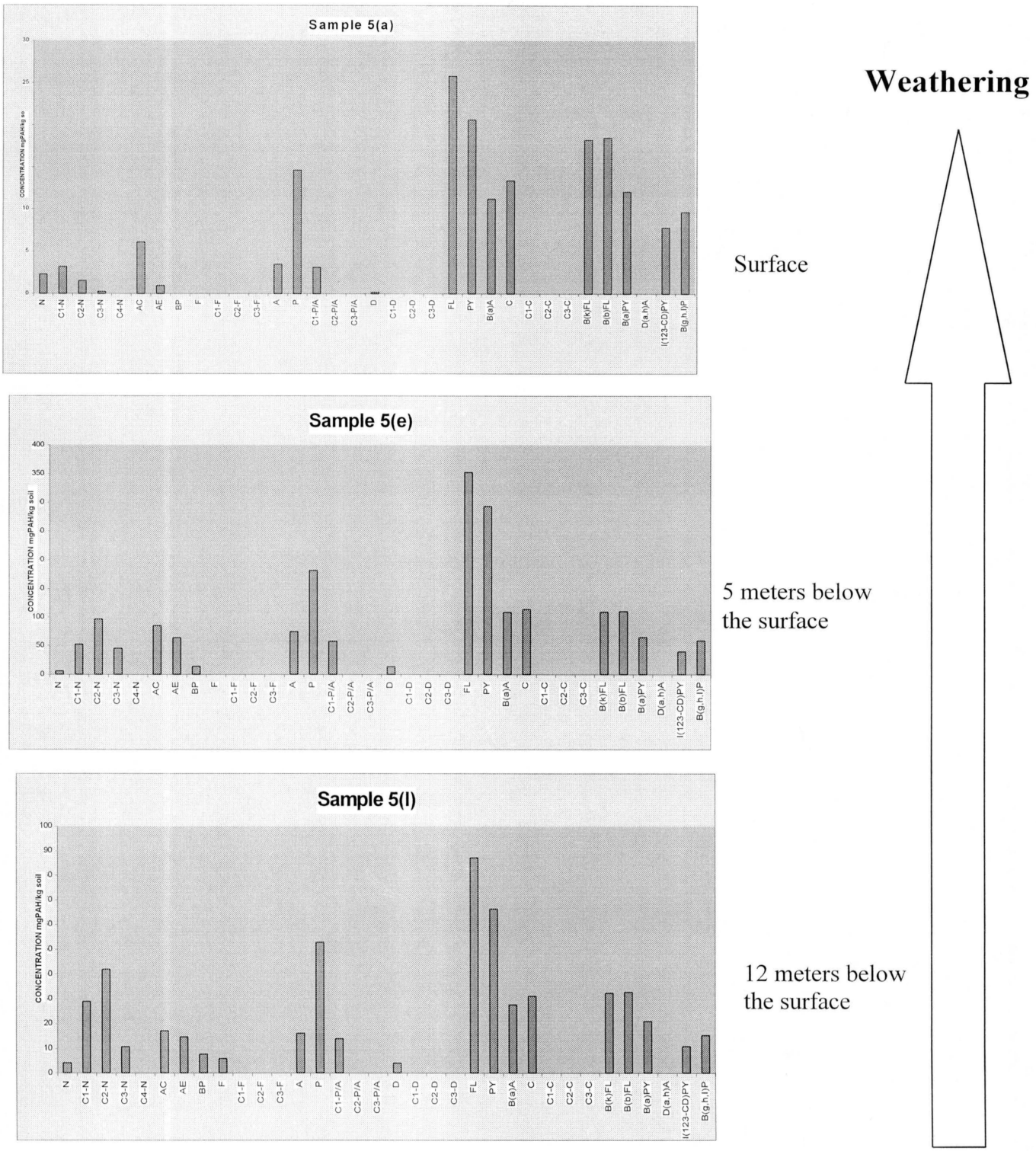

Figure 9.16: Weathering of coal tar with depth

Analyte distribution patterns were also used to identify the pollution source of soil samples contaminated with coal tar and mineral oil respectively. The fingerprints of these samples are shown in Figure 9.17. This example illustrates that the fundamental differences in the distributions of PAHs according to the number of rings and degree of alkylation, is effective to qualitatively determine the type of hydrocarbon pollution. The two soil samples used in this example were specifically chosen because they were contaminated to the same degree but with different distributions. The total PAH concentration found in these samples were < 25 mg/kg. The coal tar contaminated sample was characterised by a relatively high abundance of fluoranthene, pyrene and the 5- and 6-ring structures, with a low dibenzothiophene to phenantrene ratio. The mineral oil contaminated sample was characterised by a relatively high abundance of naphthalenes, phenenthrenes, dibenzothiophenes and chrysenes, with a high dibenzothiophene to phenantrene ratio. However, a more quantitative technique is needed to allocate the contribution of the two sources to the PAH contaminated soils, such as the double ratio plots illustrated in Figure 9.15.

CONCLUSIONS

The quality of PAH data generated with respect to accuracy and precision is critical for the successful determination of diagnostic ratios. The simplified method that was developed to determine source and weathering ratios by using only one isomer peak in an alkyl homologue, was found to be accurate and precise enough for this purpose. In the case of soil samples investigated in this study, the relative abundance of alkyl-naphthalenes (C_1-C_3), alkyl-phenanthrenes (C_1-C_2), alkyl-dibenzothiophenes (C_1-C_2) and C_1-chrysenes were found in high enough concentrations to develop source ratios based on these isomers. Substantial differences were also found in source ratios between petrogenic and pyrogenic sources to allow the ability to distinguish between different sources. These differences were further enhanced when a double ratio plot of C_2-N/C_1-P (source ratio) versus C_3-N/C_2-P (weathering ratio) is used.

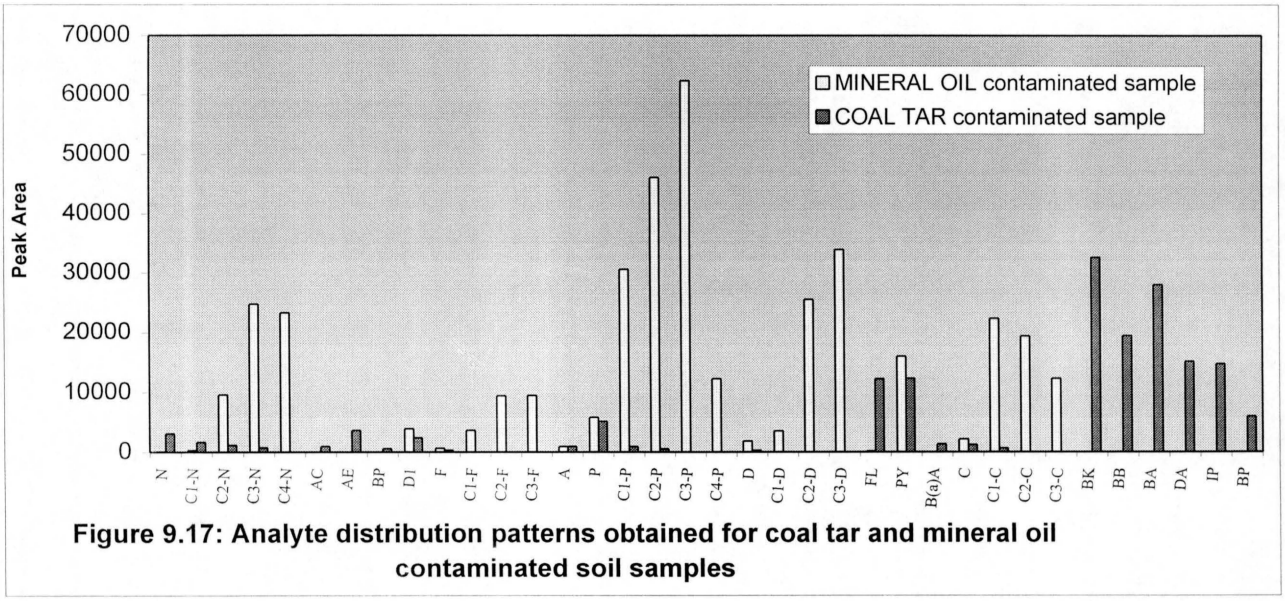

Figure 9.17: Analyte distribution patterns obtained for coal tar and mineral oil contaminated soil samples

This plot is also a useful indicator of weathering and degradation.

The determination of source ratios in water samples is subject to some inherent limitations:

- **Limited data:** The abundance of alkyl-PAHs in water samples was generally found to be lower than the detection limit.

- **Weathering:** Source ratios based on parent PAHs are inaccurate because these compounds weather rapidly at different rates losing their fingerprint. Ratio calculations can be useful in the case of fresh and unaltered pollution.

- **Lack of repeatability:** Interferences from co-extracted compounds complicated the determination of certain isomers. The manual integration of analytical data further limited the repeatability.

Chapter 10

FINAL CONCLUSIONS AND RECOMMENDATIONS

INTRODUCTION

In the preceding chapters of this thesis, analytical methods have been developed and evaluated for the determination of specific target analytes in water and soil samples, and their suitability for hazard identification, health risk assessments and implementation for high quality chemical fingerprinting. Special attention was given to the analytical performance, method detection limits and the ability of these methods to distinguish target analytes from co-extracted compounds that often have concentrations of up to orders of magnitude higher than the target analytes. The ability of the methods to differentiate among the various isomers of the alkyl substituted polycyclic aromatic hydrocarbons (alkyl-PAHs) was also important.

Based on the low guideline concentrations specified by the USEPA (see **Table 3.1**), the sensitivity and reliability of the method for carcinogenic PAHs is critical for risk assessments. On the other hand low detection limits for all the PAHs (including alkyl-PAHs) are required for chemical fingerprinting and to link pollutants positively to their sources. In the following sections, the limitations and strengths of the developed chemical analyses and interpretative methods are discussed. Recommendations are given for future development work in the field of analytical methods to determine poly aromatic hydrocarbons (PAHs) in soil and water samples.

STATE OF THE ART ANALYTICAL METHODOLOGY

The determination of PAHs in groundwater and surface water samples

Considering the present level of sophisticated analytical equipment used in conjunction with modern sample preparation technologies such as Solid Phase Microextraction (SPME), it can be concluded that PAHs in water samples can be analysed with a high level of reliability. SPME was compared to liquid-liquid extraction (LLE) and found to be superior to traditional extraction methods with regard to many aspects. The main advantages of the SPME-GC/MS method include:

- The elimination of toxic solvents and increased automation reduced analytical costs and improved turnover times.
- The simple pre-treatment procedure reduced the uncertainty of the overall results.
- The small amount of sample required was better suited for sampling, sample handling and transportation.
- The method showed superior analytical performance when compared to the liquid-liquid extraction method with much lower Method Detection Limits (MDLs) and procedural blank values.
- The technique was characterised by excellent selectivity and the ability to distinguish target analytes from interfering compounds

- It was possible to differentiate among various alkyl-PAH isomers that could be used for the calculation of source and weathering ratios.

- Detection limits found with SPME-GC/MS were all lower than the health risk based guideline concentrations of PAHs specified by the USEPA (see **Table 3**), which make the method suitable for health risk assessments.

The following disadvantages were identified when using SPME:

- The quantification of alkyl-PAHs is complicated by the fact that SPME is based on partition equilibrium with significant differences among the extraction efficiencies of the target analytes. Two consecutive analyses are required (multiple extraction SPME) for the application of advanced chemical fingerprinting.

- The technique (as used under the conditions specified in this study) is not reliable for the accurate quantification of 5-ring PAH compounds (indeno[123-cd]pyrene, dibenzo[a,h]anthracene and benzo[g,h,I]perylene, which show poor analytical performance.

- The concentrations of dibenzothiophene and phenanthrene isomers in coal tar contaminated samples (used for diagnostic ratios) were often found to occur in concentrations lower than the MDL.

Based on the advantages and disadvantages listed above, SPME coupled with Gas Chromatography and Mass Spectrometry (SPME-GC/MS) is the preferred method for the analysis of trace quantities (< 10 ng/cm^3) PAHs in water samples. For samples containing larger amounts of PAHs the liquid-liquid extraction method would be better suited, especially if the results are required for advanced chemical fingerprinting, or if accurate results for the 5-ring PAHs are required.

The analyses of soil and sediment samples

The development of more efficient analytical equipment for the extraction of organic compounds from soil and sediment samples (Accelerated Solvent Extraction - ASE) used in conjunction with GC/MS, resulted in a reliable method for the determination of PAHs. The ASE method was found to be superior to traditional extraction methods, for example Soxhlet extractions in many respects. The main advantages include:

- The system is automated and exhibits similar or improved recoveries of target compounds.

- Compared to Soxhlet, the procedure is significantly less time- and solvent-consuming.

- Savings in labour and time are possible due to the large sample capacity and high efficiency of the ASE system.

The only drawback that was observed, which is not related to the ASE technique but to the nature of the pollution source is that the isomers of C_2-P, C_3-P, C_2-D and C_3-N often occur in soils and sediments in concentrations below the method detection limit (MDL). Advanced chemical fingerprinting (ACF) is, therefore, not always possible.

Headspace SPME (HSSPME) was found to be a fast, efficient and selective screening method to extract PAH compounds from polluted soil and sediments, but the sensitivity of the method decreases sharply with an increase

in the ring size. The technique does not require any sample pre-treatment, other than grinding, drying and homogenising, and is very useful as a fast screening technique. Savings on chemical analyses and sampling can be realised as the results can be used to identify samples that must be analysed with a more detailed technique such as ASE-GC/MS, or to adapt the sampling and analysis strategy. The technique is associated with the following disadvantages:

- Due to their low vapor pressures, the 4- and 5-ring PAHs cannot be analysed. Information on these compounds is, however, vital for risk analysis and advanced chemical fingerprinting.
- Due to differences in extraction efficiency with the degree of alkylation, the method is not suitable for the quantitative determination of alkyl-PAHs.
- The determination of source ratios and weathering ratios is limited to compounds with similar physico-chemical properties (e.g., C_1-P/C_1-D) for the same reasons as mentioned above.

Advanced chemical fingerprinting analyses

Distinct differences between the PAH analyte distribution patterns of refined oil and coal tar fingerprints have been shown, using results obtained from methods developed during this study. The PAH distribution patterns obtained with these methods are suitable for the differentiation among multiple sources.

The determination of source and weathering ratios in coal tar contaminated samples was associated with several disadvantages. Pyrogenic sources have a decrease in alkyl-PAH concentrations with an increase in the degree of alkylation, which means that certain alkyl-PAHs are normally present in levels lower than the MDL, especially in slightly contaminated samples. Co-extracted compounds are, therefore, often found at levels of a few orders of magnitude higher than the alkyl-PAH isomers. This complicates the determination of reliable diagnostic ratios in coal tar contaminated samples that are only slightly contaminated. The following difficulties were observed with the quantification of trace level alkyl-PAHs:

- Peak overlap of the interfering compounds with the isomer peaks
- Continuous background mass spectral interference
- Poor resolution among certain isomer peaks belonging to the same alkyl homologue
- Low signal to noise ratios
- The time involved in manual integration of each isomer peak

An alternative approach has been investigated to overcome these problems, which is based on the ratio of individual isomers in two different alkyl homologues. One specific isomer was selected in each alkyl homologue, which was used throughout the study to determine isomer-to-isomer ratios. This approach was found to be very efficient, much less time consuming, subjected to less interferences and more reliable. Substantial differences were found in source ratios between petrogenic and pyrogenic sources, which made it possible to successfully distinguish between them. The use of double ratio plots was found to be useful to further enhance these differences.

