APPENDIX 4

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

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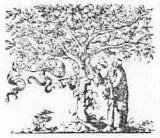

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Abstract

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

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

1. Introduction

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

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

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fulfill the needs for an expedited screening and characterisation procedure.

1.2. Extraction of organic compounds from soil samples

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

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

1.3. Target analytes

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

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

Compound	Rings in structure	Quantitating ion (*m/z*)	Confirmatory ion (*m/z*)	Amount absorbed (ng) (C_o = 24 ng)	Extraction effectiveness (%)
Naphthalene (N)	2	128	127	3.07	12.80
C_1-naphthalenes (C1-N)	2	142	141	3.47	14.50
C_2-naphthalenes (C2-N)	2	156	141	1.93	8.05
C_3-naphthalenes (C3-N)	2	170	155	1.12	4.67
C_4-naphthalenes (C4-N)	2	184	169	0.42	1.77
Biphenyl (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[*e*]pyrene	5	252	253	n.d.	–
Dibenz[*ah*]anthracene (DA)	5	228	226	n.d.	–
Benzo[*ghi*]perylene (BP)	6	276	277	n.d.	–
Indeno[1,2,3-*cd*]perylene (IP)	6	276	277	n.d.	–

n.d. = not detected.

1.4. Physical–chemical parameters of coal tar components

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

1.5. Optimisation of headspace extraction parameters

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

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

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

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

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

1.6.1. Source discrimination based on relative PAH abundance

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

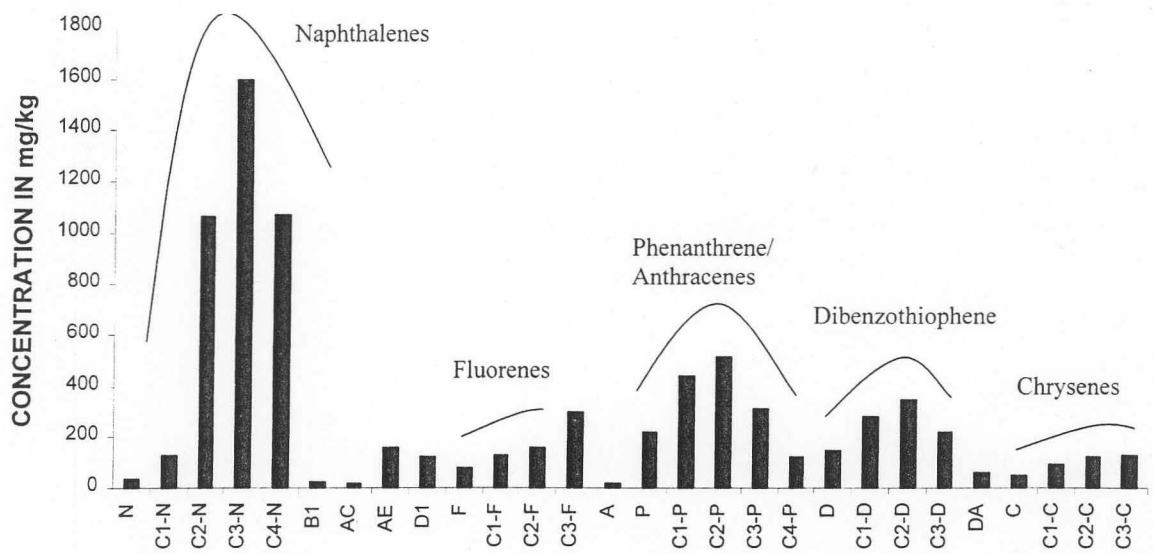

Fig. 1. Characteristic petrogenic profile obtained from a typical mineral oil contaminated soil sample with a PLE and GC–MS analysis. The distributions of the alkylated homologues of N, F, P, D and C where the parent PAH for each series is least abundant, compares with previously reported profiles [15].

