# 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 µg/cm$^3$ 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).

## 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[15], 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[16]:

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

(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 % :

$$\%P = (C_1 / C_0)x100 \quad \text{.....(4)}$$

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)[8]. 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.

$$n = C_0 V_{MT} = C_f V_f + C_w V_w + \sum C_{Mi} V_{Mi} \quad (5)$$

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

$$P_f = C_f V_f / C_0 V_{MT} \quad (6)$$

The amount of solute which can partition into the sample matrix ($\sum C_{Mi} V_{Mi}$), can have an effect on $C_f V_f$ 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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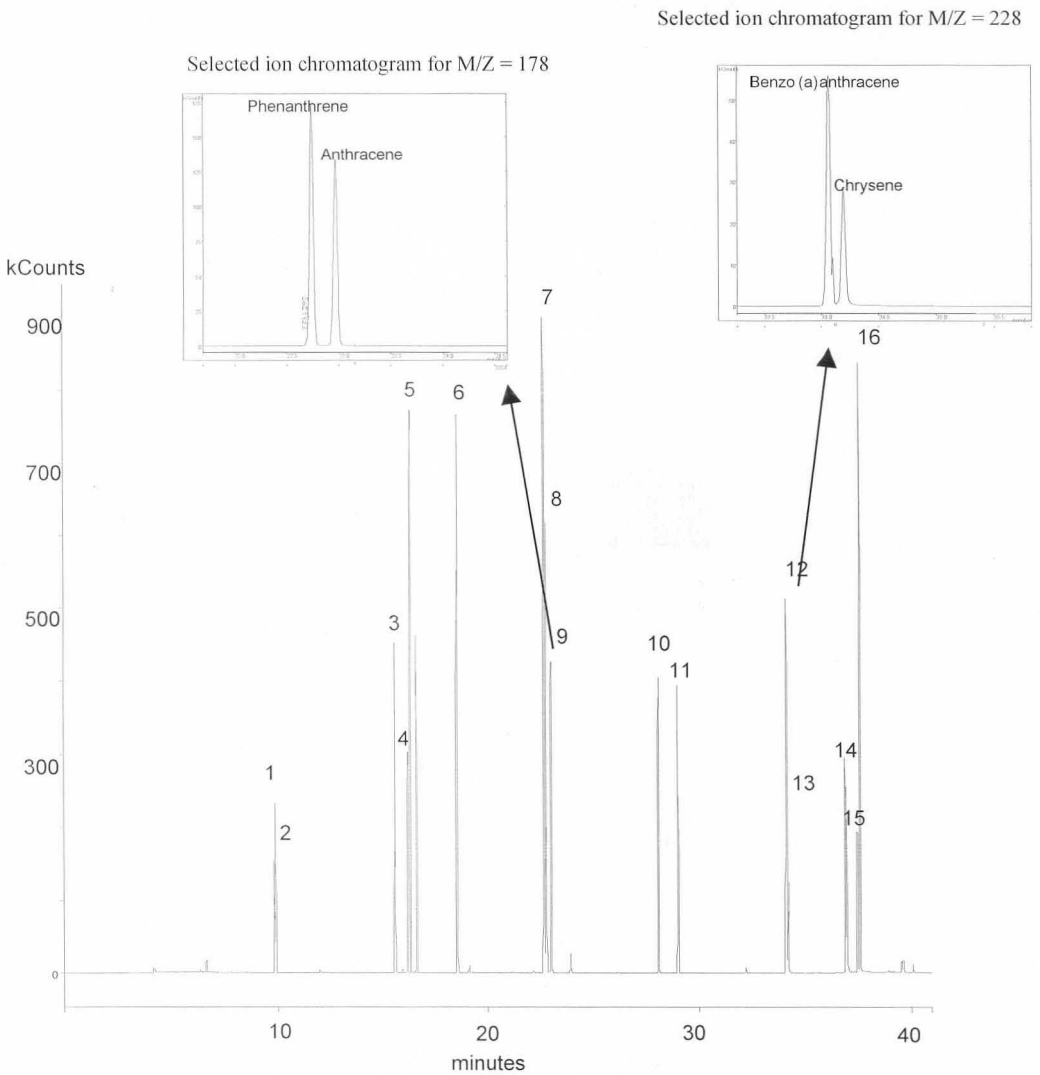


Figure 1: SIS Chromatogram of 2 ng/cm$^3$ PAHs illustrating chromatographic and inertness performance. (1)$d_8$-naphthalene (2) naphthalene (3) acenaphthylene (4) $d_{10}$-acenaphthene (5) acenaphthene (6) fluorene (7) $d_{10}$-phenanthrene (9) anthracene (10) fluoranthene (11) pyrene (12) benzo[a]anthracene (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

