Chapter 8

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

INTRODUCTION

Extraction of organic compounds from soil samples

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

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

Optimisation of headspace extraction parameters

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

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

Hyphenated MS determination of PAHs

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

The requirements for fingerprinting and interpretative methods

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

EXPERIMENTAL

Reagents and Materials

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

HSSPME Extraction Procedure

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

Fiber selection

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

Sample and headspace volumes

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

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

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

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

Temperature

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

Accelerated Solvent Extraction

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

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

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

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

Analytical performance

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

RESULTS AND DISCUSSION

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

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

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

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

Analytical performance

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

TABLE 8.1 : Extraction efficiency of PAHs using the headspace technique

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

n.d. = not detected.

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

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

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

[a] - concentration as mg/kg in brackets

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

Source discrimination based on relative PAH abundance

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

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

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

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

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

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

Source ratios

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

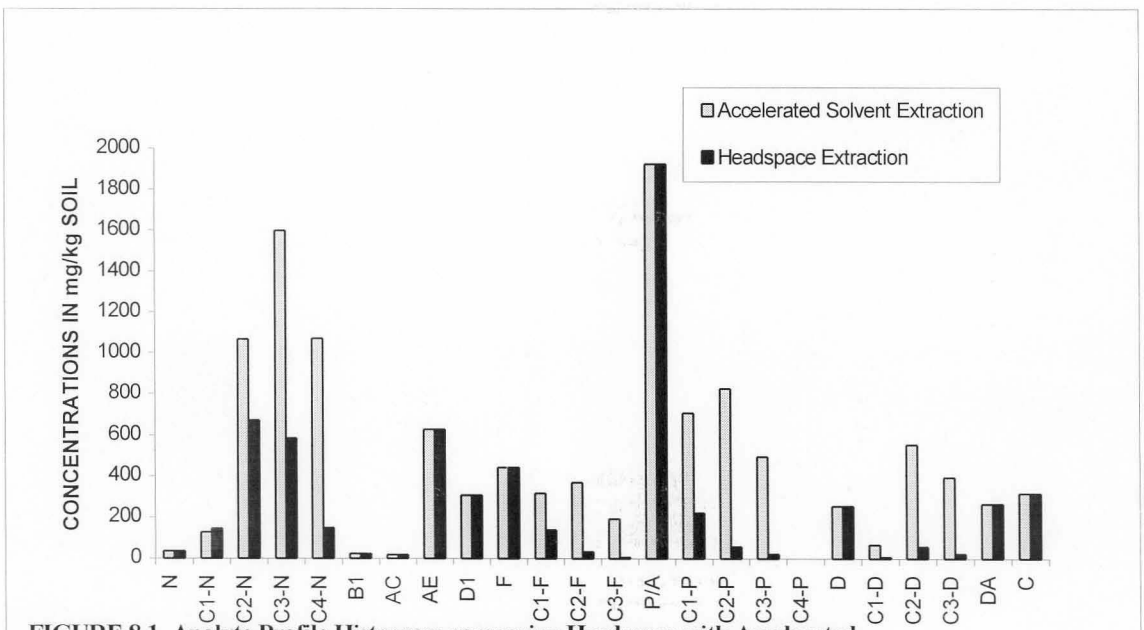

FIGURE 8.1 Analyte Profile Histogram comparing Headspace with Accelerated Solvent Extraction for CRM-103-100