FUTURE NEEDS AND DEVELOPMENTS

The implications of inaccurate environmental analyses are severe, because mistakes can lead to hazards being undetected or the spurious detection of unreal hazards. It is for this reason that the need to develop more reliable en sensitive analytical methods will continue. Laboratories also face continued pressure to

develop environmental methods that are less complicated and can produce analyses at lower costs and faster turnover times, using inexpensive instrumentation. There is also a need for environmental laboratories to have a stronger focus on quality assurance (QA) and quality control (QC) and to become engaged in accreditation programmes. Participation in inter-laboratory studies might offer the possibility to improve the current state of the art methodologies, but is also of strategic importance for laboratories to maintain/increase their level of competitiveness.

Considering the certainties and uncertainties of the current state of the art methodologies, the following developments are recommended:

- Further refinements to the SPME-GC/MS method discussed in **Chapter 6** with the aim to further improve detection limits, repeatability and the analysis of the 5-ring compounds.
- Optimisation of the SPME extraction conditions, such as the adjustment of pH and ionic strength of the sample, and optimisation of the ion trap conditions can achieve this.
- The determination of alkyl-PAHs using GC/MS/MS and chemical ionisation (soft ionisation technique) to create a stable ion for MS/MS isolation. This method will allow lower detection limits and reliable spectral identification of individual isomers for even the most difficult cases.
- The extraction of PAHs from water samples using multi-channel silicone rubber tubes and thermal desorption as an alternative method to SPME. This technique has the advantage that target analytes are retained quantitatively, opposed to the single equilibrium absorption process of a SPME analysis. The technique will also allow the quantification of alkyl-PAHs with much less complications.
- The investigation into the correlation between PAHs and inorganic contaminants found in groundwater samples.

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APPENDIX 1

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The use of SPME and GC/MS for the Chemical Characterisation and Assessment of PAH Pollution in Aqueous Environmental Samples

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THE USE OF SPME AND GC/MS FOR THE CHEMICAL CHARACTERISATION AND ASSESSMENT OF PAH POLLUTION IN AQUEOUS ENVIRONMENTAL SAMPLES

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Abstract

In this study, direct solid-phase microextraction (DISPME), followed by capillary gas chromatography (GC) and mass spectrometry (MS) in the selected ion storage (SIS) mode was investigated for the determination of polycyclic aromatic hydrocarbons (PAHs) and their alkylated homologues in environmental water samples. It was found that several factors affected the amount absorbed with a single stage extraction, such as the degree of alkylation, fiber condition, absorption time, sample pH, sample matrix, sample temperature, agitation method etc. The technique of multiple extractions (MESPME) was investigated and found to compensate for variations in analytical conditions or sample matrix. The linearity of spiked PAH samples was established in the low concentration range with correlation coefficients of about 0.99. Relative standard deviations (%RSD) of between 1.6 and 17.8% were obtained for relative response factors (RRFs). The limits of detection were estimated at the pg/cm^3 levels that were considerably lower than the maximum concentration level (MCL) specified by the United States Environmental Protection Agency (USEPA). The results demonstrate the potential of MESPME for screening PAHs in environmental waters. The method was also developed to include the quantification of alkyl substituted PAHs which is important for interpretative methods such as chemical fingerprinting (source identification) and hazard, exposure and risk characterisation.

Keywords : Environmental water, Solid-phase micro-extraction, Polynuclear aromatic hydrocarbons, Chemical characterisation, Extraction methods, Environmental analysis.

INTRODUCTION

Sources and occurrence of PAHs in natural waters

The discharge of coal tar products, refined petroleum products and lubricating oils into the environment is among the common anthropogenic sources that have degraded the quality of water and sediment, impacting on health and biota. Coal tar polluted aqueous samples contain a wide variety of chemical components, such as volatile aromatic compounds (VACs), PAHs and their alkyl homologues. The concentration of these pollutants in aqueous samples is usually in the low ng/cm^3 to pg/cm^3 range due to the low solubility of heavy PAHs and partitioning of all PAHs back into stream sediments. Certain aromatic compounds have the potential to damage resources at low levels and can affect the health of animals and humans in a contaminated area. The European Community directive 80/778/EEC states a maximum contaminant level of 0.2 ng/cm^3 for some individual PAHs. The following compounds serve as reference compounds: fluoranthene, benzo[α]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene. There is a constant demand for analytical methods capable of analysing at lower levels, with shorter turnaround times, lower analysis costs, and with better analytical performance. Inaccurate environmental analyses can lead to severe economic and social implications, such as undetected hazards and identification of unreal hazards. Environmental methods should also be reliable enough to characterise the type and source of contamination, as this forms the basis of sound decisions and action required to protect public health and to improve the quality of the environment.

Extraction of PAHs from aqueous samples

Since the introduction of the SPME technique by Pawliszyn [1] in 1989, the application for the extraction of PAHs in environmental samples has been shown [2,3] and the basic theory behind SPME has been detailed [4,5]. PAHs can be extracted from aqueous samples with SPME using a non-polar phase fiber such as the 100μm polydimethylsiloxane (PDMS). It has also been reported [6] that some alkyl substituted PAHs show much higher distribution coefficient (K) values than non-substituted PAHs. This is because PAHs with side chains are more soluble in the hydrophobic

stationary phase, improving the partitioning into this phase. In a previous study, the effect of vapor pressure differences between parent and alkylated PAHs was investigated in the context of SPME headspace analysis[7]. Because of differences in extraction efficiency between PAHs with different degrees of alkylation, it was concluded that headspace SPME is not a very efficient method to establish chemical matches based on the profile of the alkyl homologous series. With a direct or headspace SPME extraction from an aqueous matrix, however, it is possible to use the technique of MESPME to allow for differences between the extraction efficiency of parent and alkylated PAHs. The application of MESPME-GC/MS is investigated in this work, with emphasis on the following aspects:

(1) Selectivity of SPME for PAHs

(2) Extraction efficiency

(3) Depletion in a complex matrix

(4) Hazard identification and characterisation

(5) Chemical characterisation of pollutants

(6) Method detection limits and method validation

The characterisation of PAH pollution

Advanced hydrocarbon fingerprinting, source identification and interpretation methods were developed during the *Exxon Valdez* investigations[8] which serve as a basis for environmental pollution characterisations. *Chemical characterisation* or fingerprinting involves the comparison of specific chemical patterns that will distinguish potential sources from each other and from background levels. For example, conventional gas chromatograms of diesel fuel, lubricating oil, crude oil and coal tar can reveal the presence of PAHs in all cases, but they exhibit different chromatographic profiles. For more detailed analysis, the identities and proportions of the aromatic compounds in a potential source are usually determined by GC/MS to provide a fingerprint of the source, which is then compared to the aromatic profile of the sample[9-12]. It has been indicated, for example, that alkylated naphthalenes and phenanthrenes, as well as C_1 - C_3-dibenzothiophenes are typical of petroleum contamination. The ratios of certain compounds with different degradation rates can be used for weathering studies[13]. Compounds that are most resistant to weathering, such as the alkylated PAHs and especially the heavier compounds such as

phenanthrenes and chrysenes will dominate weathered samples. Thus, the proportions of marker compounds such as alkylated PAHs, as well as the proportions of other aromatic compounds, provide a fingerprint that can be used to identify the source and degree of weathering in environmental water samples. The application of HSSPME-GC MS for fingerprinting and interpretative methods has been discussed in a previous publication[7]. It was shown that chemical characterisation of alkylated PAHs can be approached in two ways:

(1) Profiling an *alkyl substituted homologous series*[14], e.g. C_1 - C_4 naphthalenes, C_1 - C_4 phenanthrenes, C_1 - C_4 fluorenes and C_1 - C_4 chrysenes together with the respective unsubstituted PAHs. The results are normally presented as an analyte profile histogram and accurate quantitative data for each alkyl homologue is necessary for this purpose. The parent PAH is accurately quantified with the help of internal standards and the alkyl homologue concentrations are then calculated, assuming the same RRF for each respective molecular ion signal. All the isomers within an alkyl homologue are grouped together for this purpose.

(2) Profiling the *isomers* within a certain alkyl homologue[8], e.g. isomers of C_2-phenanthrenes. For this purpose, an accurate quantitative result is not required for each isomer, but the result is presented as a single ion chromatogram, based on the major ion of the homologue, showing the relative intensities of all the isomers.

Other interpretative uses of the results include hazard identification and hazard, exposure and risk characterisation. Hazard identification is based on the confirmation of the presence or absence of PAHs, especially the marker compounds. The hazard characterisation is determined by comparing the contaminant levels found to that of the MCL allowed by institutions such as the USEPA. Oral exposure characterisation of drinking water is calculated based on body weight, exposure duration and amount ingested.

Due to the important role of alkyl substituted PAHs in the assessment use of results, the application of direct SPME-GC MS for analysing these components was investigated.

EXPERIMENTAL

Chemicals

Nanopure water was employed throughout. An analytical reference standard mixture of 16 priority PAHs, 2000 $\mu g/cm^3$ each and the isotopically labelled PAH mixture, 4000 $\mu g/cm^3$ each of naphthalene-d8, phenanthrene-d10, chrysene-d12 and perylene-d12 were obtained from Ultra Scientific (Anatech, South Africa). Methylene chloride (analytical grade) was purchased from Riedel-de Haen (Sigma Aldrich, South Africa).

Gas chromatography conditions

The gas chromatograph was a Varian model 3800 GC operated under the following conditions: Injection: Varian 1071 Injector in the splitless mode, Injector Temperature: 280 °C, Column: J&W fused silica DB5 MS column, 30 m, with a 0.25-mm internal diameter and 0.25-μm film thickness, Carrier gas: He, 1 cm^3/minute, Column Oven: initial 60 °C, then 60-130 °C at 7 °C/minute, 130-200 °C at 5 °C/minute, 200-260 °C at 6 °C/minute, 260-320 °C at 20 °C/minute, final temperature 320 °C - hold 4 minutes.

GC/MS analytical conditions

The mass spectrometer was a Varian Saturn model 2000 Ion Trap system operated under the following conditions: Selected Ion Storage, Scan rate: 3 scans per second, Delay time: 3 minutes, Peak threshold: 2 counts, Background mass: 43u, Scan segments: 10-99/100-209/210-399/400-650, Tune factors: 100/140/120/35, Emission current: 15 μA, Multiplier gain: 10^5, Ion trap temperature: 150 °C, Transfer line temperature: 300 °C.

Solid Phase Microextraction

A 100μm PDMS fiber was obtained from Supelco (Sigma Aldrich, South Africa). For optimum repeatability the technique was automated using a Varian Model 8200 autosampler. Organic compounds were extracted at room temperature from aqueous samples by sampling in the liquid phase, using a 1.2 cm^3 sample in a 1.8 cm^3 sample vial sealed with a teflon coated septum. The fibre was immersed into the agitated liquid for 30 minutes and then immediately inserted into the GC injector at 280°C for thermal desorption, followed by GC/MS analysis.

RESULTS AND DISCUSSION

Selectivity for PAHs

The hydrophobic nature of PAHs suggests high distribution coefficients between the non-polar PDMS-fiber and the water matrix. The selectivity of SPME for individual PAHs is illustrated in Figure 1, which is a standard chromatogram obtained from a water sample spiked with 2 ng/cm^3 each priority PAH. Certain chromatographic and inertness performance criteria as specified in USEPA method 525 are illustrated in Figure 1. This method requires (1) a baseline separation for anthracene and phenanthrene and (2) separation of benzo[a]anthracene and chrysene by a valley less than 25% of average peak height. Both these requirements were met with this method as illustrated in Figure 1.

{Figure 1}

Efficiency of a SPME fiber extraction

The absorption of analytes into the polymeric phase is described by the conventional volume-based distribution coefficient[10]:

$$K_{dv} = \frac{M_f / V_f}{M_w \; V_w} \qquad \text{.....(1)}$$

where M_f is the mass of analyte extracted by the fiber at equilibrium, M_w is the mass of analyte remaining in the water, V_f and V_w are the volumes of the fiber and water respectively. Another parameter, which can be used to predict SPME fiber-water partitioning behaviour, is the octanol-water partition coefficients (K_{ow}). Good agreement between K_{ow} and K_{dv}, obtained with the 100µm PDMS fiber, has been reported in the literature for low molecular weight analytes (such as benzene, toluene and xylenes). Yang and co-workers[3] reported negative correlations between K_{ow} and K_{dv} for analytes with higher molecular weights. Based on the experimental data found, they concluded that K_{ow} cannot be used to anticipate the K_{dv} trend in SPME for PAHs with molecular weights higher than naphthalene. They also found disagreement between K_{dv} values with different coating thicknesses and

demonstrated that K_{dv} is not valid to describe the sorption behavior of these analytes. Better agreement was found when using a surface-based sorption partitioning coefficient (K_{ds}).

In this study, for simplicity, the fractional amount of analyte sorbed onto the 100µm PDMS fiber (extraction efficiency and sensitivity) was determined experimentally. Analytes included several PAHs and their alkyl homologues. It is very useful to define the fractional amounts of solute in each phase after extraction. The investigation was therefore not based on extractions where equilibrium has been reached. As shown in a previous study[115], equilibrium can take as long as a few hours to days, which is not practical for a routine method. It was also shown that proportional relationship exists between the absorbed analyte and its initial concentration in non-equilibrium conditions. A non-equilibrium extraction time of 30 minutes was adopted for the purpose of this study. Extraction efficiency was then determined by averaging four independent determinations of different concentrations ranging between 0.2 and 8 ng/cm^3. Due to limits imposed by aqueous solubilities, concentrations of chrysene, benzo[a]anthracene, benzo[k]fluoranthene and benzo[a]pyrene are limited to a maximum concentration of 2 ng/cm^3 in standards. The amount of analytes absorbed into the fibre was determined as follows:

(1) the sum of peak areas $\sum A_i$ for a known quantity of analyte (C^0_{aq}) was determined from two successive extraction steps, using the following equation[116]:

$$\sum A_i = A_1^2/(A_1 - A_2) \qquad \text{..... (2)}$$

(2) The amount extracted with a single extraction (C_1) was then determined using:

$$C_1 = A_1/\sum A_i \times C^0_{aq} \qquad \text{.....(3)}$$

(3) The efficiency of a single stage extraction was then determined as the fractional amount found in the fibre phase after equilibrium, and expressed as % :

$$\%P = (C_1 / C_0) \times 100 \quad \text{.....(4)}$$

The extraction efficiency found for selected PAHs and alkyl substituted PAHs under the conditions used in this study are shown in **Table 1**. The ranges of %P values depicted in the table were obtained during several experiments over a period of one year, using the non-equilibrium conditions outlined in the experimental section. The purpose of presenting these results is to illustrate the variation in %P and is dependent on various factors, such as the fiber condition (number of times used), absorption time, sample pH, sample matrix, sample temperature, agitation method, etc.

{Table 1}

Examining the results in **Table 1** reveals that the average %P for PAHs range between 30% and 66%. A general trend of an increase in extraction efficiency with an increase in the degree of alkylation was observed. This agrees with the findings of Liu et. al.[6] that alkyl substituted PAHs show much higher K values than the parent PAHs, because PAHs with side chains are more soluble in the hydrophobic stationary phase and, hence, more completely extracted. A decline in extraction efficiency was, however, found for C_4-N. This could be due to the fact that the experiment was performed in non-equilibrium conditions (relatively short absorption time) and that the heavier compounds diffuse more slowly into the fiber.

