# 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]:

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

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.

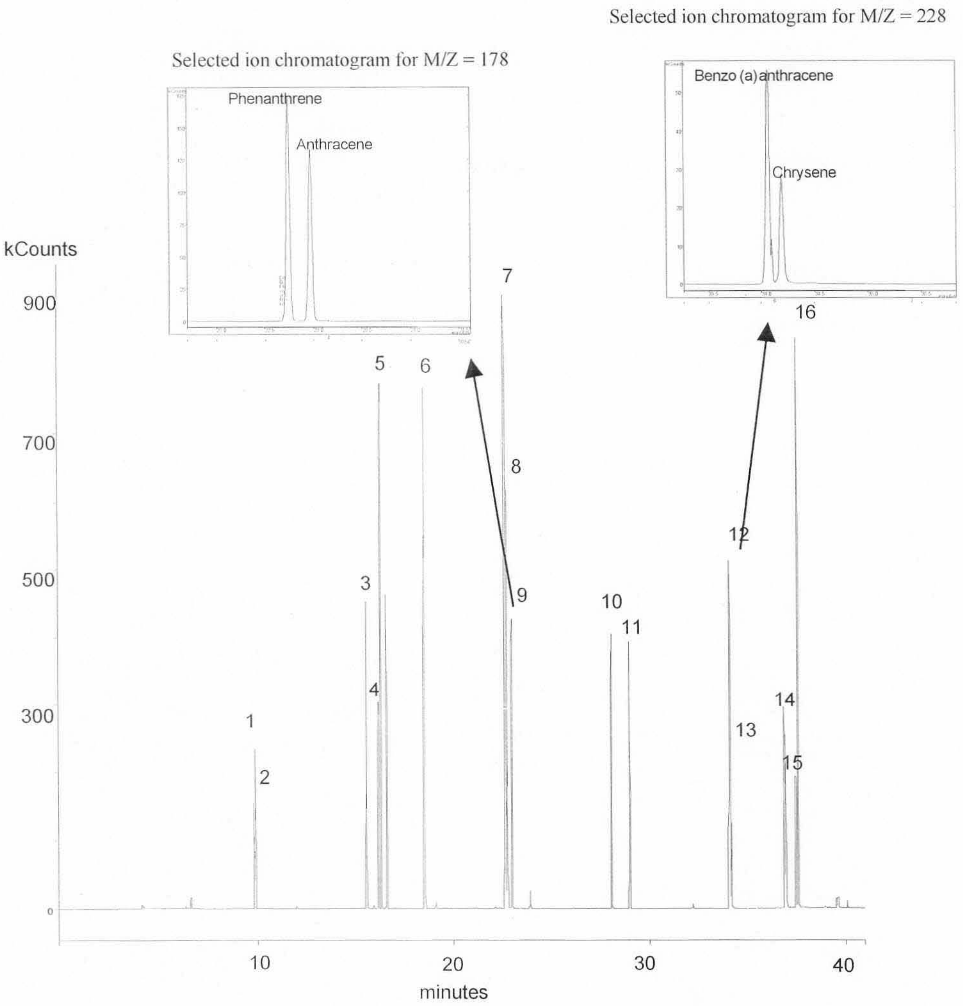

**Figure 6.1: Chromatogram of 2 ng/cm$^3$ PAHs illustrating chromatographic and inertness performance. (1)d$_8$-naphthalene (2) naphthalene (3) acenaphthylene (4) d$_{10}$-acenaphthene (5) acenaphthene (6) fluorene (7) d$_{10}$-phenanthrene (9) anthracene (10) fluoranthene (11) pyrene (12) benzo[a]anthracene (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]

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

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

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

(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 % :

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

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.

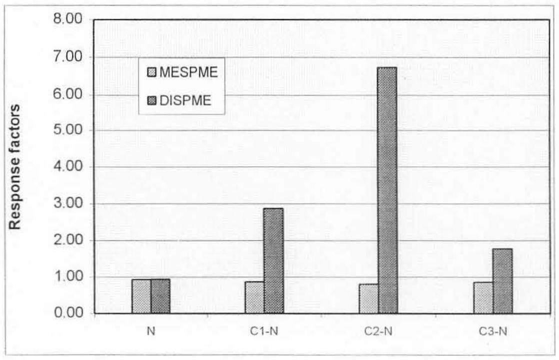

**Figure 6.2: Response factors for the naphthalene homologous series using a sample of known concentrations**

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].

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

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

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

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.