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

Weathering ratios

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

Individual isomer distributions

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

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

Hyphenated MS determination of PAHs

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

CRM 105 - 100

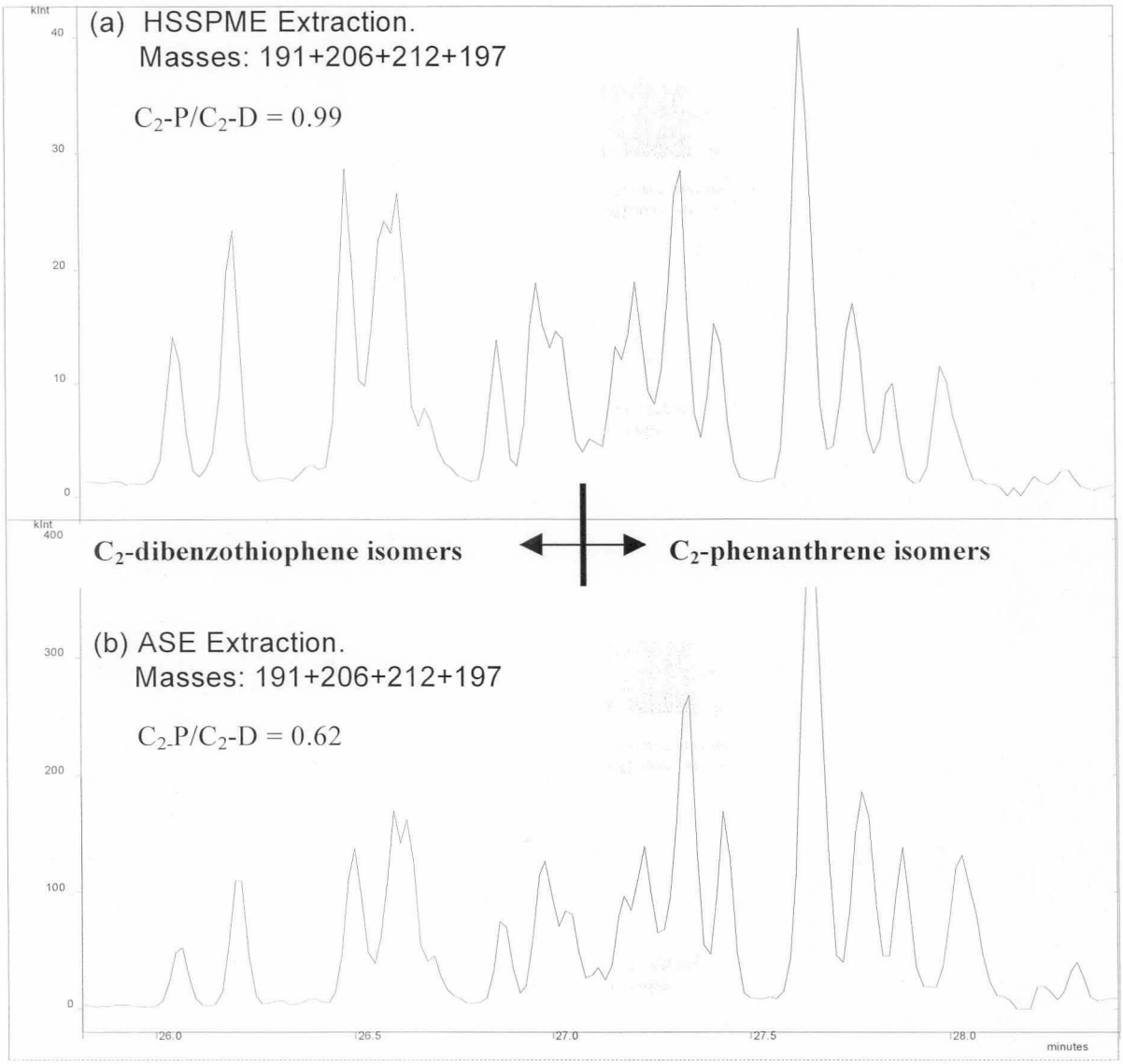

FIGURE 8.2: Selected ion mass chromatograms for C_2-phenanthrenes and C_2-dibenzothiophenes, comparing the relative isomer ratios using (a) HSSPME and (b) ASE