Chemical Characterisation of pollutants by means of MESPME

Chemical mixtures that leak into water leave behind a characteristic pattern, and the main purpose of estimating the concentrations of alkyl substituted PAHs is to match the PAH distribution pattern of a sample to that of a potential source. Modified solvent extraction techniques have been reported for this purpose [13]. Because standards for alkylated PAHs are presently unavailable, the concentration of these compounds are normally calculated based on the total peak area of all the isomers in an alkyl homologue and using the RRF of the corresponding parent PAH. Solvent extraction techniques have been used for this calculation method because similar extraction efficiencies are obtained for all PAHs. In the case of an SPME analysis the variation of extraction efficiencies with the degree of

alkylation is the main reason why the relative response of alkyl substituted PAHs cannot be compared to the response of the corresponding parent PAH. Other factors that can contribute to these differences are changes in sample matrix and small changes in analytical conditions. The analytical error will be similar to the difference between the extraction efficiency of the parent PAH and alkylated PAH respectively.

To compensate for these effects, the method of using MESPME was investigated using an aqueous sample spiked with trace levels of naphthalene to C_3-naphthalenes. The $\sum A_1$ of individual components was obtained with MESPME and calculated using equation 2 and the data from two extraction steps. The $\sum A_1$ is not affected by the extraction efficiency and is proportional to the analyte concentration. The recovery of naphthalene and alkyl substituted naphthalenes is determined by a calculation using the ratios between analyte peak and the peak of the sensitivity internal standard (d8-naphthalene). In the case of the homologues series, the response of the most abundant isotope peak are used. By dividing these ratios obtained with MESPME by those observed for a solvent extraction analysis, the recoveries can be calculated. The recoveries of naphthalene and the C_1 to C_4-naphthalenes are shown in Figure 2. Mean recoveries ranged between 109 and 124% were obtained, based on the average of six determinations. In the case of a single extraction the recoveries ranged between 110 and 272%. The results demonstrate the suitability of MESPME to estimate PAH and alkyl substituted PAH concentrations for the purpose of profiling PAH distribution patterns.

{Figure 2}

The main assessment use of alkyl substituted PAH profiles is source identification. The results obtained with MESPME was found to suitable to construct an analyte profile histogram to establish similarities and differences between the sample and potential sources as well as for comparison with literature profiles. The basic use is to match the profile to a typical combustion process profile (pyrogenic) or a typical crude oil/refined products profile (petrogenic)[18]. Another use is to ratio the relative abundance of the alkylated homologues of one PAH family (e.g. C_2-phenanthrene) to that of another PAH family (e.g. C_2-dibenzothiophene). These ratios are then used to distinguish between different sources. An ideal source ratio would be unique to that particular source, and the two

analytes would degrade at similar rates[117]. Weathering ratios are determined in a similar way except that two alkylated homologues from two different PAH families are chosen that degrade at a different rate, e.g. C_3-N/C_2-P, where C_3-N will degrade faster than C_2-P.

Depletion Studies for SPME in a Complex Matrix

Aqueous environmental samples normally contain diverse and highly complex matrices in which multiphase systems exist. An example of such a system is water contaminated with a dense non-aqueous phase liquid (DNAPL). It was shown in a previous study[118] that less of the target analytes are sorbed on a SPME fiber when analysing in matrices other than water, such as biological fluids, urine, milk or blood. Since SPME is an equilibrium partitioning process, a fractional amount of solute will be extracted at equilibrium or at any other period in time. This amount is linearly related to the concentration of the analyte, as long as the analysis procedure is standardised. In a typical mutiphase environmental sample, the total number of moles (n) of analyte in the system can be described by Equation 5, where C_0 is the initial analyte concentration, V_{MT} is the total matrix volume, C_f and V_f is the moles of solute in the fiber, C_w V_w is the moles of solute in the water phase and $\sum C_{Mi}V_{Mi}$ is the moles of solute in the ith phase of the matrix.

$$n = C_0V_{MT} = C_fV_f + C_wV_w + \sum C_{Mi}V_{Mi} \quad (5)$$

The fractional amount of solute absorbed on the fiber (P_f) at equilibrium can then be determined using the following equation:

$$P_f = C_fV_f / C_0V_{MT} \quad (6)$$

The amount of solute which can partition into the sample matrix ($\sum C_{Mi}V_{Mi}$), can have an effect on C_fV_f and, hence, on P_f. The amount of analyte absorbed normally decreases as the matrix become more complex, i.e. an increase in the number of phases in the sample and the volume (V_{Mi}) of each phase according to equation 5. In the steel industry, for example, a contaminated water sample can contain lipids (rolling oils), mineral oil (lubricants) and coal

tar (coke making process). A previously characterised water sample found to be contaminated with coal tar and mineral oil was used to investigate the multiple extraction of naphthalene in a complex matrix. The results are shown in Figure 3, comparing the extraction profile with that of a clean water matrix. The results illustrate that in the case of the complex matrix, a portion of the analyte partitioned into the mineral oil and coal tar phase resulting in smaller extraction efficiency of the SPME fiber. The total organic concentration in this water sample was 0.01% and illustrates changes in extraction efficiency in low concentrations of organic compounds. It can, however, be accounted for by using quantitation methods such as internal standards or standard addition. This laboratory uses deuterated internal standards and the average response factors generated from a linear 3-point calibration graph, to quantify the target parent PAHs. Alkylated PAHs are quantified by using the technique of MESPME, straight baseline integration of each level of alkylation and RRF of the respective unsubstituted parent PAH. The combination of these methods significantly improves the quality and reliability of analytical data.

{Figure 3}

Improvement in signal to noise ratio using Selected Ion Storage (SIS)

As illustrated in this study, the complexity of the sample is an issue when dealing with trace level analysis. A high level of selectivity is required for this purpose, which is a distinction of the analytes of interest from compounds that are co-extracted by the SPME fiber and may possibly interfere with the analysis. In this method a degree of selectivity is achieved during each the following analytical stages:

- SPME extraction: the selective extraction of non-polar compounds using a PDMS SPME extraction
- Gas chromatography: separation between target analytes and from interfering compounds
- Mass spectrometry: reconstruction of the mass spectrum based on the selected ion current of the analyte.

The signal to noise ratio is improved during each of these analytical stages. The technique of SIS was investigated to further improve signal to noise ratios as it removes interfering matrix ions from the ion trap leading to greater sensitivity and less spectral noise. The results are shown in Figure 4 where the chromatograms for a typical environmental sample is shown comparing the result of a solvent extraction analysis, SPME extraction and GC/MS (full scan) and a SPME extraction and GC/MS in the SIS mode. The signal to noise ratios are shown on the

chromatograms and the improvement in the SIS mode can be seen. The sample used in this study was contaminated with various aromatic compounds from an unknown source and contained naphthalene, C_1-naphthalenes and C_2-naphthalenes. In the case of the solvent extraction, quantification of the C_2-naphthalenes was difficult due to the small signal and high noise interference from the other aromatic compounds. The SPME extraction was found to be more specific towards the PAHs, leading to less interference and a higher signal to noise ratio. Best results were obtained in the SIS mode and this technique is preferred when dealing with the determination of PAHs in water samples with complex matrixes. Also notice the increase in sensitivity with increasing alkylation in the case of the SPME extraction.

{Figure 4}

Method Linearity, Recovery, Repeatability and Sensitivity Study

The objective for the SPME GC/MS method developed in this study is to obtain reliable measurements at low concentrations in complex matrixes. Reference materials for PAHs in environmental water samples are not currently available and the analytical performance studies were performed using laboratory prepared standards. The method was optimised at the lower concentration ranges and calibration standards were obtained by spiking ultra-pure water with a certified PAH standard mixture to obtain calibration standards with concentrations ranging from 0.2 ng/cm^3 to 8 ng/cm^3. Straight-line calibration curves were constructed and a good linearity was characterised by correlation coefficients of about 0.99.

{Table 2}

The accuracy and repeatability has been determined by the addition of a known amount of PAHs (6 ng/cm^3) to ultra-pure water. The recovery obtained (calculated amount divided by added amount) for each PAH ranged from 96 to 142%. Relative standard deviations (%RSD) were better than 20% in all instances. A general trend of an increase in RSD with an increase in the size of the PAH was observed.

The detection and quantification limits stated in Table II are estimated from the signal to noise ratios. The method was found to be the most sensitive for naphthalene, signal to noise ratio of 8961 (signal = 112985 counts, noise = 13 counts) at the 2 ng/cm^3 level, and an estimated corresponding detection limit of 0.0006 ng/cm^3. Chrysene showed the lowest signal to noise level and highest detection limit. All the PAHs exhibit detection limits and blank values well below the maximum concentration levels specified by the USEPA. Blank values were obtained on ultra-pure water samples spiked with internal standards for quantification. Some of the observed blank values were found to be higher than the detection limits, indicating that the detection limits reported in Table II cannot be reached in practice due to sample carry-over. These values were relatively low and indicate minimal carry-over from the SPME fiber when analysing samples with low contamination levels. Analysis of severely contaminated samples may lead to carry-over problems.

Conclusions

The technique of SPME GC/MS was found to be a selective and efficient method for the determination of PAHs in aqueous environmental samples. SPME can be applied at non-equilibrium conditions with resulting shorter analysis times. Other major advantages of this technique is the use of much smaller samples, elimination of solvent extraction techniques and automation of the extraction process which together reduce analytical costs and turnover times and avoid disposal of toxic solvents.

The extraction efficiency of parent PAHs ranged between 38 and 59% and is found to be dependent on various conditions, such as fiber condition, absorption time, sample pH, sample matrix, sample temperature, agitation method etc. Most of these conditions are under the control of the analyst, except the sample matrix. The technique of internal standards together with multiple extraction SPME was found to be suitable to compensate for differences in extraction efficiency. Using the mass spectrometer in the Selected Ion Storage mode can reduce matrix effects. The quantification of alkylated PAHs, which plays an important role in assessment use of results, can be carried out with sufficient accuracy to allow the characterisation of polluted water samples. Potential uses of this MESPME GC/MS include the hydrocarbon source identification, weathering processes and risk assessments associated with public health and biota. The method has good linearity in the low concentration range investigated and has the sensitivity required to

characterise the chemical hazard. Detection limits were found to be orders of magnitude lower than the maximum concentration levels stated in the USEPA drinking water standard.

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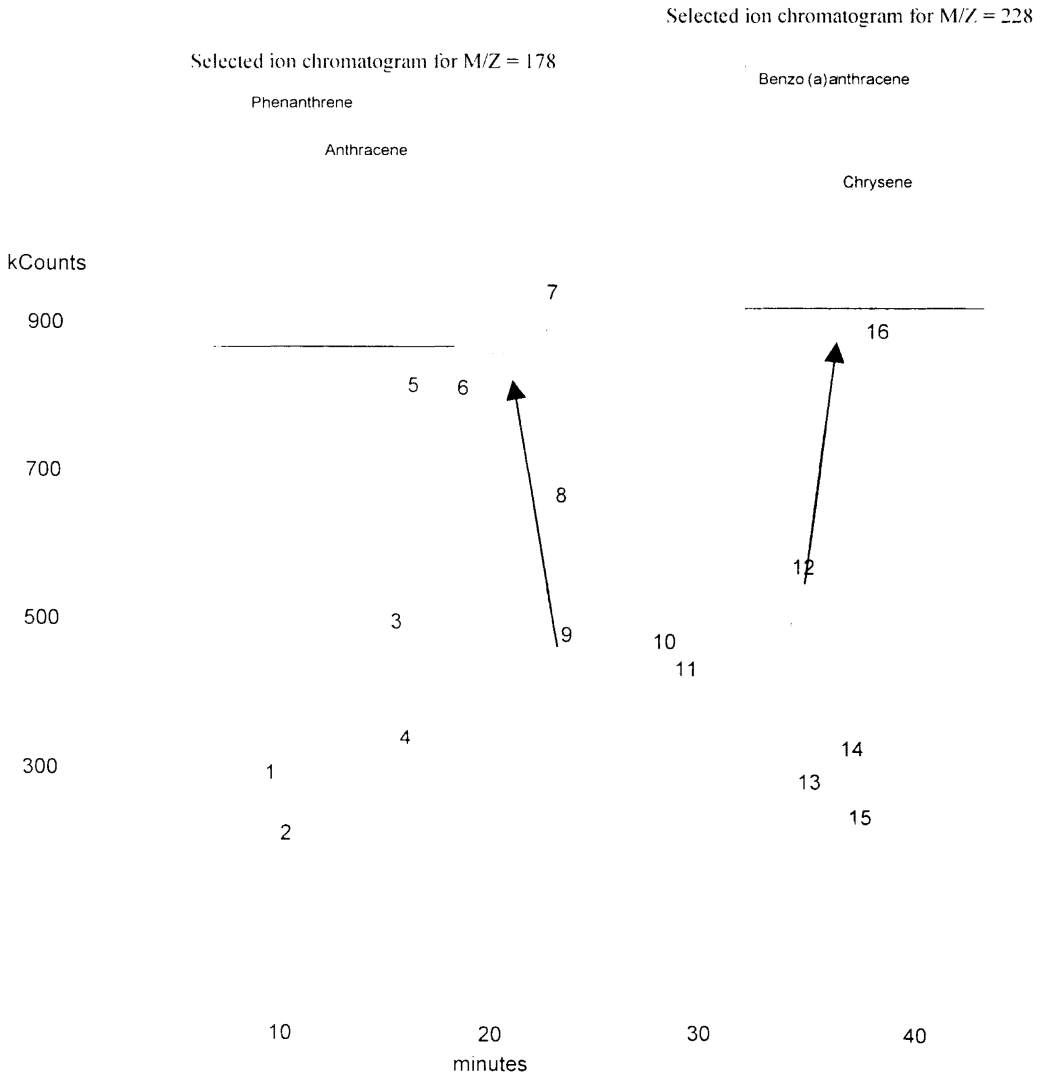

Figure 1: Chromatogram of 2 ng/cm^3 PAHs illustrating chromatographic and inertness performance. (1)d_8-naphthalene (2) naphthalene (3) acenaphthylene (4) d_{10}-acenaphthene (5) acenaphthene (6) fluorene (7) d_{10}-phenanthrene (9) anthracene (10) fluoranthene (11) pyrene (12) benzo[a]anthracene (13) chrysene (14) benzo[b]fluoranthene, benzo[k]fluoranthene (15) d_{12}-perylene (16) benzo[a]pyrene.
Segment 2 (3 – 12 minutes): m/z = 126 – 130 and 134 – 138
Segment 3 (12 – 22 minutes): m/z = 162 – 168 and 176 - 180
Segment 4 (22 – 25 minutes): m/z = 164 – 168 and 176 - 180
Segment 5 (25 – 31 minutes): m/z = 199 – 205
Segment 6 (31 – 35 minutes): m/z = 226 – 230 and 238 – 242
Segment 7 (35 – 41 minutes): m/z = 250 –254, 262 – 266 and 274 - 280

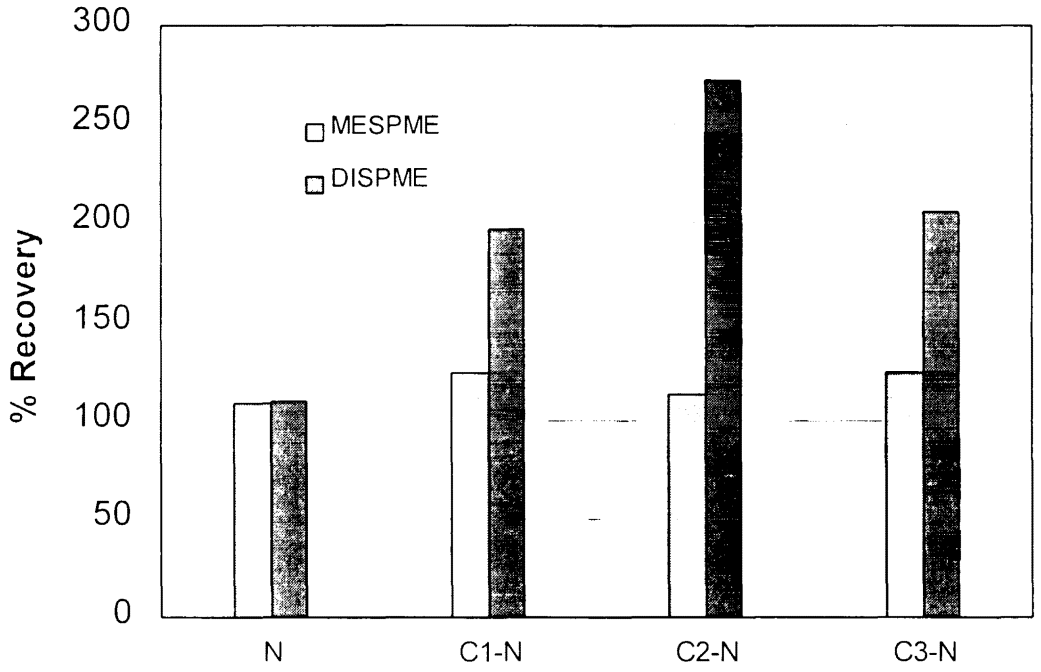

Figure 2: Recovery of the naphthalene homologues series added to pure water at levels of 6 – 12 ng/cm^3 using MESPME. Results are based on six determinations.