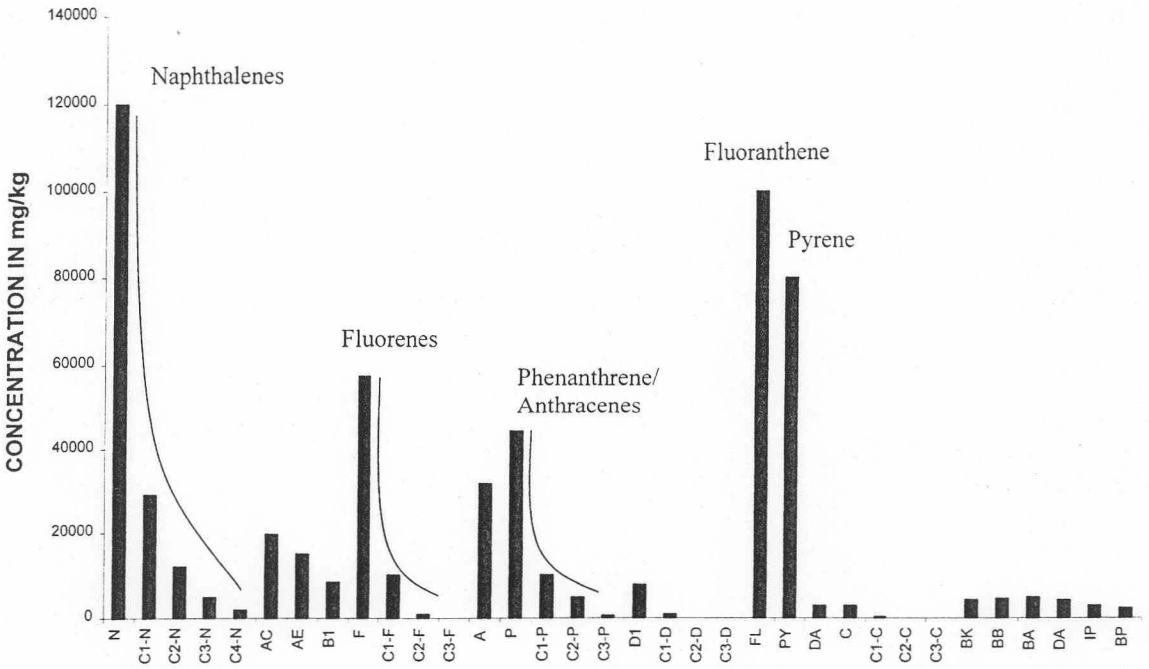

Fig. 2. Characteristic pyrogenic profile obtained from a typical coal tar contaminated sample with a PLE and GC–MS analysis. The PAH distributions which are dominated by parent compounds of two- to four-ring compounds and contains large quantities of Fl and PY, compares with previously reported profiles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

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

1.6.2. Relative amounts of alkylated phenanthrene and dibenzothiophene and chrysene

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

1.6.3. Source ratios

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

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

1.6.4. Weathering ratio

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

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

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

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

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

1.6.5. Individual isomer distributions

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

2. Experimental

2.1. Reagents and materials

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

2.2. Headspace SPME extraction procedure

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

2.2.1. Fiber selection

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

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

2.2.2. Sample and headspace volumes

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

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

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

2.2.3. Temperature

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

2.3. Pressurized liquid extraction

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

2.4. GC–MS analysis conditions

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

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

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

2.5. Estimation of saturated vapor pressures

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

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

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

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

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

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

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

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

2.7. Analytical performance

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

3. Results and discussion

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

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

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

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

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

Vapor pressure is one of the parameters which

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

3.2. Physical–chemical parameters of coal tar components

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

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

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

Table 2
Physical–chemical properties of selected coal tar pollutants

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

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

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

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

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

3.3. Analytical performance

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

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

Table 3
Calibration results for headspace SPME of PAH contaminated soils

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

[a] Concentration as mg/kg in brackets.