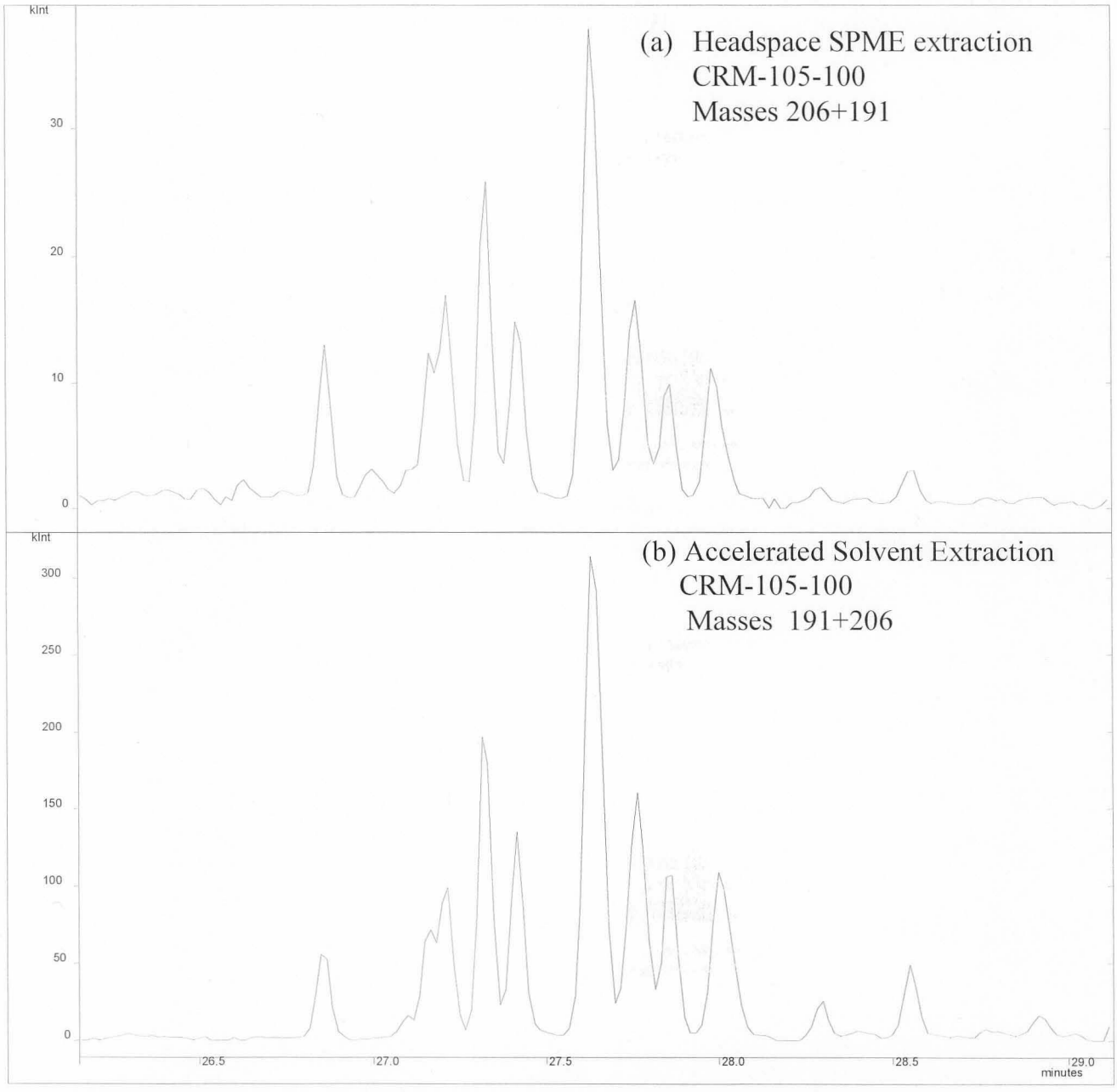

FIGURE 8.3: Selected ion mass chromatograms for C_2-phenanthrenes of (a) headspace SPME (b) Accelerated Solvent Extraction