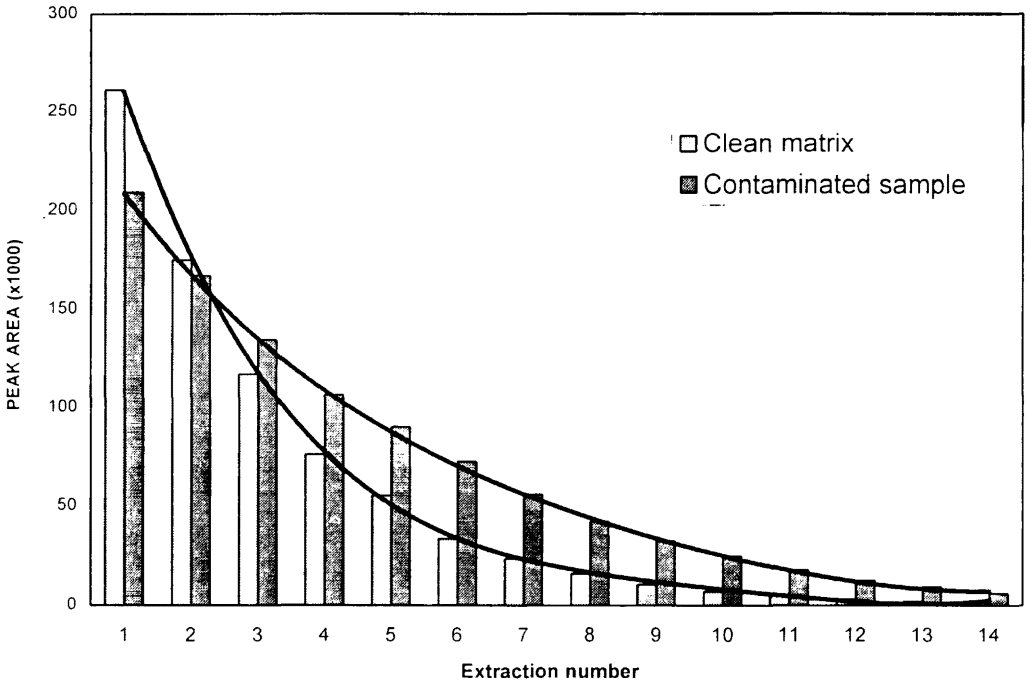

Figure 3: MESPME-extraction of naphthalene from (1) a clean matrix and (2) a contaminated sample

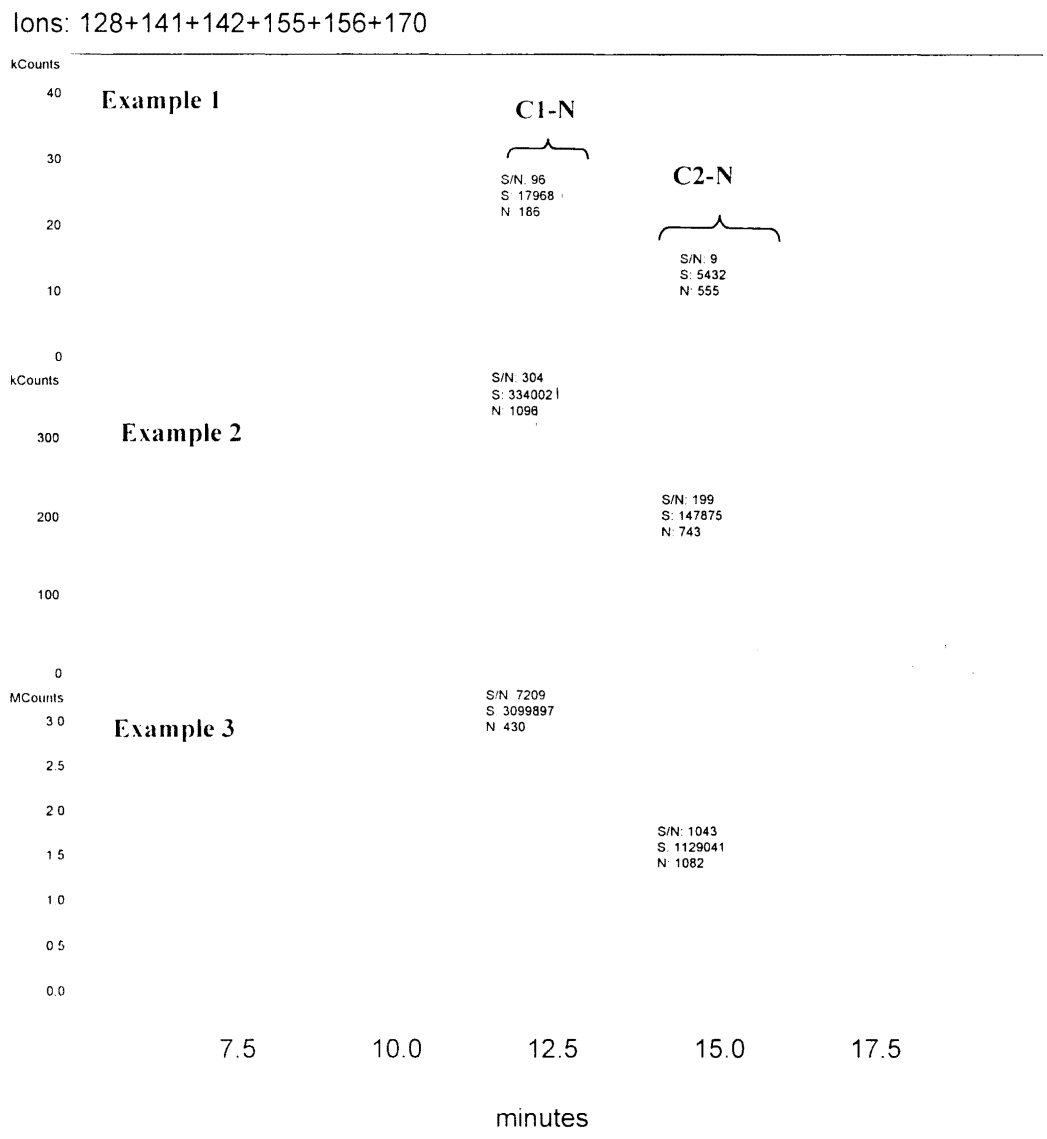

Figure 4: GC/MS chromatograms of naphthalene, C_1-naphthalenes and C_2-naphthalenes in a contaminated water sample showing signal to noise ratios. (1) solvent extraction and full-scan MS (2) SPME extraction and full-scan MS (3) SPME extraction and SIS MS mode.

TABLE I: Extraction efficiency of various PAHs at low ng/cm^3 levels from ultrapure water

Analyte	% P range
Naphthalene	20 – 35
C_1-Naphthalenes	35 – 45
C_2-Naphthalenes	55 – 65
C_3-Naphthalenes	50 – 60
C_4-Naphthalenes	40 – 50
Biphenyl	45 – 55
Acenaphthylene	45 – 55
Acenaphthene	45 – 55
Fluorene	45 – 55
Dibenzofuran	45 – 55
Dibenzothiophene	30 – 40
Phenanthrene	40 – 60
Anthracene	40 – 60
Fluoranthene	40 – 60
Pyrene	40 – 60
Benzo[a]anthracene	40 – 60
Chrysene	40 – 60
Benzo[k]fluoranthene	35 – 60
Benzo[a]pyrene	35 – 60
Benzo[g,h,i]perylene	35 – 60
Dibenz[a,h]anthracene	35 – 60
Indeno[1,2,3-cd]pyrene	35 – 60

Table II: Calibration and analytical results

	CALIBRATION (4 levels: 2 - 8 ng cm^3)		ACCURACY AND PRECISION			SENSITIVITY			REPRESENTATIVINESS	WATER STANDARDS
Compound	Regression Coefficients (R^2)	% RSD	Value found for a 6 ng/cm^3 spiked sample	% Recovery	% RSD for 6 ng cm^3 (n=10)	Signal to Noise (S/N) At 2 ng/cm^3	Quant. Limit [(a)] ng/cm^3	Detection limit [(b)] ng/cm^3	Procedural Blank Values ng/cm^3	MCL[(c)] USEPA ng/cm^3
Naphthalene	0.997	2.21	6.12	102	8.9	8961	0.002	0.0006	0.000	70.0
Acenaphthylene	0.993	5.21	5.95	99	3.0	6143	0.003	0.0009	0.000	-
Acenaphthene	0.991	3.59	5.88	98	3.5	5940	0.003	0.0009	0.000	-
Fluorene	0.996	1.81	6.42	107	7.0	6254	0.003	0.0009	0.000	-
Phenanthrene	0.996	2.31	5.99	100	1.6	1407	0.014	0.0040	0.021	5.0
Anthracene	0.997	2.48	5.78	96	3.5	1856	0.010	0.0030	0.000	
Fluoranthene	0.997	1.13	6.27	105	11.3	2725	0.007	0.0020	0.015	1.0
Pyrene	0.995	3.78	6.41	107	12.5	2970	0.007	0.0020	0.012	-
Benzo[a]anthracene	0.992	23.9	8.42	140	6.3	1019	0.020	0.0060	0.000	0.100
Chrysene	0.993	41.3	8.54	142	4.1	866	0.046	0.0070	0.031	0.200
Benzo[k]fluoranthene	0.999	54.3	7.07	118	11.8	1945	0.012	0.0030	0.000	0.200
Benzo[a]pyrene	0.993	43.2	7.71	129	17.8	1355	0.017	0.0045	0.000	0.200

(a) - Signal to noise = 10
(b) - Signal to noise = 3
(c) - Maximum concentration level, US Environmental Protection Agency.

APPENDIX 2

Paper presented during the 3 rd Euroconference on Analytical Environmental Chemistry, Chalkikdiki, Greece, 9 – 15 October 1999.

3rd Euroconference on Environmental Analytical Chemistry

Chalkidiki (Greece) October 9-15, 1999

W.J. Haveniga

has participated in the **3rd Euroconference on Environmental Analytical Chemistry**

For the Organizing Committee

Prof. A. Voulgaropoulos
Chairman

Z. Loukou
Conference Secratery

The use of SPME and GC-MS for the chemical characterisation and assessment of PAH pollution in aqueous environmental samples

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Coal tar polluted samples contain a wide variety of chemical components, such as volatile aromatic compounds (VACs) and polycyclic aromatic hydrocarbons (PAHs) with their alkyl homologues. Certain aromatic compounds have the potential to damage resources and affect the health of animals and humans in a contaminated area. Chemical analyses are needed to determine of the extent of contamination in water resources, damage assessments, the prevention of contaminated water from reaching consumers and identification of the source of contamination. In the case of source identification the method must be specific and sensitive enough to reveal special chemical characteristics that will distinguish potential sources from each other and from background levels. For example, the gas chromatograms of diesel fuel, lubricating oil, crude oil and coal tar can reveal the presence of PAHs in all cases, but they exhibit different characteristic chromatographic profiles. For more detailed analyses, the identities and proportions of the aromatic compounds in a potential source are usually determined by GC-MS to provide a fingerprint of the source, which is then compared to the aromatic profile of the sample. It has been indicated, for example, that alkylated naphthalenes and phenanthrenes, as well as C_1 - C_3 dibenzothiopenes are typical of petroleum contamination. In weathered samples, compounds most resistant to weathering, such as the alkylated PAHs and especially the heavier compounds such as phenanthrenes and chrysenes, will dominate. Thus, the proportions of marker compounds such as alkylated PAHs, as well as the proportions of other aromatic compounds, provide a fingerprint that can be used to identify the source and degree of weathering in environmental water samples

Analysis of the alkyl substituted PAHs therefore play an important role in the assessment use of results, such as hydrocarbon source identification, oil weathering processes and short- and long-term biological effects relationship. Using a non-polar phase fiber such as the 100µ polidimethylsiloxane these compounds can be extracted from an aqueous sample with the technique of Solid Phase Micro-extraction (SPME). It has , however, been reported that some alkyl substituted PAHs show much higher distribution coefficient (K) values than non-substituted PAHs. The reason for this is because PAHs with side chains are more soluble in the hydrophobic stationary phase and with increasing alkylation, the amount of analyte is more completely extracted. Using a direct SPME extraction from an aqueous matrix it is possible to use the technique of multiple extraction (ME) SPME to allow for differences between the extraction effectiveness of parent and alkylated PAHs. Chemical characterisation and the modelling of coal tar pollution in environmental samples using the technique of ME-SPME-GC/MS is discussed.

APPENDIX 3

Paper presented during the Chromatography/Mass Spectrometry Conference, 16 – 18 October 2000, Warmbaths.

Advanced Chemical Fingerprinting of Polluted Water Samples Using SPME-GC/MS

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Due to its sensitivity, selectivity, specificity and discriminatory power, the potential of using GC/MS data for tracing coal tar or petrochemical pollution to suspected sources is recognised by many workers in the field of hazardous waste management. Spill identification in groundwater relies on the extraction and pre-concentration of organic compounds from the sample followed by a detailed analysis of poly aromatic hydrocarbons (PAHs) and alkyl substituted PAHs using GC/MS. SPME has been investigated in this study as a possible alternative to conventional extraction methods that are normally expensive and labor- and time consuming. The objective was to develop a simple sample preparation procedure that could be automated and coupled on-line with the final GC/MS analytical measurement. The advantages of SPME include a solvent free extraction, a high degree of selectivity, much shorter analysis time and a small sample volume. The results (analytical data for selected PAHs) obtained was used to develop interpretative methods (Advanced Chemical Fingerprinting) capable of tracing contamination in the environment to its source. The analyses of data were based on the principles that (1) each source has a unique chemical composition and (2) has a unique analyte distribution pattern. The technique of multiple extraction SPME is proposed to compensate for differences in extraction efficiencies among different PAHs when analysing characteristic analyte distribution patterns. The application was further developed to determine diagnostic (source) ratios between two PAH isomers. Using the C_1-D/C_1-P ratio of two single isomer peaks in each of these two different alkyl homologues, an alternative approach to hydrocarbon fingerprinting was developed. The results of source ratios that were determined on several ground water samples are discussed. The conclusion is made that the determination of the C_1-D/C_1-P source ratio in groundwater samples is useful, but is limited to samples containing these isomers in concentration of > 0.07 ng/cm^3. The advanced technique of MS-MS was investigated to increase the detection limits of the method and allow the determination of source ratios in samples with lower pollution levels. The results are discussed.

