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

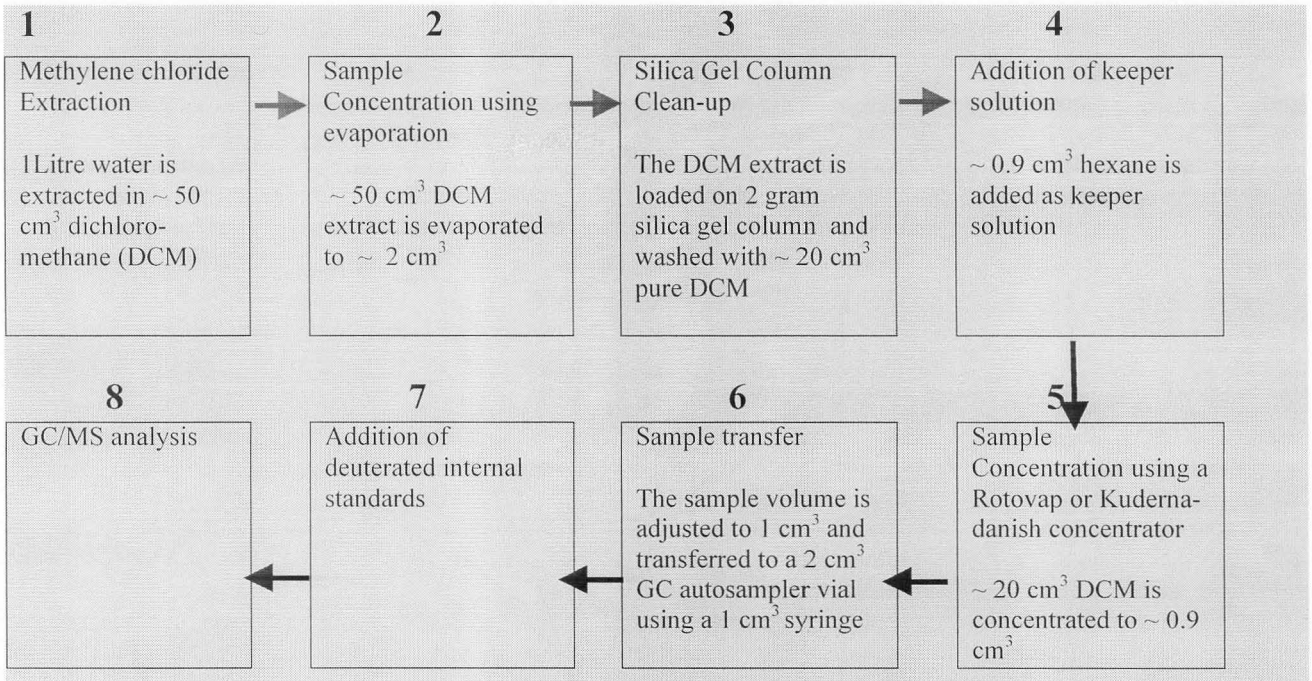

Figure 5.1: The sample purification and enrichment scheme for the analysis of groundwater samples

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).