3.4. The use of headspace SPME for chemical fingerprinting

3.4.1. Source discrimination based on relative PAH abundance

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

3.4.2. Relative amounts of alkylated phenanthrenes and dibenzothiophenes and chrysenes

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

3.4.3. Source ratios

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

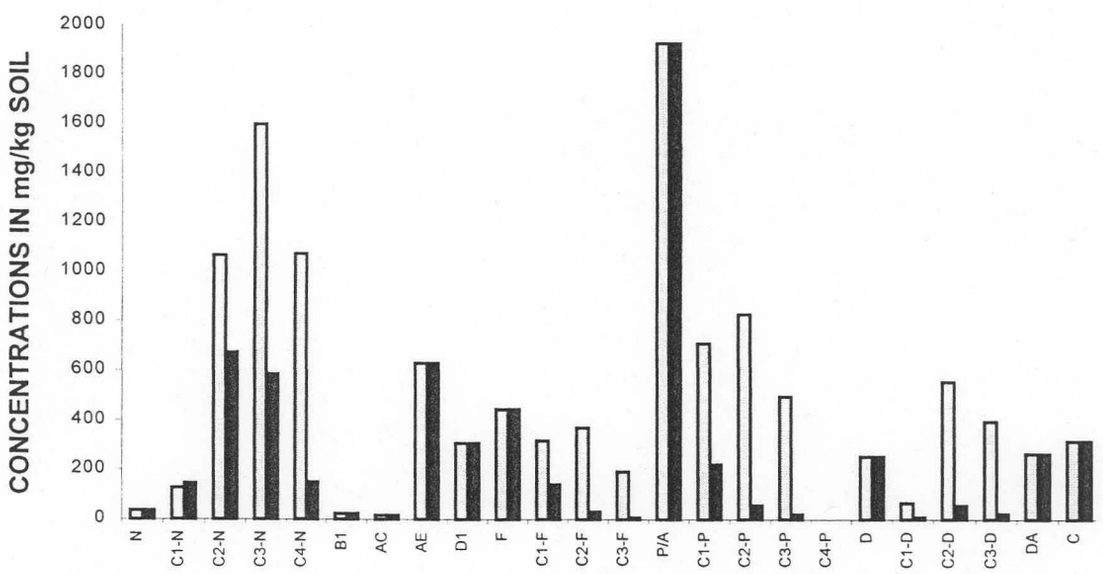

Fig. 3. Analyte profile histogram comparing headspace (grey bars) with PLE (black bars) for CRM-103–100.