APPENDIX 4

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Chemical Characterization and Screening of Hydrocarbon Pollution in Industrial Soils by Headspace Solid-Phase Microextraction

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Chemical characterization and screening of hydrocarbon pollution in industrial soils by headspace solid-phase microextraction

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Chemical characterization and screening of hydrocarbon pollution in industrial soils by headspace solid-phase microextraction

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Abstract

A headspace solid-phase microextraction method, followed by a gas chromatographic–mass spectrometric analysis, has been developed for the screening of soil samples polluted by coal tar or refined petroleum products. Vapor pressures of target analytes were determined using a capillary GC method to identify environmentally important components with a sufficiently high vapor pressure to be analyzed in the headspace mode. The method was optimized under non-equilibrium conditions with simplicity and automation in mind and does not require any extraction procedure or sample preparation, other than grinding, drying and homogenizing. The analytical performance and the significance of the results for the purpose of chemical characterization, source discrimination, determination of individual isomer distributions and to calculate source or weathering ratios, is discussed.

Keywords: Soil; Environmental analysis; Extraction methods; Headspace analysis; Pressurized liquid extraction; Petroleum products; Tars; Solid-phase microextraction; Polynuclear aromatic hydrocarbons; Hydrocarbons

1. Introduction

1.1. The need for a screening method for hydrocarbons in soil

In literature, the term 'screening' refers to a fast semi-quantitative method to determine if contaminants are present above a preset concentration threshold. Typically, the first indication that a site may have a potential DNAPL (dense non-aqueous phase liquid) problem occurs during a phase 1 site assessment. A key element of a phase 1 site assessment is a detailed review of the site's history and use, including a record of all chemicals that may have been released on this site. If the site history reveals significant releases of DNAPL compounds, then the next phase of site characterisation should include an actual soil analysis (screening) to determine if DNAPLs are present in the soil. The need for analytical methods that can provide expedited site characterisation of hazardous waste sites is critical. Slow sample turn-around times can cause unnecessary delay in site remediation. Methods that minimise sample handling and holding times are needed to improve data quality, as chemical integrity after sampling is always a concern. Once a DNAPL problem has been identified, then more elaborate analytical methods are required to measure the severity and extent of contamination. The analytical methodology developed in this study is targeted to

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fulfill the needs for an expedited screening and characterisation procedure.

1.2. Extraction of organic compounds from soil samples

Before a screening analysis can be performed, it is first necessary to extract the organic compounds from the soil matrix. The extraction technique is then followed by an appropriate analytical technique such as liquid chromatography (HPLC), gas chromatography (GC) or gas chromatography–mass spectrometry (GC–MS). The extraction process of contaminants such as polycyclic aromatic hydrocarbons (PAHs) in soil samples is traditionally performed using a solvent extraction technique. A critical requirement for the extraction method used, is to have good recovery of analytes. Noordkamp et al. [1] investigated and compared various methods for the extraction of PAHs from sludge and sediments, namely microwave-, ultrasonic-, various solvents- and soxhlet extraction. Other techniques such as supercritical fluid extraction (SFE) [2] and pressurized liquid extraction (PLE; Dionex trade name Accelerated Solvent Extraction) [3] have also been reported. Although both PLE and SFE are available as automated techniques, their application for routine screening is inhibited by the difficulty of automation, time consuming procedures and long analysis turnover times. The performance of these extraction methods may also change because of the nature of the soil being extracted, since the complexity of the matrix and the presence of large amounts of many pollutants may alter the performance of previously successful procedures. Traditional extraction techniques have the additional disadvantage of requiring large amounts of solvent while changes in environmental regulations place increasingly severe restrictions on solvent use in laboratories worldwide.

The technique of solid-phase microextraction (SPME) was introduced by Pawliszyn [4] in 1989 and has shown advantages such as solvent free extraction, relatively short analysis turnover time and possibilities for automation. Typically, a fused-silica fiber coated with a thin layer of polymeric stationary phase is used to extract various analytes from air, water and soil samples. Phases such as polydimethylsiloxane and polyacrylate are currently commercially available. The applications of these phases for the analysis of a variety of semi-volatile components, including PAHs [5,6] have been reported. Liu et al. [7] investigated solid-phase microextraction using porous layer-coated metal fibers. Zhang and Pawliszyn [8] showed the potential of applying headspace SPME for analysing organic compounds in a variety of matrices, including soils and sludges. The technique has since been developed for a variety compound classes and has earned a reputation for its simplicity, speed, high sensitivity and reproducibility. In the work reported here the extraction of organic compounds from a contaminated soil sample using headspace extraction with a polymer-coated silica fibre and followed by GC–MS was investigated. The main objectives were to design an uncomplicated and efficient method with the following requirements: (1) selectivity towards target PAH analytes, ranging from at least two- to four-ring structures and including heterocyclic compounds, (2) sensitivity towards environmentally important hydrocarbons for pollution assessment purposes and determination of environmental risks, (3) inclusion of alkylated PAHs in the target analyte list to determine toxicological effects, as some alkylated constituents are more toxic than the parent PAH, (4) low analytical variability to allow chemical fingerprinting, (5) avoidance of special sample preparation, other than grinding, drying and homogenising, (6) solvent free extraction, (7) possibility of automation, (8) elimination of the matrix interferences as the presence of a complex environmental matrix very often causes severe analytical problems.

1.3. Target analytes

This study is focused on the screening of soil samples polluted by coal tar or refined petroleum products (diesels, mineral oils, fuel oils, and lubricating oils), containing environmentally important polycyclic aromatic hydrocarbons (PAHs), alkylated PAHs and selected heterocyclic compounds. In the case of the alkylated PAHs, a C_3–PAH, for example, indicates the sum of all trimethyl, methylethyl and propyl isomers. Analytes measured in this work are listed in Table 1.

Table 1
Target analytes, primary and secondary ions used for GC–MS analysis and extraction efficiency of PAHs using the headspace technique

Compound	Rings in structure	Quantitating ion (m/z)	Confirmatory ion (m/z)	Amount absorbed (ng) (C_0 = 24 ng)	Extraction effectiveness (%)
Naphthalene (N)	2	128	127	3.07	12.80
C_1-naphthalenes (C1-N)	2	142	141	3.47	14.50
C_2-naphthalenes (C2-N)	2	156	141	1.93	8.05
C_3-naphthalenes (C3-N)	2	170	155	1.12	4.67
C_4-naphthalenes (C4-N)	2	184	169	0.42	1.77
Biphenyl (BI)	2	154	152	2.50	10.40
Acenaphthylene (AC)	3	152	153	2.42	10.10
Acenaphthene (AE)	3	154	153	2.27	9.50
Dibenzofuran (DI)	3	168	169	1.92	8.00
Fluorene (F)	3	180	165	1.43	6.00
C_1-fluorene (C1-F)	3	180	165	0.62	2.62
C_2-fluorene (C2-F)	3	194	179	0.12	0.51
C_3-fluorene (C3-F)	3	208	193	0.05	0.19
Phenanthrene (P)	3	178	176	0.91	3.80
Anthracene (A)	3	178	176	0.88	3.70
C_1-phen/anthracene (C1-P)	3	192	191	0.28	1.16
C_2-phen/anthracene (C2-P)	3	206	191	0.06	0.25
C_3-phen/anthracene (C3-P)	3	220	205	0.04	0.15
Dibenzothiophene (D)	3	184	152	0.95	3.96
C_1-dibenzothiophene (C1-D)	3	198	184	0.12	0.49
C_2-dibenzothiophene (C2-D)	3	212	197	0.09	0.38
C_3-dibenzothiophene (C3-D)	3	226	211	0.05	0.22
Fluoranthene (FL)	4	202	101	0.36	1.50
Pyrene (PY)	4	202	101	0.30	1.30
Chrysene (C)	4	228	226	n.d.	–
Benzo[*a*]anthracene	4	228	226	n.d.	–
Benzo[*k*]fluoranthene (BK)	5	252	253	n.d.	–
Benzo[*e*]pyrene	5	252	253	n.d.	–
Dibenz[*ah*]anthracene (DA)	5	228	226	n.d.	–
Benzo[*ghi*]perylene (BP)	6	276	277	n.d.	–
Indeno[1,2,3-*cd*]perylene (IP)	6	276	277	n.d.	–

n.d. = not detected.

1.4. Physical–chemical parameters of coal tar components

Headspace sampling with SPME is limited to substances with sufficient vapor pressure, especially when sampling is performed at room temperature. Vapor pressure governs the vaporisation of the analyte from soil, and strongly influences the amount adsorbed onto the SPME fiber. Knowledge of the vapor pressure is therefore necessary to understand the behaviour of a given organic compound during the headspace sampling process and to predict the equilibrium distribution between the soil, air and fiber. Compounds occurring in coal tar generally have a low volatility (boiling points ranges between 200 and 400°C) and experimental data on vapor pressures of compounds such as the alkylated PAHs is very scarce. Capillary GC has been reported [9,10] as a practical method to at least get a good estimate of vapor pressures of low volatility compounds.

1.5. Optimisation of headspace extraction parameters

The objective was to optimise selective extraction conditions for the determination of polycyclic aromatic hydrocarbons of environmental interest, namely those with sufficiently high aqueous solubilities

and vapor pressures to partition into water reserves and the atmosphere. Optimum headspace parameters were investigated and reported in previous papers [8,11], and are beyond the scope of this study. It was necessary to optimise the method at non-equilibrium conditions to keep sample analysis to a reasonable time.

1.6. The use of PAH data for fingerprinting and interpretive methods

In order to characterise pollution it is necessary to establish the concentration of major environmentally important constituents in environmental soil samples. As indicated by several authors [12,13], the determination of the 19 priority pollutant aromatic and polycyclic aromatic hydrocarbons does not generate sufficient data to permit appropriate interpretation of environmental impact such as toxicological or biological effects, source allocation, degree of weathering and long-term impact prediction. Additional data, such as the concentration of alkylated PAHs and dibenzothiophenes, are necessary for this purpose and have a wide interpretative use. One such use is to distinguish among sources of hydrocarbons in the environment.

Chemical fingerprinting has, over the last two decades, evolved into a science by which original source(s) of complex chemical mixtures (e.g., petroleum or coal tar) can often be identified [14]. The relative abundance of key individual compounds (especially two- to four-ring polycyclic aromatic hydrocarbons, and three-ring heterocyclic dibenzothiophenes) forms a chemical pattern that can be used for source identification. The following advances in chemical fingerprinting techniques have been reported:

1.6.1. Source discrimination based on relative PAH abundance

Petrogenic hydrocarbons are characterized by their distributions of alkylated homologues of naphthalene (N), fluorene (F), phenanthrene (P), dibenzothiophene (D) and chrysene (C), where the parent PAH for each series is least abundant [15]. A characteristic petrogenic profile is illustrated in Fig. 1. Combustion related sources (pyrogenic) produce a PAH distribution dominated by the parent compounds of two- to four-ring PAHs and containing large quantities of fluoranthene (FL) and pyrene (PY) [15]. A characteristic pyrogenic profile is illustrated in Fig. 2. These two types of profiles, also

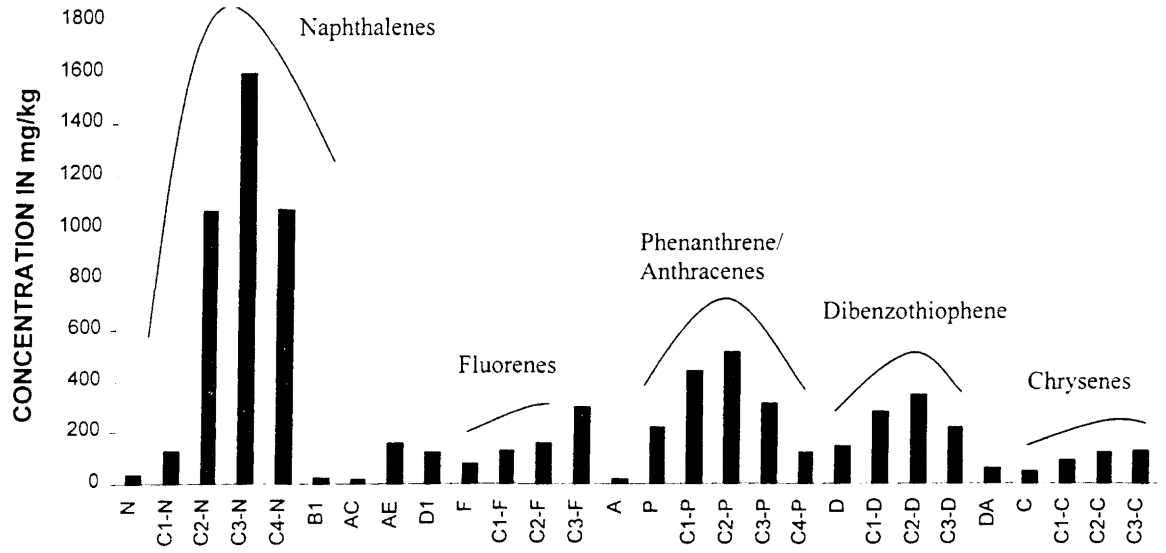

Fig. 1. Characteristic petrogenic profile obtained from a typical mineral oil contaminated soil sample with a PLE and GC–MS analysis. The distributions of the alkylated homologues of N, F, P, D and C where the parent PAH for each series is least abundant, compares with previously reported profiles [15].