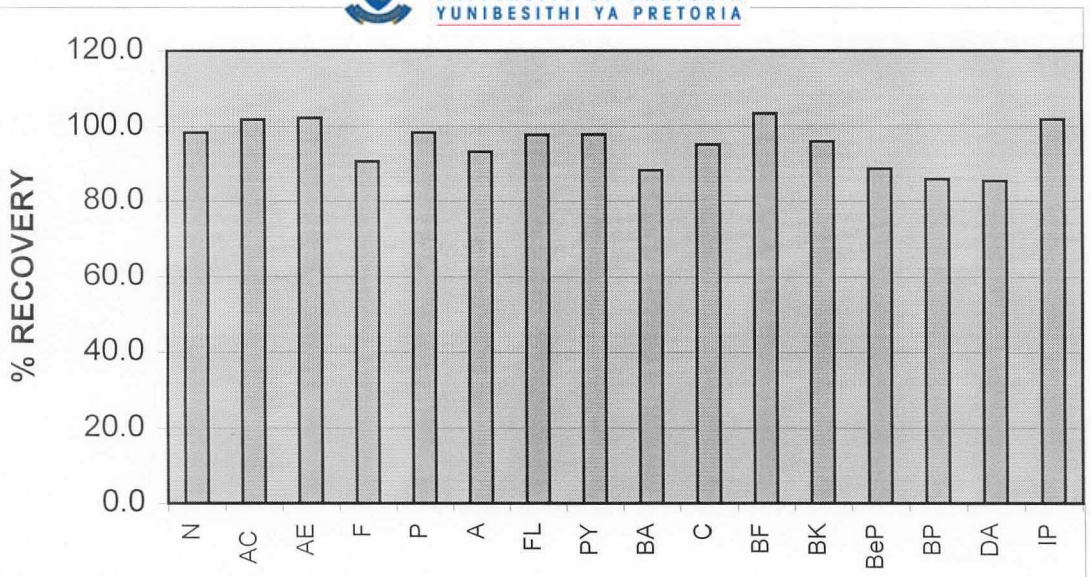

Figure 5.2: Recovery of PAHs added to water at a 40 ng/cm3 level. Results are based on 10 independent determinations.

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.