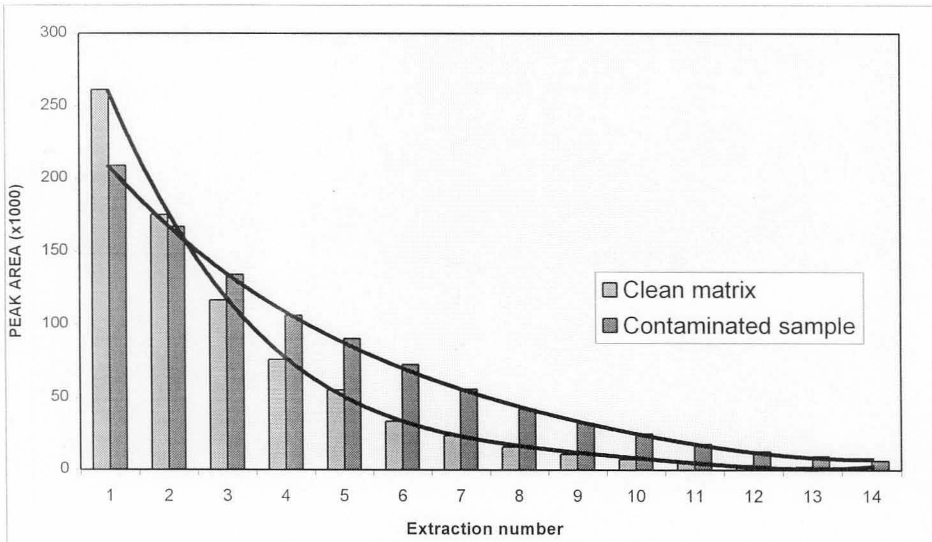

Figure 6.3: MESPME-extraction of naphthalene from (1) a clean matrix and (2) a contaminated sample

## 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.

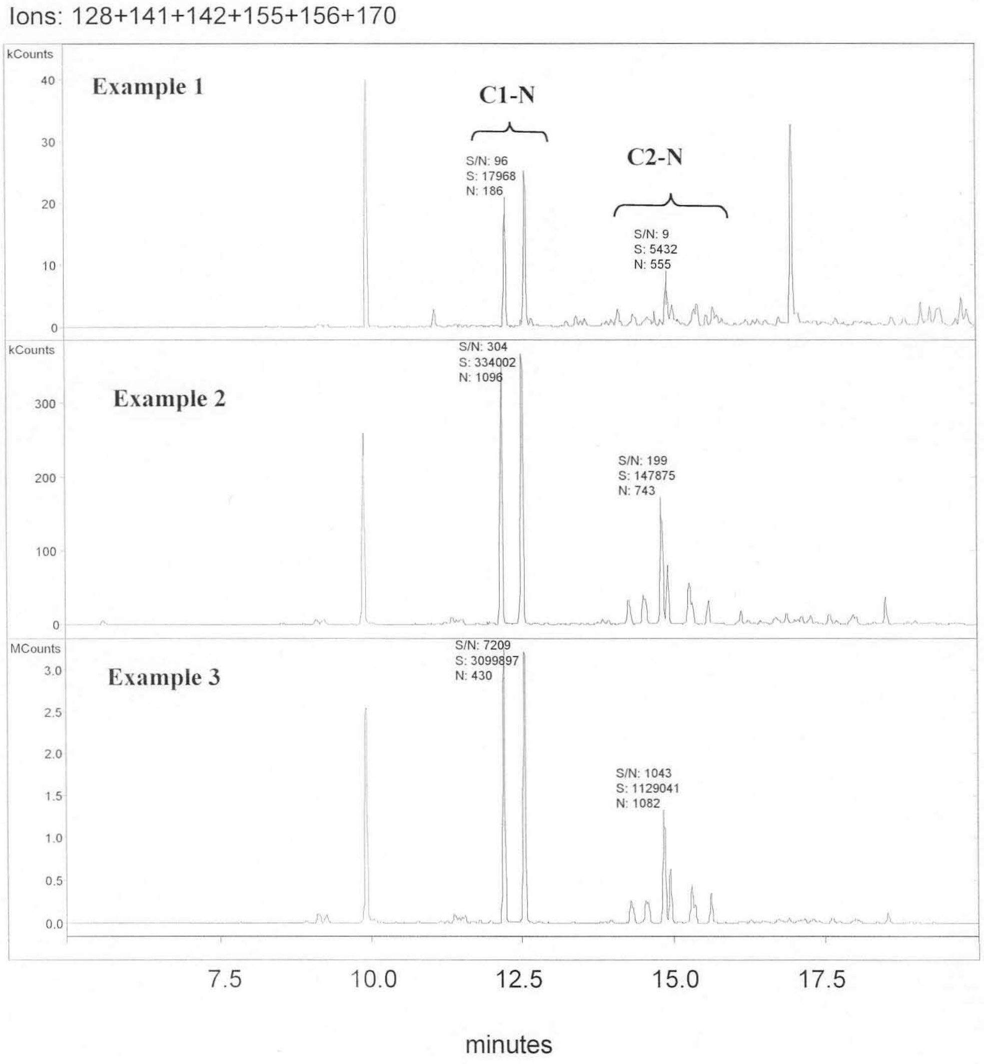

**Figure 6.4: Reconstructed ion chromatograms of naphthalene, $C_1$-naphthalenes and $C_2$-naphthalenes in contaminated water sample showing signal to noise ratios. (1) Solvent extraction and full-scan MS mode (2) SPME extraction and full-scan MS mode (3) SPME extraction and SIS MS mode. (sum of ions: 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 | | | x | |
| C1-D/C1-P | | | x | |
| C2-D/C2-P | x | | | |
| C2-N/C1-P | | | x | |
| C3-N/C2-P | x | | | |
| C2-P/C2-C | x | | | |
| Suitability for advanced chemical fingerprinting | | | x | |