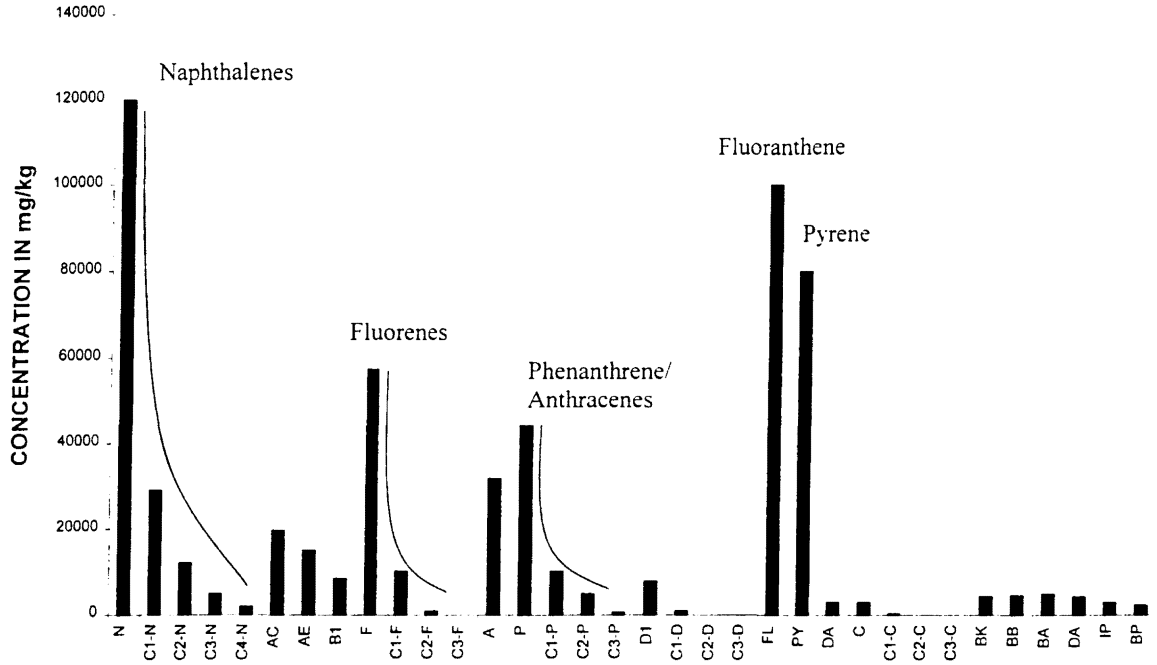

Fig. 2. Characteristic pyrogenic profile obtained from a typical coal tar contaminated sample with a PLE and GC–MS analysis. The PAH distributions which are dominated by parent compounds of two- to four-ring compounds and contains large quantities of Fl and PY, compares with previously reported profiles [15].

referred to as analyte profile histograms, are used to establish chemical matches between one 'suspect' oil and the petroleum in an environmental sample, and to distinguish between petrogenic and non-petrogenic sources [14].

1.6.2. Relative amounts of alkylated phenanthrene and dibenzothiophene and chrysene

The relative amounts of these compounds in an environmental sample are used to differentiate among different crude oils, petroleums and refined petroleums [14,16]. In crude oil, for example, similar abundances of phenanthrenes and dibenzothiophenes are found, with the chrysene series largely absent in some cases (e.g., Exxon Valdez crude oil) [14]. Creosote, on the other hand, contains significant amounts of five- to six-ringed PAHs with a low relative abundance of dibenzothiophenes. Major differences in the PAH fingerprints between petroleum sources have previously been found in the relative amounts of dibenzothiophenes [14].

1.6.3. Source ratios

A source ratio is a ratio between two characteristic analytes or group of analytes in a source, which ideally must be unique to that particular source, and where the two analytes degrade at similar rates, i.e. the ratio stays constant. Boehm et al. [14] reported that selected alkyl-PAH homologues are (1) relatively resistant to weathering influences and (2) occur in relatively different concentrations in different petroleum sources. Douglas et al. [17] reported that the ratios of C_2-dibenzothiophenes to C_2-phenanthrenes (C_2-D/C_2-P) and ratios of C_3-dibenzothiophenes to C_3-phenanthrenes (C_3-D/C_3-P) stay relatively constant, even when weathering has degraded up to 98% of the total PAHs. They have also demonstrated the stability and usefulness of the source ratio over a wide range of weathering and biodegradation of different oils using double ratio plots of C_3-D/C_3-C (weathering ratio) versus C_3-D/C_3-P (source ratio). The dibenzothiophene group of compounds (C_0-D to C_4-D) was found to vary the most widely in different sources, as their concen-

trations reflect the sulfur content of the source. The resistances to weathering, combined with the source specific nature of the C_3-D/C_3-P ratio in spilled oil, make them especially useful for the identification of multiple sources of hydrocarbons.

1.6.4. Weathering ratio

Ratios of compounds that change substantially with weathering and biodegradation are termed 'weathering ratios'. Weathering is the combined effect of dissolution, biodegradation and photo-oxidation. The bacterial degradation order within a PAH homologous series is as follows:

$$C_0\text{-PAH} > C_1\text{-PAH} > C_2\text{-PAH} > C_3\text{-PAH} > C_4\text{-PAH}$$

During a study of hydrocarbon sources following the Exxon Valdez oil spill, Page and co-workers [15] reported the following major compositional changes:

1. Pronounced decrease in naphthalenes (N) relative to other PAHs, which occurs rapidly in the first few days of exposure to the atmosphere.
2. Development of a 'water-washed' profile for each of the petrogenic groups so that each group has the following distribution: Parent (C_0)<C_1<C_2<C_3.
3. Gradual build-ups in the relative abundances of the phenanthrenes, dibenzothiophenes, and chrysenes as the more soluble components are lost. Because of their low solubilities in water, and resistance to microbial degradation, the chrysenes exhibit the most pronounced relative increase.

In the study by Douglas et al. [17] concerning the environmental stability of petroleum hydrocarbons, they reported that compounds that weather to below their respective detection limits during the early stages of oil degradation cannot provide reliable weathering ratios. They developed weathering indicators of varying sensitivity for different stages of the weathering process. The ratio of C_3-naphthalens/C_2-phenanthrenes is a sensitive ratio and can for example be used for light product degradation such as diesel fuel. A less sensitive weathering ratio such as C_3-dibenzothiophene/C_3-chrysene may be used for crude oil degradation.

1.6.5. Individual isomer distributions

Boehm et al. [14] have shown that the differences in the relative distribution of individual isomers within a homologous series, such as the C_3-dibenzothiophene isomers, present opportunities for fingerprinting similar petroleum hydrocarbon sources. They indicated that (1) the C_3-dibenzothiophenes as a group, represent more than 20 individual isomers that are present at different abundances in oils from different sources and that (2) these isomer distributions reflect the source carbon, depositional environment during formation and the existence of any diagenic sources.

2. Experimental

2.1. Reagents and materials

Experiments were carried out using US environmental Protection Agency (EPA) certified PAH contaminated soil samples, CRM-103–100, CRM-104–100 and CRM-105–100, obtained from Resource Technology. A standard mixture containing 2000 ppm each of the 16 EPA priority PAHs, was purchased from Supelco (Sigma–Aldrich, South Africa).

2.2. Headspace SPME extraction procedure

A 100-μm polydimethylsiloxane (PDMS) fiber was obtained from Supelco (Sigma–Aldrich, South Africa) and used to extract soil samples by headspace. A 0.1-g soil sample was transferred into a 1.8-ml sample vial that was sealed with a PTFE-faced septum. At least 2 h was allowed for thermal equilibrium to be reached throughout the soil and headspace. The fibre was exposed for 40 min to the headspace without making contact with the soil and then immediately inserted into the GC injector for thermal desorption and GC–MS analyses. Attention was given to the following parameters, and the chosen conditions were used to verify analytical performance:

2.2.1. Fiber selection

A 100-μm PDMS fibre was chosen because it showed the highest extraction efficiency and, therefore, lowest detection limit in a previous inves-

tigation [18]. Detection limits of at least 1 mg/kg were desired in this study.

2.2.2. Sample and headspace volumes

As indicated by Zhang and Pawliszyn [8] SPME is mainly an equilibrium analytical method, and in the case of headspace sampling the amount of analytes absorbed by the liquid polymeric coating is related to the overall equilibrium of analytes in a three phase system, namely sample, air and polymer phase.

$$n_{hs/spme} = \frac{K_1 K_2 V_p V_s C_0}{(K_1 K_2 V_p) + (K_2 V_{HS}) + V_S} \quad (1)$$

where K_1 is the partition coefficient of the analyte between the sample and gas phases and K_2 the equilibrium constant of the analyte between gas and polymer phase. V_p, V_S and V_{HS} are the polymer fiber, sample and headspace volumes, respectively. C_0 is the concentration of the analyte in the sample. The K_2 value and the volume ratios between the fiber and headspace and headspace and sample affect the amount of analyte sorbed from the headspace. In the case of this study the fibre volume is fixed ($Vp=$ 0.000621 ml) and a headspace volume (V_{HS}) of 1.2 cm^3 was chosen, resulting in a large volume ratio of 1932. The technique can be made more sensitive by using a larger sample size or a larger headspace volume. The volume ratio is, however, only within limited control of the analyst. A standard 1.8-ml glass vial was used in this study. The concentration of analytes will be homogeneous within each of the three phases once equilibrium has been reached. Although the principle behind SPME is an equilibrium partitioning process, it is not necessary to wait until full equilibrium is reached. As long as the extraction time is standardised, reproducible and sufficiently sensitive analysis is possible. For optimum repeatability it is, however, necessary to choose an equilibrium time in the region where small changes will not have a dramatic effect on detector response. Zhang also showed that extraction times can be reduced by sampling analytes indirectly from the headspace above the sample instead of sampling directly from the aqueous solution, because the diffusion of analytes in the vapor phase is four orders of magnitude higher than in the aqueous phase. Since the chromatographic run time is 45 min (including cool down time), an exposure time of 40 min was adopted in our study.

2.2.3. Temperature

It is known that by increasing the temperature of the sample, the vapor pressure of the analyte is increased, and partition equilibrium between the sample and headspace will be reached more quickly. A higher temperature was, however, not considered for the purpose of this investigation, as it complicates automation. To determine the extraction effectiveness of the fiber under the chosen experimental conditions, the GC response was calibrated by injecting a 40 ng (1 μl of 40 μg/ml) PAH standard.

2.3. Pressurized liquid extraction

Extraction experiments were performed with an ASE-200 system (Dionex, CA, USA). A certified reference soil sample, CRM-103–100, PAH contaminated soil, EPA certified, was extracted using a similar procedure as described in EPA Method 3545. A 1-g air dried and finely ground sample was placed in a 11-ml stainless steel extraction vessel. The sample was then extracted for 10 min at 100°C, at pressure of 14 MPa (2000 p.s.i.) in the extraction apparatus, using acetone–methylene chloride (1:1). The extractions were carried out in two cycles and a flush volume of 60% of the extraction cell volume was also used. The extracted analytes were purged from the cell for 90 s using pressurised nitrogen 1 MPa (150 p.s.i.). The extract was then concentrated to a final volume of 10 ml, of which 1 μl was injected into the GC–MS system. Alkylated PAH concentrations were determined by a manual integration of peaks in the selected ion mass chromatogram.

2.4. GC–MS analysis conditions

The gas chromatograph was a Varian model 3800 GC operated under the following conditions: Injection: Varian 1071 injector operated in the splitless mode, injector temperature: 280°C, column: J&W fused-silica DB5 MS column, 30 m×0.25 mm I.D., and 0.25-μm film thickness, carrier gas: He, 1 ml/min, column oven: 60°C (0 min), 7°C/min to 130°C, 5°C/min to 200°C, 6°C/min to 260°C, 20°C/min to 320°C (4 min).

A Varian 8200 autosampler was used under the following conditions: SPME mode, headspace, 40-min adsorption, 5-min desorption.

The mass spectrometer was a Varian Saturn model 2000 Ion Trap system operated under the following conditions: mass range: 45–450 u, scan rate: 0.81 s/scan, delay time: 3 min, peak threshold: two counts, background mass: 43 u, scan segments: 10-99/100-250/251-399/400-650, tune factors: 80/140/70/25, emission current: 10 μA, multiplier gain: 10^5, ion trap temperature: 150°C, transfer line temperature: 300°C.

2.5. Estimation of saturated vapor pressures

The Kovats [19] retention index was determined for each component using a GC method operated under the following conditions: Injection: Varian 1071 Injector operated with a 1:25 split, injector temperature: 280°C, column: J&W fused-silica DB5 MS column, 30 m×0.25 mm I.D. 0.25-μm film thickness, carrier gas: He, 1 ml/min, column oven: 60°C (0 min), 10°C/min to 320°C (4 min).

The following formula was used to calculate the retention index for each PAH:

$$I = 100n + 100[t_R(x) - t_R(n)/t_R(n+1) - t_R(n)] \quad (2)$$

I: temperature programmed retention index; n: carbon number of n-alkane eluting before substance x; $n+1$: carbon number of n-alkane eluting after substance x; t_R: retention time.

Using the assumption that vapor pressure is proportional to the retention index the vapor pressures for the PAHs were calculated at 298 K by linear regression [9]:

$$-\log P_L^0 = a.I + b \quad (3)$$

2.6. Amount of analytes absorbed into the fiber at optimum conditions

The GC–MS response for some parent PAHs were determined with liquid injections of a 40 μg/ml each PAH standard solution. Equal amounts of 40 ng/ml PAHs were spiked into a water matrix, of which a sample size of 0.6 ml (24 ng) was then analysed using the headspace technique. The headspace volume was 1.2 ml. The amount of analytes absorbed into the fibre was determined from their GC–MS response.

2.7. Analytical performance

The series of PAH contaminated soil standards, with certified parent PAH concentrations, were used to determine analytical performance parameters. The study was limited to PAHs with certified concentrations. The study was further limited to the range of concentrations in the standards. Calibration curves were constructed from peak areas, obtained from different analyte concentration in the three soil standards and the linearity illustrated.

3. Results and discussion

3.1. Amount of analytes absorbed into the fiber at optimum conditions

The amount of analyte absorbed by the fiber in the headspace is governed by the fiber-headspace distribution constant K_2 (Eq. 1), the vapor pressure of the analyte and on the degree by which the compounds are released by the soil to partition into the headspace. The effectiveness of a single stage extraction of PAHs was determined as the fractional amount found in the fibre phase after accumulation, and expressed as %:

$$\%P = (C_2/C_0)100 \quad (4)$$

where C_2 and C_0 are the mass of solute in the fibre and initial mass in the sample, respectively. The results are given in Table 1. The relative extraction effectiveness of alkylated PAHs was determined by comparing the concentration of the isomers obtained with HS–SPME, with the concentration of the isomers obtained with PLE, relative to the efficiency of the parent PAH. The assumption was made that that 100% extraction effectiveness was obtained with PLE, since PLE extracts total residue. In the case of headspace (HS) SPME, the effectiveness decreased very sharply with an increase in degree of alkylation:

C_0-PAH > C_1-PAH > C_2-PAH > C_3-PAH.

Vapor pressure is one of the parameters which

governs the HS–SPME effectiveness, and follows the trend of lower effectiveness with lower vapor pressures. Analytes, which could be extracted from the headspace, are naphthalene through pyrene with extraction effectiveness of 12.8% and 1.3%, respectively. Compounds with a vapor pressure lower than $2.4 \cdot 10^{-10}$ (pyrene) could not be detected using the analytical conditions under which this experiment was performed. The detection limits can be improved by modifying the experimental conditions to result in a larger amount of analyte present in the headspace, but due to complications with automation, it was not considered in this study.

3.2. Physical–chemical parameters of coal tar components

A graph was constructed for saturated vapor pressures of *n*-alkanes as a function of Kovats index (20 data points), and the following linear regression data were obtained using Eq. 3:

$y = 0.0071x - 5.5463$ and $R^2 = 0.9887$.