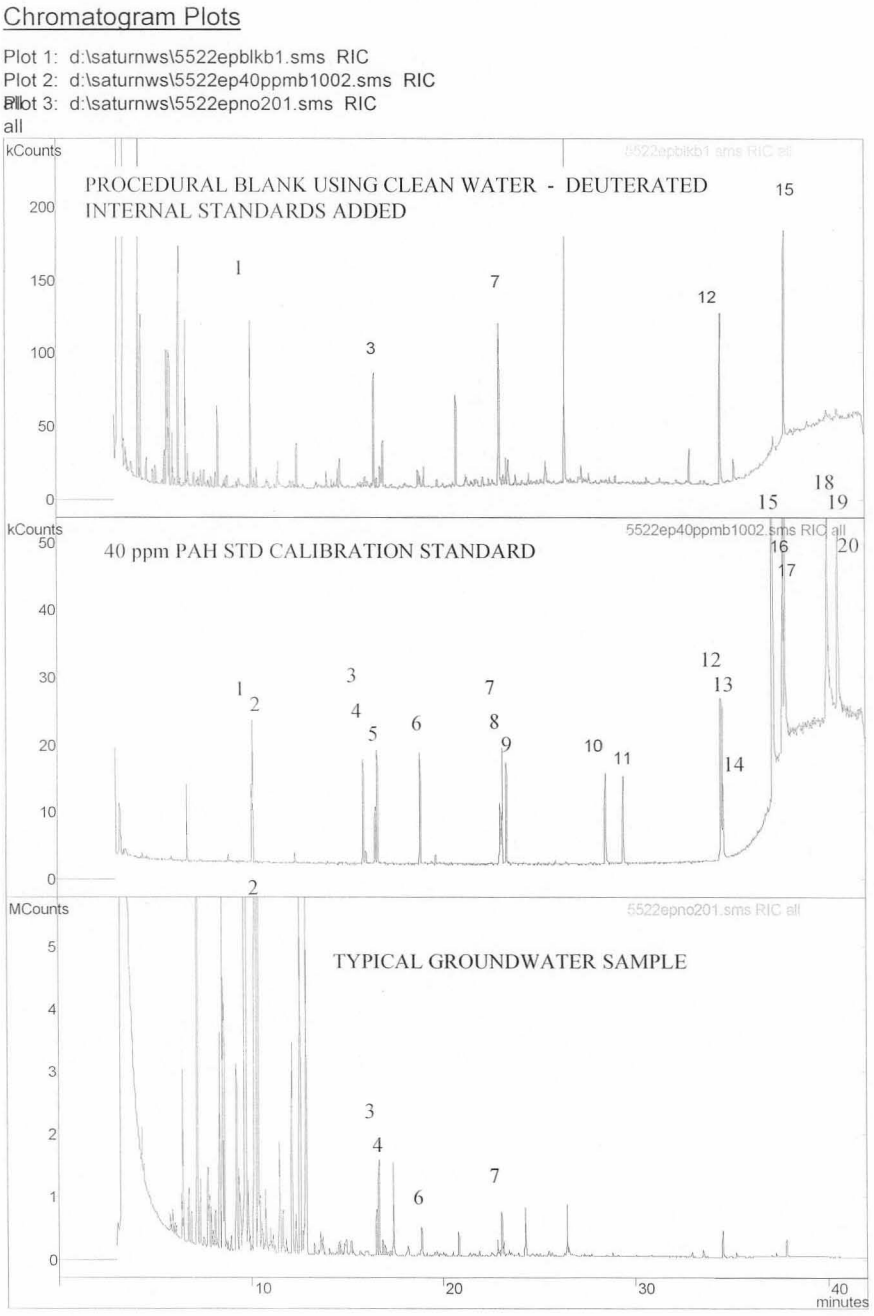

Figure 5.3: Typical total ion chromatograms of a Procedural Blank, PAH standard and a contaminated groundwater sample : (1)d10-naphthalene (2) naphthalene (3) d8-acenaphthene (4) acenaphthene (5) acenaphthylene (6) fluorene (7) d10-phenenthrene (8)phenenthrene (9) anthracene (10) fluoranthene (11) pyrene (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.

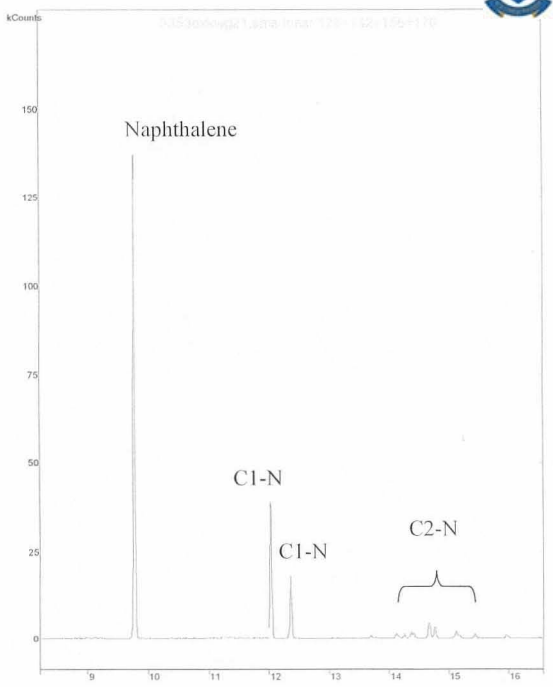

Figure 5.4 (a): Selected ion chromatogram for the naphthalenes - sample containing > 1 µg/cm3 PAHs

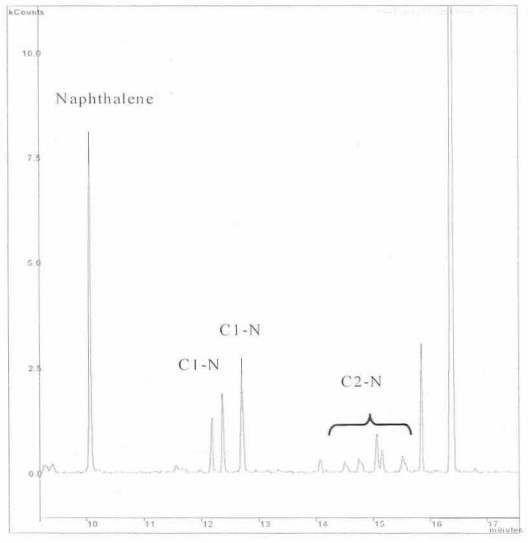

Figure 5.4 (b): Selected ion chromatogram for the naphthalenes – sample containing < 10 ng/cm3 PAHs