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

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

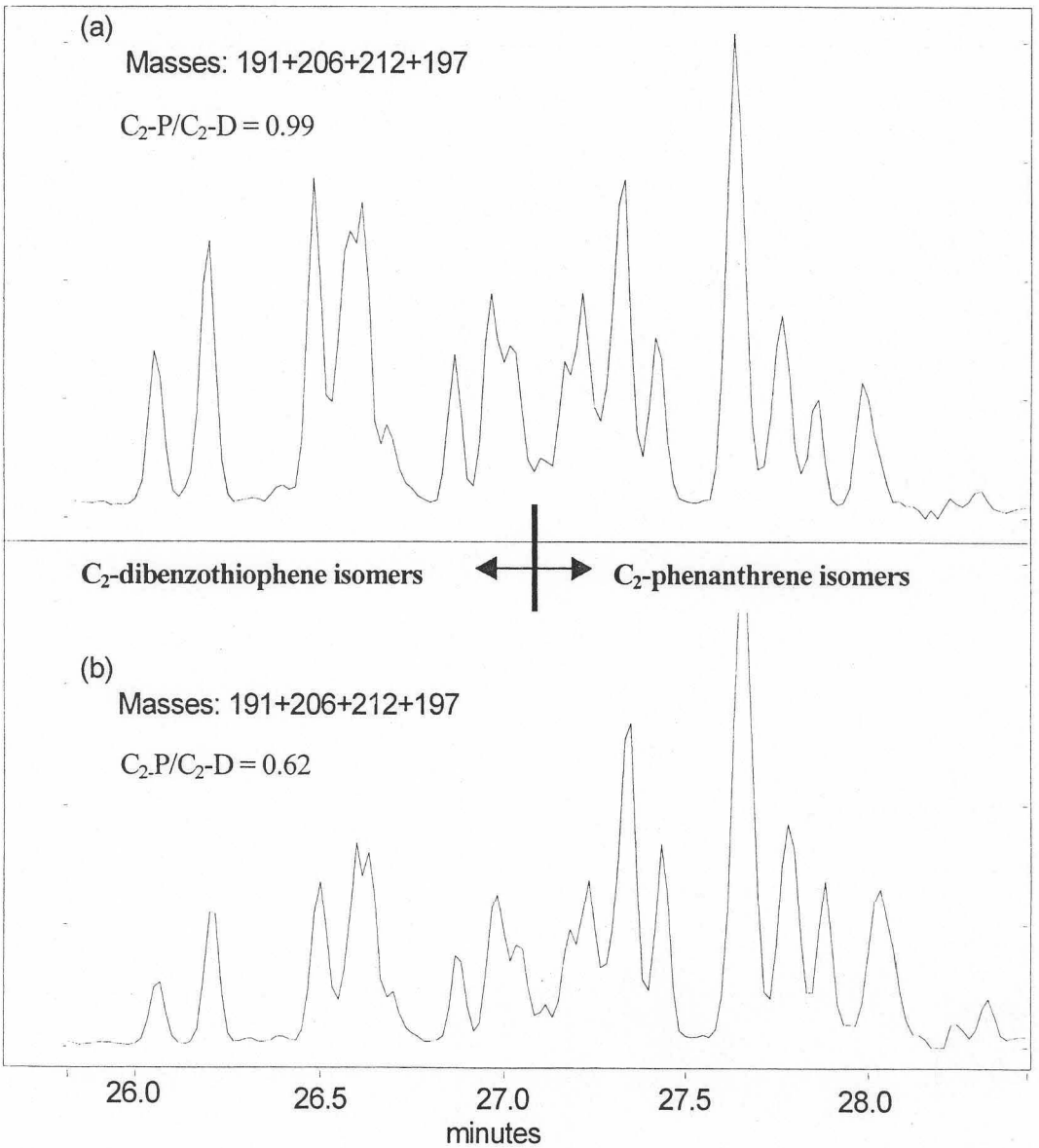

Fig. 4. Selected ion mass chromatograms for C_2-phenanthrenes and C_2-dibenzothiophenes, comparing the relative isomer ratios using (a) HS–SPME and (b) PLE. (Note the slight bias against later eluters with lower P^0).

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

3.4.4. Weathering ratios

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

3.4.5. Individual isomer distributions

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

3.5. Hyphenated MS determination of PAHs

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

3.6. Conclusions

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

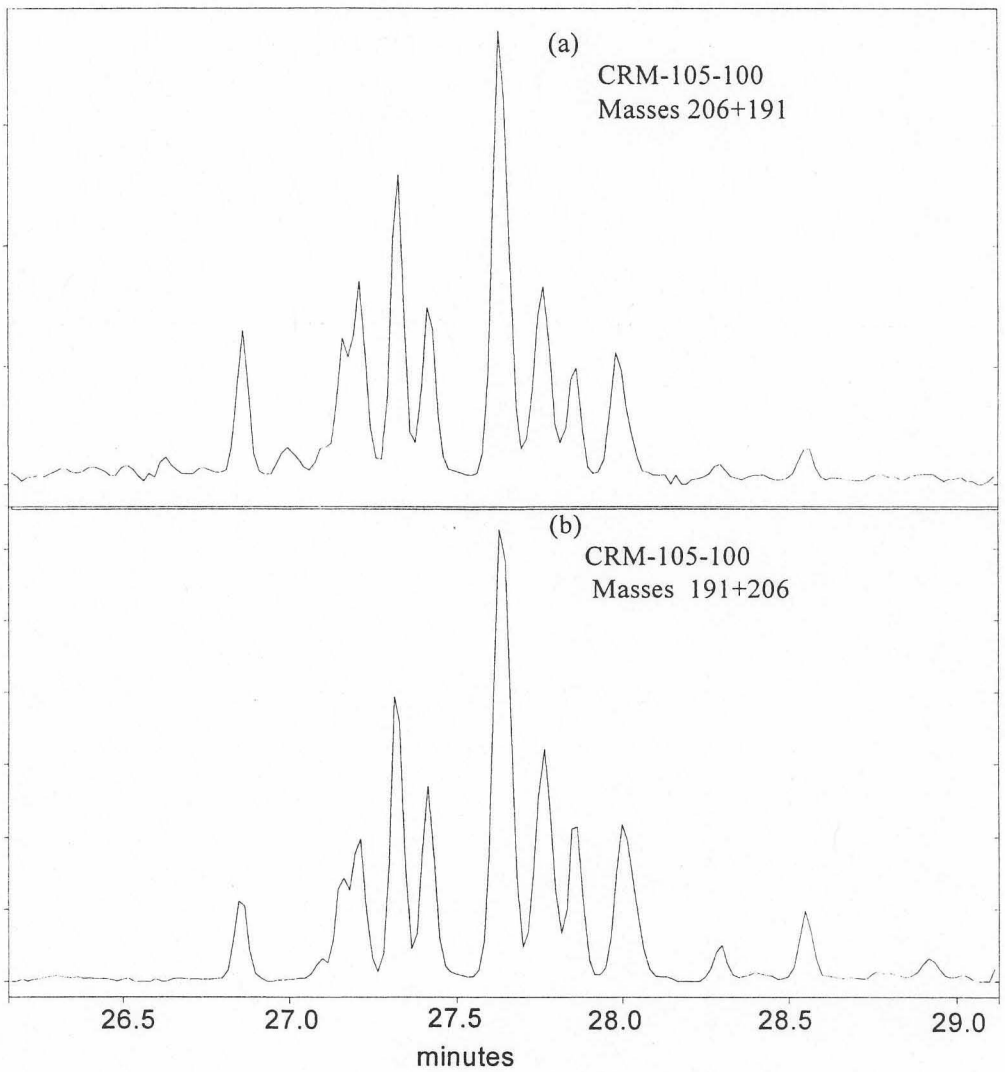

Fig. 5. Selected ion mass chromatograms for C_2-phenanthrenes of (a) HS–SPME (b) PLE.