The ($P^0_{L,}$ values obtained (298 K) for target analytes are shown in Table 2 and range from $4.3 \cdot 10^{-4}$ mmHg for naphthalene to $9.0 \cdot 10^{-19}$ mmHg for

Table 2
Physical–chemical properties of selected coal tar pollutants

No.	Compound	Rings in structure	Kovats index	Log P^0_L (mmHg)	P^0_L (mmHg)	Log molar[a] solubility	Water solubility (mg/l)
1	Indene	1	1161	2.70	2.0E-03	−3.034	110
2	Naphthalene	2	1255	3.36	4.3E-04	−3.606	32
3	2-Methylnaphthalene	2	1314	3.78	1.7E-04	−3.748	28
4	1-Methylnaphthalene	2	1330	3.90	1.3E-04	−3.705	25
5	Biphenyl	2	1397	4.38	4.2E-05	−4.345	6.6
6	1-Ethylnaphthalene	2	1413	4.49	3.3E-05	−4.162	10.7
7	1,3-Dimethylnaphthalene	2	1458	4.81	1.6E-05	−4.292	8.0
8	1,5-Dimethylnaphthalene	2	1425	4.57	2.7E-05	−4.679	3.3
9	2,3-Dimethylnaphthalene	2	1438	4.66	2.2E-05	−4.716	3.0
10	2,6-Dimethylnaphthalene	2	1443	4.70	2.0E-05	−4.888	2.0
11	1,2,5-Trimethylnaphthalene	2	1556	5.50	3.2E-06	−4.923	2.0
12	Acenaphthylene	3	1470	4.89	1.3E-05	–	–
13	Acenaphthene	3	1503	5.13	7.5E-06	−4.594	3.9
14	Dibenzofuran	3	1537	5.37	4.3E-06	–	–
15	Fluorene	3	1604	5.84	1.4E-06	−4.925	2.0
16	4-Methyldibenzofuran	3	1639	6.09	8.1E-07	–	–
17	3,4-Diethyl-1,1-biphenyl	2	1692	6.47	3.4E-07	–	–
18	2-Methylfluorene	3	1720	6.67	2.2E-07	–	–
19	2-Ethylfluorene	3	1823	7.40	4.0E-08	–	–
20	Methylethylfluorene	3	1910	8.02	9.6E-09	–	–
21	Dibenzothiophene	3	1775	7.06	8.7E-08	–	–
22	Phenanthrene	3	1803	7.25	5.6E-08	−5.150	1.30
23	Anthracene	3	1815	7.34	4.6E-08	−6.377	0.08
24	Fluoranthene	4	2084	9.25	5.7E-10	−5.898	0.26
25	Pyrene	4	2136	9.62	2.4E-10	−6.176	0.14
26	1,2-Benzanthracene	4	2476	12.03	9.3E-13	−7.214	0.017
27	Chrysene	4	2486	12.10	7.9E-13	−8.057	0.002
28	3,4-Benzopyrene	5	2895	15.01	9.9E-16	−7.820	0.004
29	Benzo[*k*]fluoranthene	5	2780	14.19	6.4E-15	–	–
30	Dibenz[*ah*]anthracene	5	3243	17.48	3.3E-18	–	–
31	Benzo[*ghi*]perylene	6	3323	18.05	9.0E-19	−9.018	0.0003
32	Indeno[1,2,3-*cd*]perylene	6	3232	17.40	4.0E-18	–	–

[a] Data from Yalkowsky et al. [20].

benzo[*ghi*]perylene (1 mmHg = 133.322 Pa). The observed rules for the vapor pressure of target analytes are as follows:

1. There is roughly between one and four orders of magnitude difference between the P_L^0 of two- and three-ring structures, and between two and eight orders of magnitude difference between three- and four-ring structures.
2. There is a trend in decreasing P_L^0 for each methylene group added.

In this investigation compounds 1–25 which are listed in Table 2 were identified as important contaminants. Based on their physical–chemical properties, they can be determined by HS–SPME and are also environmentally important. This list of compounds includes the lower molecular mass aromatic hydrocarbons and PAHs which are of particular interest due both to their high groundwater and air transfer potentials.

3.3. Analytical performance

The results are shown in Table 3 and include linearity, precision and detection limits. All the PAHs tested exhibited good linearity and precision and regression coefficients of better than 0.99 were found in most cases, except for anthracene (0.985) and pyrene (0.982). The precision test was performed using the EPA-certified BNA contaminated soil CRM-105–100. The precision values found are shown as RSDs, together with the concentration levels at which the values were obtained. A precision of better than 10% RSD was found in all cases. The precision values are based on variations in the area counts of the signal, and not referenced to an internal standard. The certified soil standard with the lowest concentration (CRM-104–100) was used to determine the detection limit. Results for the lowest concentration analysed are used for this purpose and ranged from 0.77 mg/kg levels for naphthalene to about 25 mg/kg for fluoranthene with the analyte detectability reflecting its vapor pressure. The detectability decreases from naphthalene to phenanthrene due to a decrease in vapor pressure, which governs the amount of PAH absorbed into the SPME fiber. The certified soil standard with the highest concentration (CRM-105–100) was used to indicate the carrying capacity of the fiber when the concentration of analytes is high. The highest individual concentration analysed was 1924 mg/kg phenanthrene which was found linear up to this level (R^2 = 0.9997). Using the experimental conditions depicted in this study, the fiber demonstrated sufficient capacity to analyse the concentration ranges as stipulated in Table 3.

In this work, quantification of analyte concentrations is based on the method of external standards because internal standards are not easily used for SPME since each compound has a different partition coefficient. Isotopically labelled analytes might be useful for individual compounds but is too cumbersome for a screening method.

Table 3
Calibration results for headspace SPME of PAH contaminated soils

Compound	Concentration range (mg/kg)	Regression coefficients – R^2	Precision as % RSD[a] (n = 6)	Lowest standard tested	
				mg/kg	S/N
Naphthalene	1–35	0.9957	2.78 (15.7)	0.77	128
2-Methylnaphthalene	1–60	0.9960	4.52 (60.4)	<1	12
Dibenzofuran	1–306	0.9972	8.28 (306)	0.66	28
Acenaphthylene	1–17	0.9910	4.94 (16.7)	1.21	21
Acenaphthene	1–640	0.9988	5.51 (640)	0.77	12
Fluorene	1–443	1.0000	7.84 (368)	0.65	12
Phenanthrene	6–1924	0.9997	8.49 (1153)	5.79	53
Anthracene	1–431	0.9849	6.74 (431)	1.44	5
Fluoranthene	25–1425	0.9947	6.80 (1410)	24.6	84
Pyrene	15–1075	0.9820	7.33 (1075)	15.0	46

[a] Concentration as mg/kg in brackets.

3.4. The use of headspace SPME for chemical fingerprinting

3.4.1. Source discrimination based on relative PAH abundance

A basic requirement for the construction of analyte profile histograms as suggested in the literature [14,15], and hence to distinguish between petrogenic and pyrogenic profiles, is the accurate determination of total analyte concentrations, including the alkylated PAHs. In the case of PLE the total residue is extracted, which allow the quantification of alkylated PAHs using manual integration techniques of the isomer series and using the parent PAH response factors (RFs). The extraction process of HS–SPME involves different mechanisms than in the case of PLE and the amount extracted will differ for each analyte, as it highly depends on factors such as the partition coefficient and the vapor pressure. These differences are illustrated in Fig. 3 where analyte profile histograms were constructed using the results from CRM-103–100, for the C_0- to C_4-PAHs obtained by both HS–SPME and PLE. It is evident from these result that although HS–SPME can generate a useful profile, it cannot be compared to a total residue extraction technique such as PLE without sophisticated manipulation of results. Limited distinguishing features can be obtained from the parent PAHs, for example, a dominant abundance of PY and FL can indicate coal tar contamination while the decrease in abundance of the two- and three-ringed PAHs can indicate weathering.

3.4.2. Relative amounts of alkylated phenanthrenes and dibenzothiophenes and chrysenes

Although alkylated PAHs cannot be determined accurately with HS–SPME without sophisticated manipulation, the relative abundances between these groups of analytes can be used to differentiate between different crude oils, petroleums and refined petroleums.

3.4.3. Source ratios

The source ratio of C_2-D/C_2-P in CRM-105–100 was investigated in this study because of the stability, resistance to weathering and source-specific nature of these isomers. These compounds also have similar chromatographic retention times, vapor pressures, extraction efficiencies and low analytical variance because it can self-normalise to minor GC and MS conditions. The selected analyte ratio was found to be 0.99 on the BNA contaminated soil, CRM-105–100, using the HS–SPME technique. This value was slightly higher than the ratio of 0.62,

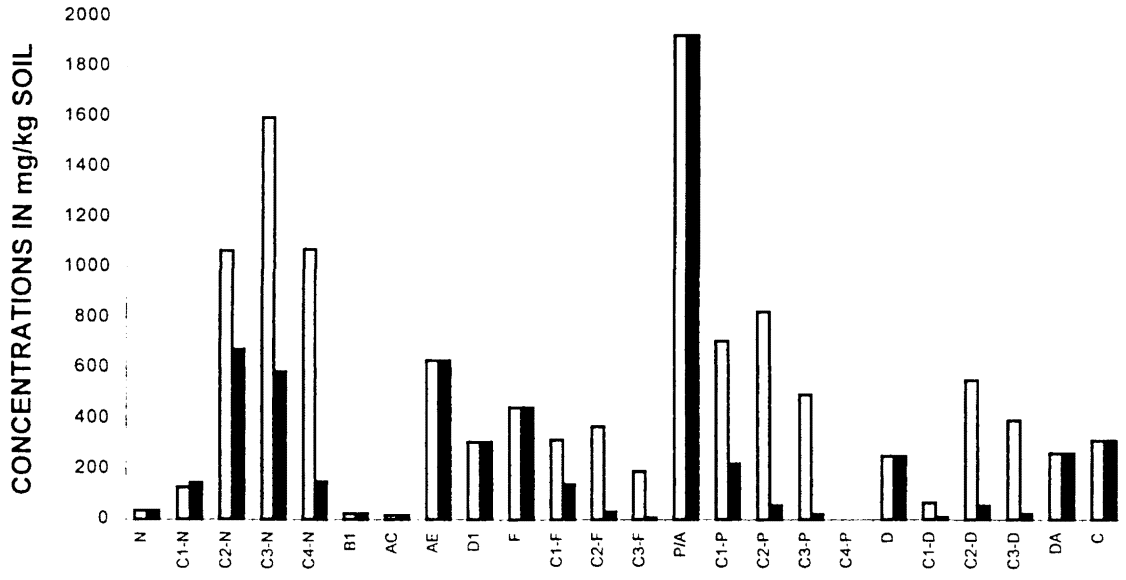

Fig. 3. Analyte profile histogram comparing headspace (grey bars) with PLE (black bars) for CRM-103–100.

found on the same sample using the PLE technique. This is due to the difference in extraction efficiencies between C_2-D (0.38%) and C_2-P (0.25%), which in turn is due to a slight vapor pressure differences. After correction for the difference in extraction efficiencies, an analyte ratio of 0.65 was found for HS–SPME, which compares very well with the ratio found using PLE. The relative standard deviation of the selected analyte ratio was calculated and found to be 5.0% ($n=6$). The results are graphically presented in Fig. 4.

This method demonstrates low analytical variance and is therefore suitable for the determination of source ratios. The successful application of source

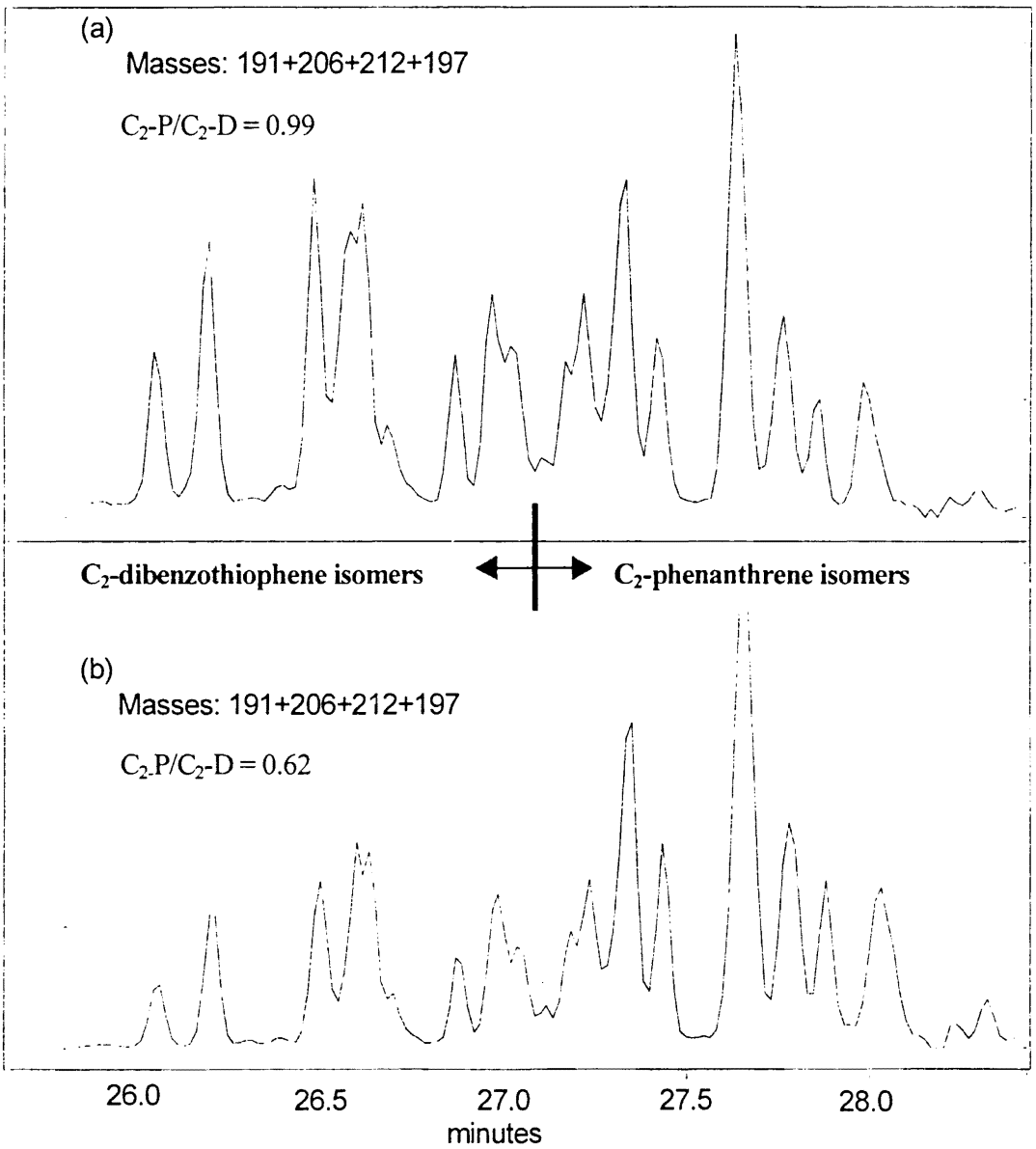

Fig. 4. Selected ion mass chromatograms for C_2-phenanthrenes and C_2-dibenzothiophenes, comparing the relative isomer ratios using (a) HS–SPME and (b) PLE. (Note the slight bias against later eluters with lower P^0).

ratio analysis using HS–SPME must include an initial investigation to establish the differences and similarities between source ratios in potential sources. To further limit the analytical variance, it is advisable to use the same instrument, set of instrumental parameters, analyst and manual peak integration procedure throughout the study. This is especially important in the case of the scan segments and tune factors of the ion-trap MS. For best results the primary and secondary ions must be assigned to the same scan segment. In the case of this study a mass range of 100–250 was chosen in segment No. 2, in order to include the primary and secondary ion masses for C_2-P (191 + 206) and C_2-D (212 + 197) in one segment.