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**

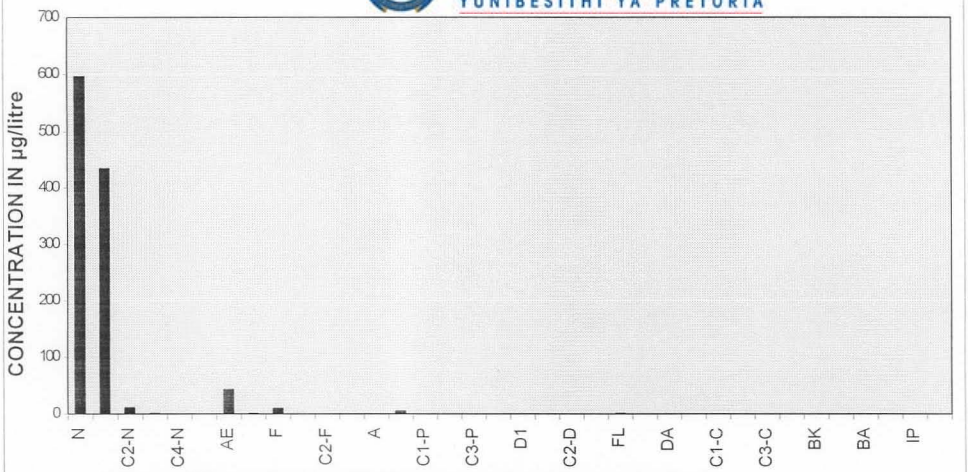

Figure 5.5: Analyte profile histogram of coal tar contaminate goundwater sample

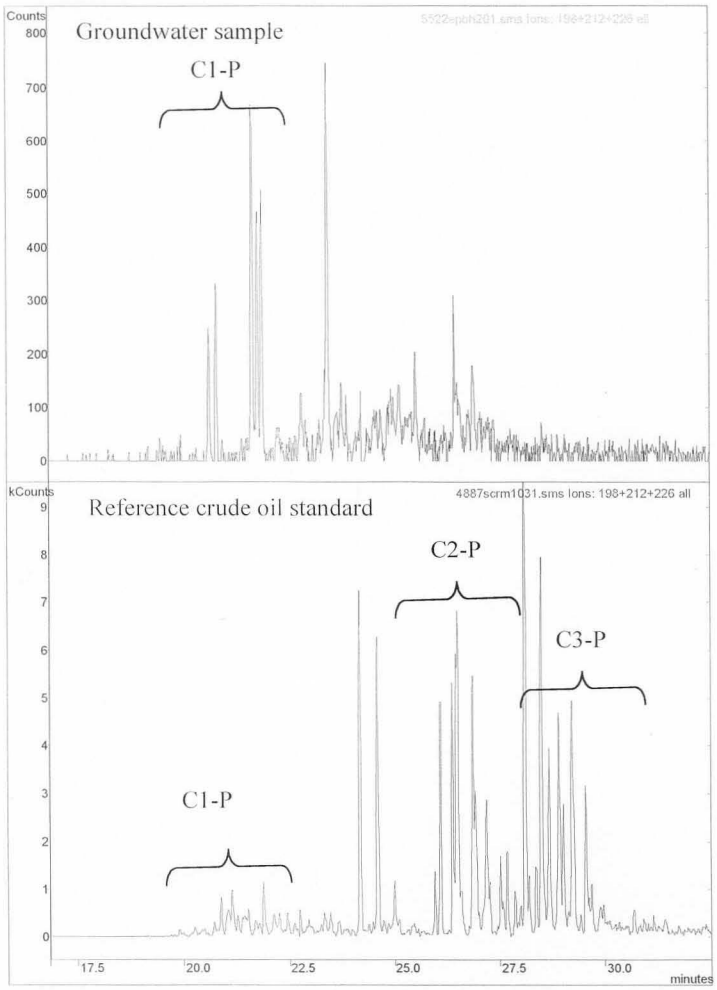

Figure 5.6: Selected ion chromatogram for the phananthrene isomers (m/z = 198, 212, 226)

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 the 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		