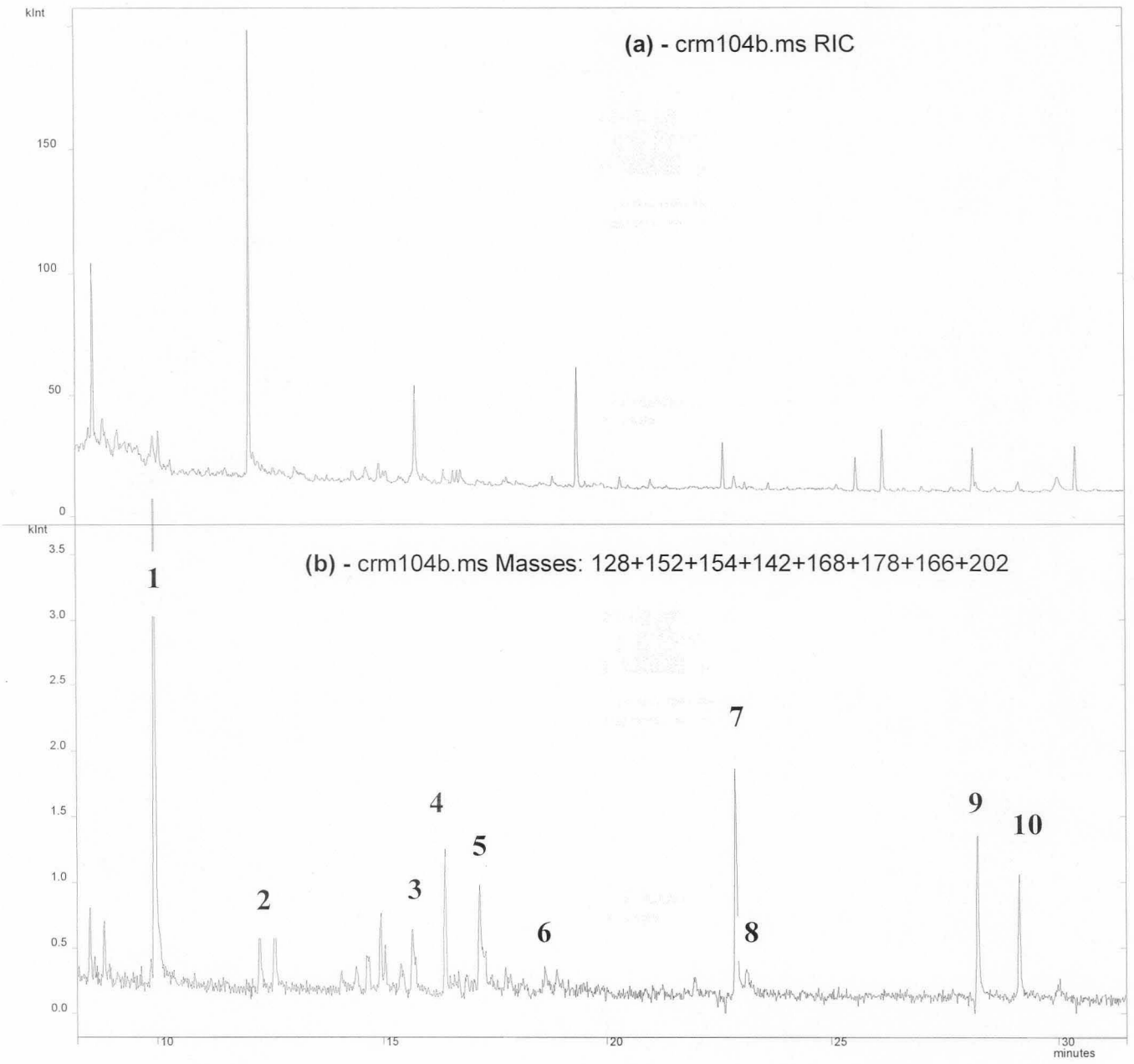

FIGURE 8.4 : Chromatogram of CRM-104-100. Sample selected to illustrate detection limits **(a)** - Reconstructed Total Ion Current **(b)** – Selected ion current of (1) naphthalene (2) 2-methyl naphthalene (3) acenaphthylene (4) acenaphthene (5) dibenzofuran (6) fluorene (7) phenenthrene (8) anthracene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