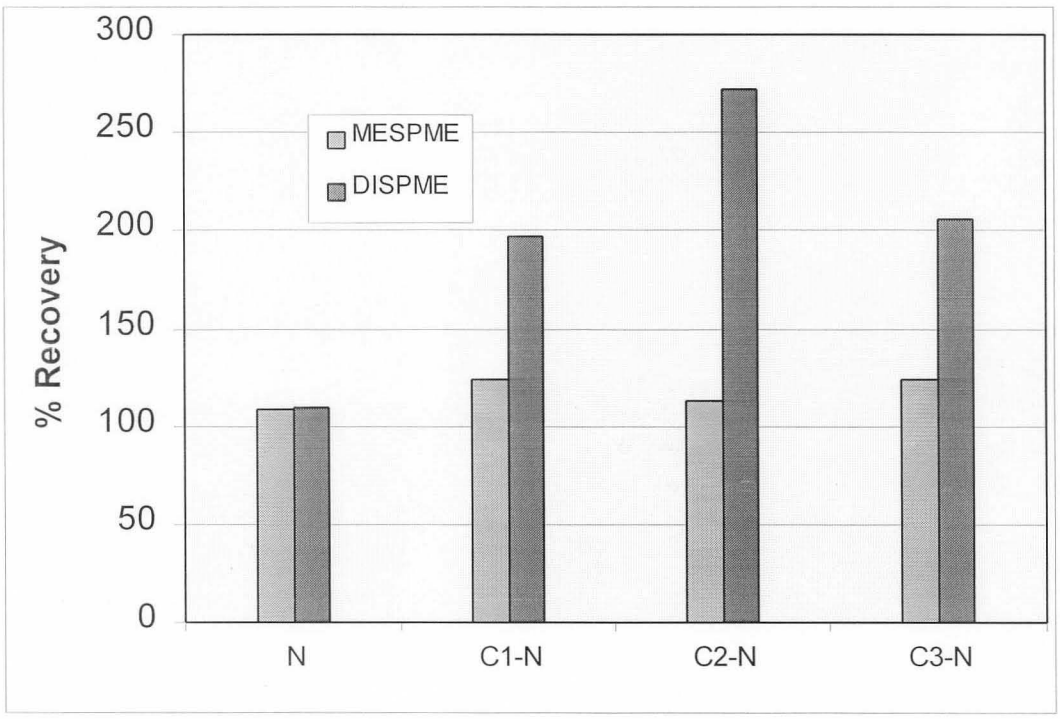


Figure 2: Recovery of the naphthalene homologues series added to pure water at levels of 6 – 12 ng/cm$^3$ using MESPME. Results are based on six determinations.

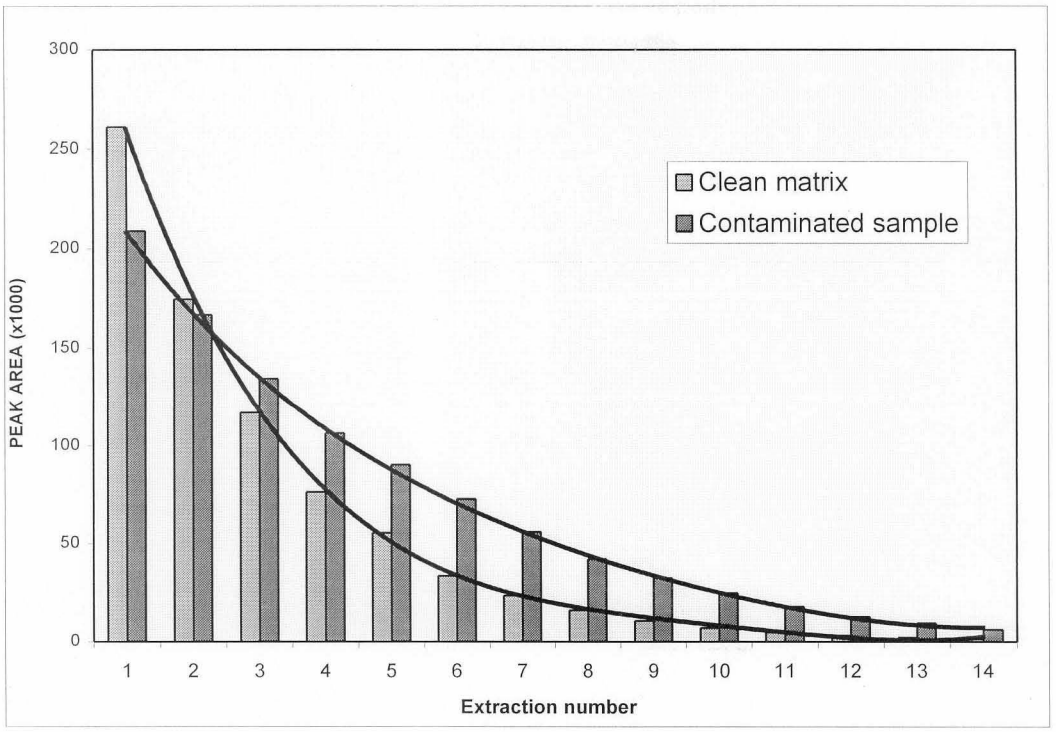


Figure 3: MESPME-extraction of naphthalene from (1) a clean matrix and (2) a contaminated sample