3.4.4. Weathering ratios

Although the determination of weathering ratios using HS–SPME is not impossible, it is associated with a lot more difficulty than in the case of source ratios. The reason for this is that the compounds which are normally used to determine ratios, such as C_3-N/C_2-P, have different chromatographic retention times, vapor pressures, partition coefficients and, therefore, a high analytical variance. A large difference also exists between value obtained between the two methods of extraction, for example, ratios of 1.29 and 11.95 were found for C_3-N/C_2-P using PLE and HS–SPME, respectively. When choosing PAHs with a large difference in vapor pressures, the resulting differences in the amount absorbed by the fiber are mainly responsible for the high ratios. In the above example, the efficiencies were 4.67% for C_3-N and 0.25% for C_2-P.

3.4.5. Individual isomer distributions

The technique was found to be suitable for the fingerprinting of the isomers in a certain alkyl homologue. Good analytical precision was found because only small physical–chemical differences, such as vapor pressure and partition coefficient, exist between the different isomers. An example of the fingerprint for CRM-105–100, which contains large proportions of C_2-phenanthrenes, is shown in Fig. 5. As evident from this example, the fingerprint obtained with HS–SPME compares very well with the fingerprint obtained with PLE. The relative distribution of individual isomers in different sources can be very subtle, but as indicated by Boehm [17], they do present further opportunities for fingerprinting similar hydrocarbon sources.

3.5. Hyphenated MS determination of PAHs

Fig. 6 shows a comparison between a total ion chromatogram (TIC) and the selected ion chromatogram of a slightly contaminated soil sample. Excellent signal-to-noise ratios are demonstrated in the single-ion mode for relative small concentrations. Using this technique it is possible to obtain a fast screening analysis of priority PAHs in contaminated soils. An example of a badly contaminated soil sample is shown in Fig. 7. A range of alkylated naphthalenes is shown in the single ion spectrum. This example is chosen to illustrate that identification and quantitation can be done in a complex matrix. In samples where background interference persists, an advanced MS technique such as selected ion storage (SIS) can theoretically be used to introduce a further selectivity step and improve results. This technique was not within the scope of this investigation but has the capability to capture groups of analyte ions (that can still be library searched) while removing interfering ions leading to greater sensitivity.

3.6. Conclusions

HS–SPME–GC–MS is found to be a fast, efficient and sensitive technique for confirmation of PAHs of up to four-ring structures. By sampling in the headspace, sampling problems related to complex matrices can be avoided and sampling in the headspace prevents oxygen or moisture from getting into the GC column. This simple means of extraction has the advantage that it does not require any special sample preparation, other than grinding, drying and homogenising. Fast analysis turnaround times can be achieved resulting in lower analysis costs and providing scientifically sound information. Information on the presence and concentration of environmentally important PAHs can be obtained in the full scan mode. Automation was found to be a major advantage when coping with large sample quantities. The benefit is that a larger number of samples can be analysed due to lower turn-around times, resulting in

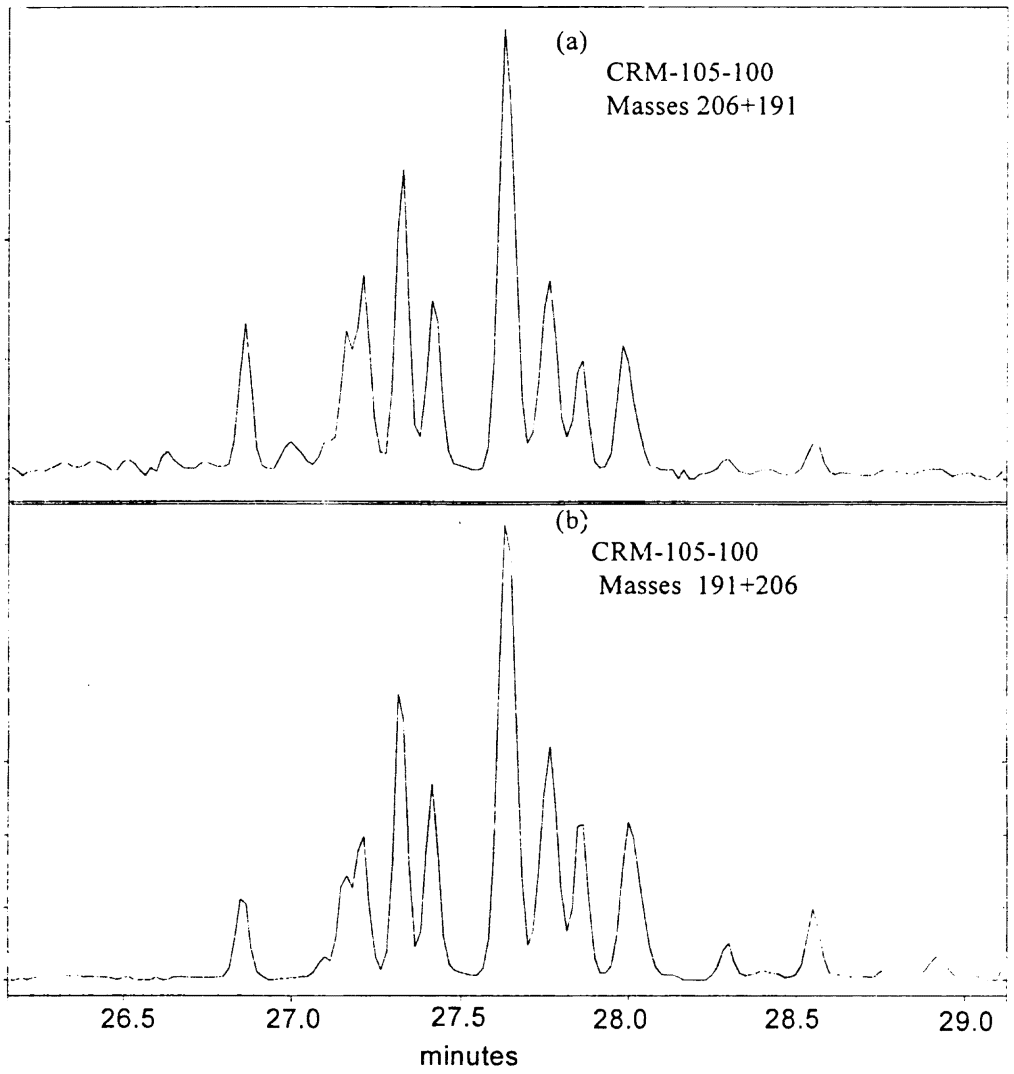

Fig. 5. Selected ion mass chromatograms for C_2-phenanthrenes of (a) HS–SPME (b) PLE.

a greater accuracy in determining the contaminant distribution throughout the site.

In addition to the efficiency and increase in the speed of the analyses, SPME–GC–MS will also decrease the cost associated with waste and hazardous site investigations. Savings will be realised in comparing the cost of headspace with conventional laboratory techniques.

The technique as a expedited screening method is suitable for:

1. The tiered approach — the screening method is used to identify samples that must be analysed with a more detailed routine technique.
2. The adaptive approach — to use the information obtained by the screening technique for the design of future sampling or analyses.

As a tool for chemical fingerprinting, this technique supplies valuable information on PAHs, alkylated PAHs, heterocyclic compounds and isomer ratios that have a wide interpretative use. The

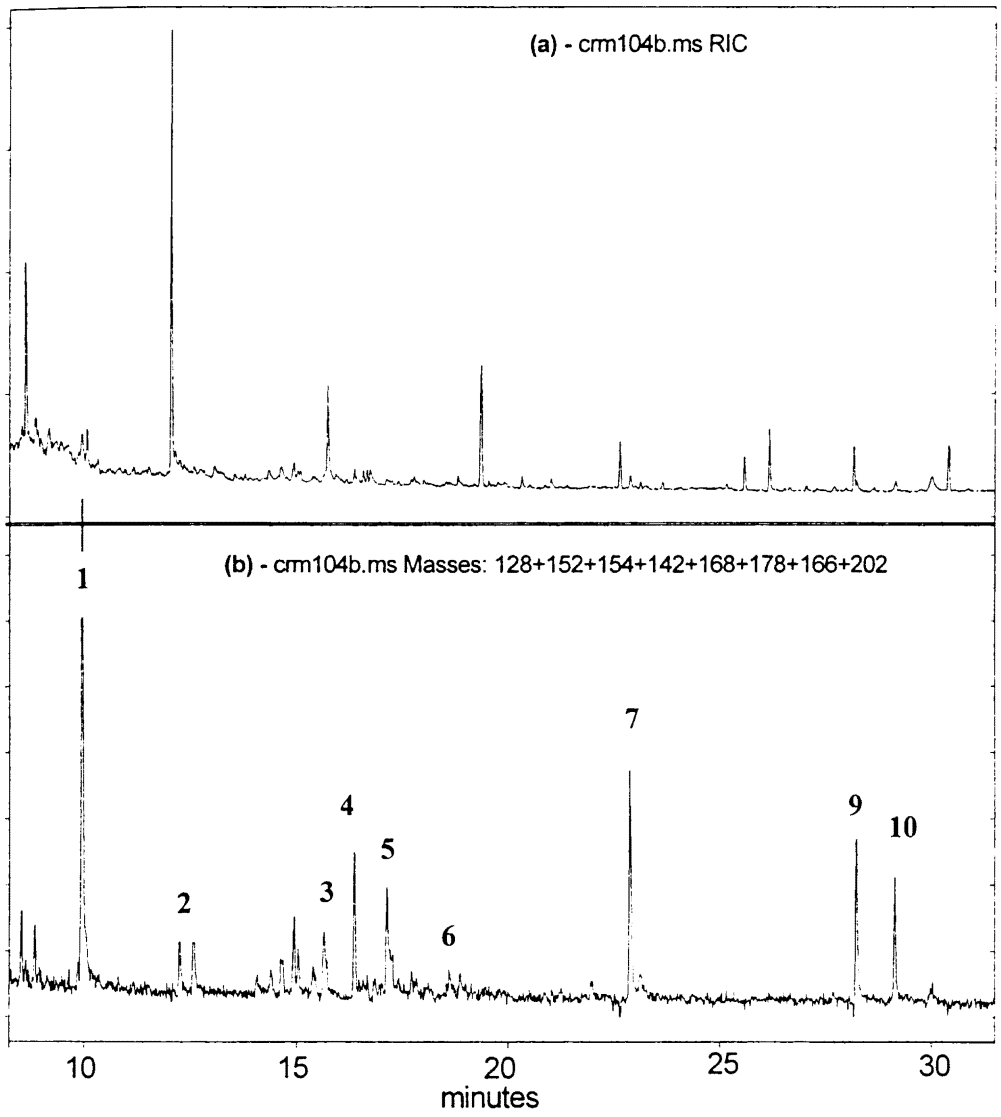

Fig. 6. Chromatogram of CRM-104–100. Sample selected to illustrate detection limits: (a) Reconstructed total ion current, (b) selected ion current of (1) naphthalene, (2) 2-methylnaphthalene, (3) acenaphthylene, (4) acenaphthene, (5) dibenzofuran, (6) fluorene, (7) phenenthrene, (8) anthracene, (9) fluoranthene and (10) pyrene.

nethod will allow the determination of relative mounts of parent PAHs, alkylated phenanthrenes, libenzothiophenes and chrysenes, source ratios beween selected homologues, and individual isomer listributions. Weathering ratios can be determined to ı limited extent.

The technique was found not to be suitable to discriminate between sources based on relative abundance of alkylated PAHs and the use of a characteristic analyte profile histogram, without using correction factors based upon extraction efficiencies. Using the experimental conditions depicted in this study, it is also not sensitive enough for accurately determining trace level concentrations of pollutants.

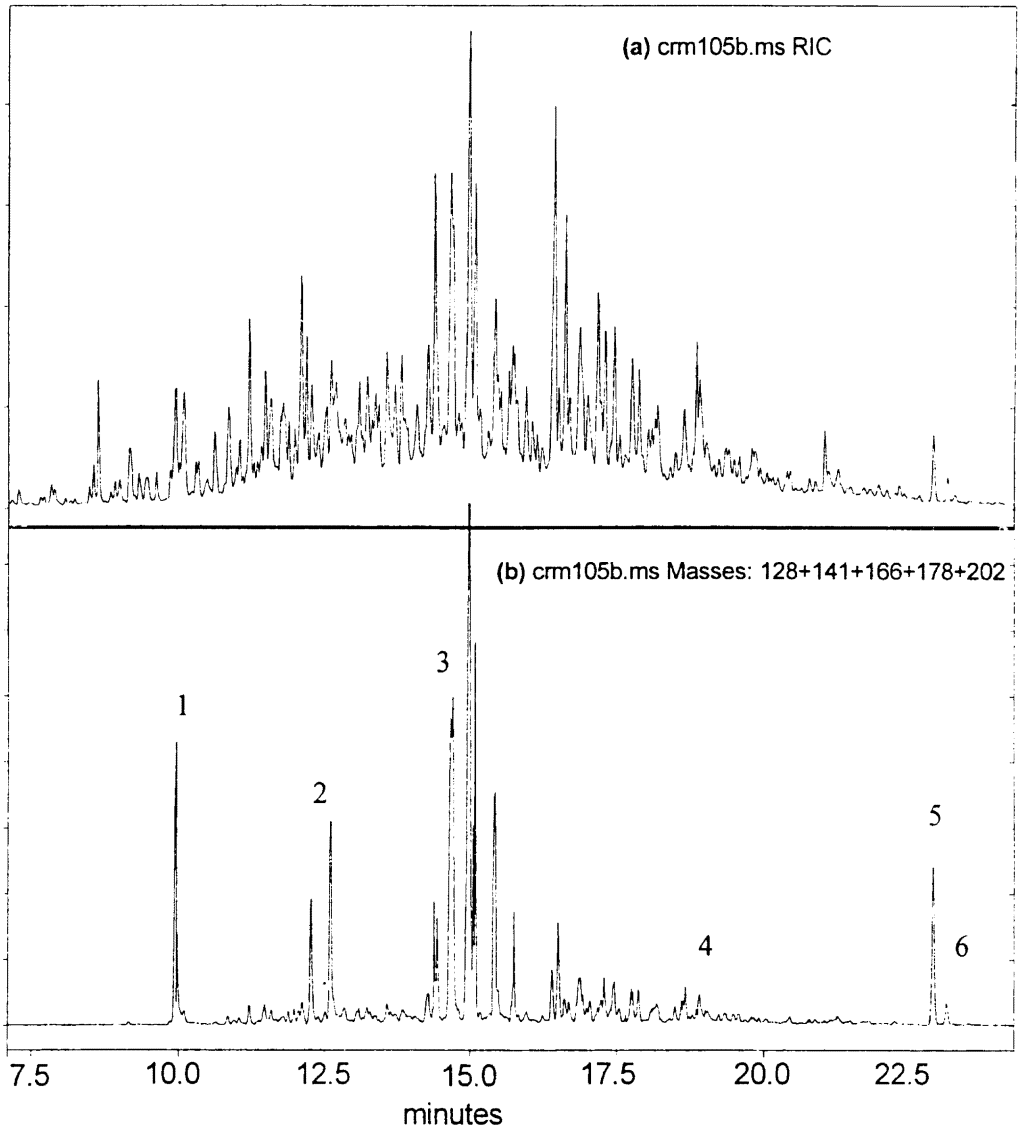

Fig. 7. Chromatograms of CRM-105–100. Sample selected to illustrate the identification of data in a complex matrix. (a) Reconstructed total ion current, (b) selected ion current of (1) naphthalene, (2) C_1-naphthalenes, (3) C_2-naphthalenes, (4) fluorene, (5) phenanthrene, (6) anthracene.

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