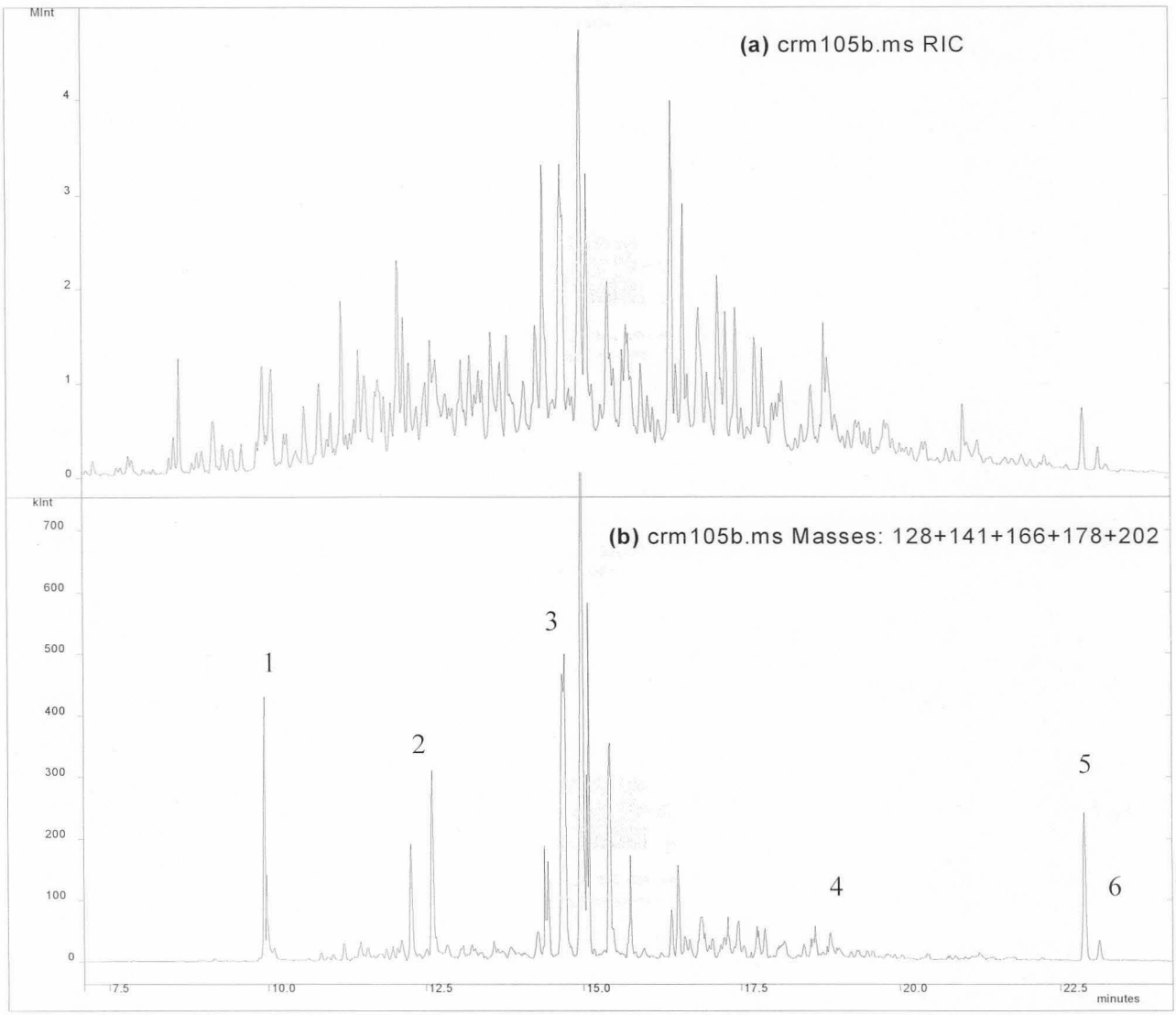

FIGURE 8.5 : Chromatograms of Crm-105-100. Sample selected to illustrate the identification of data in a complex matrix. **(a)** - Reconstructed Total Ion Current **(b)** – Selected ion current of (1) naphthalene (2) C_1-naphthalenes (3) C_2-naphthalenes (4) fluorene (5) phenenthrene (6) anthracene

CONCLUSIONS

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

The technique as a screening method is suitable for:

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

- *The adaptive approach* - to use the information obtained by the screening technique for the design of future sampling or analyses.

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

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

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

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