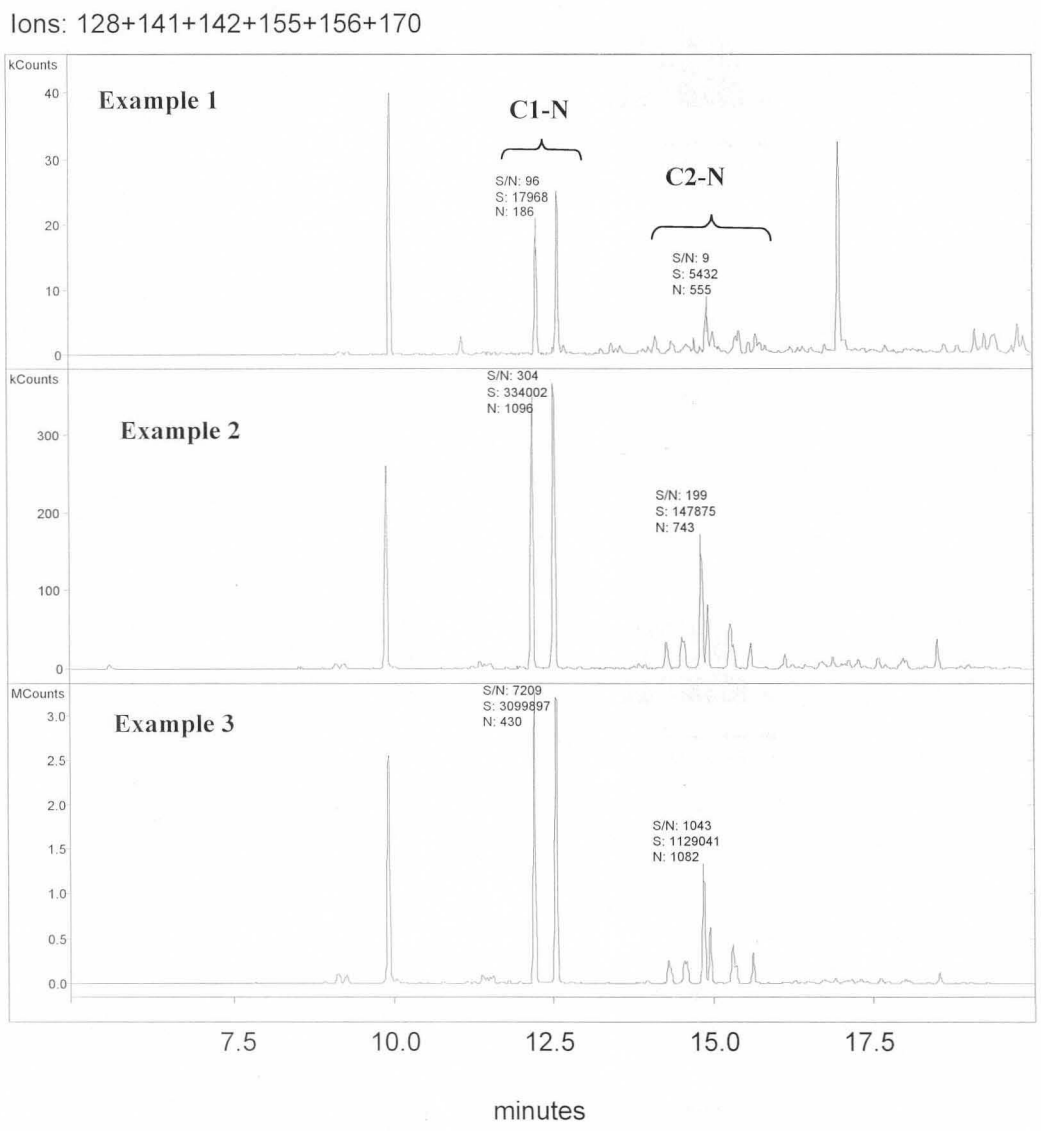


Figure 4: GC/MS chromatograms of naphthalene, $C_1$-naphthalenes and $C_2$-naphthalenes in a contaminated water sample showing signal to noise ratios. (1) solvent extraction and full-scan MS (2) SPME extraction and full-scan MS (3) SPME extraction and SIS MS mode.

**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.