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

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

The technique as a expedited screening method is suitable for:

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

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

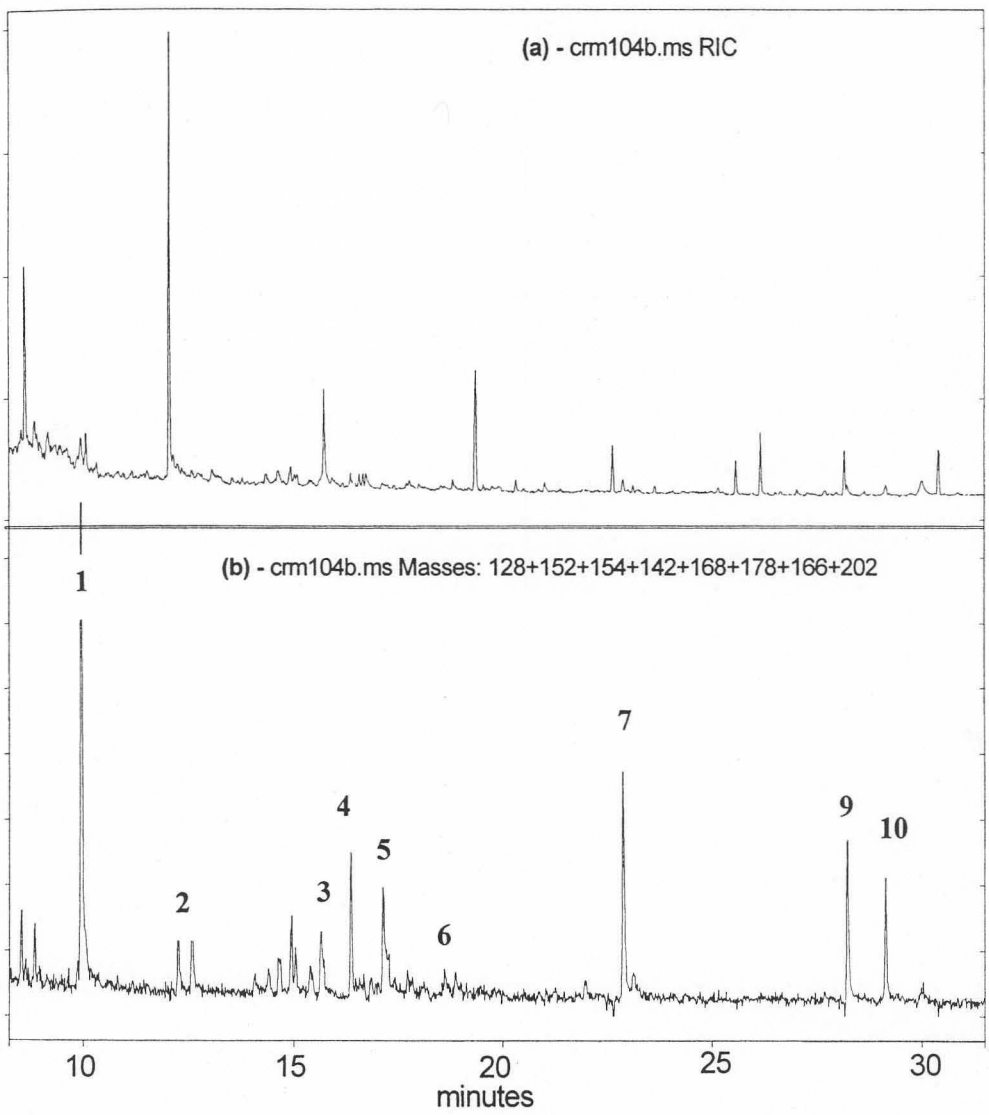

Fig. 6. Chromatogram of CRM-104–100. Sample selected to illustrate detection limits: (a) Reconstructed total ion current, (b) selected ion current of (1) naphthalene, (2) 2-methylnaphthalene, (3) acenaphthylene, (4) acenaphthene, (5) dibenzofuran, (6) fluorene, (7) phenenthrene, (8) anthracene, (9) fluoranthene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

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

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

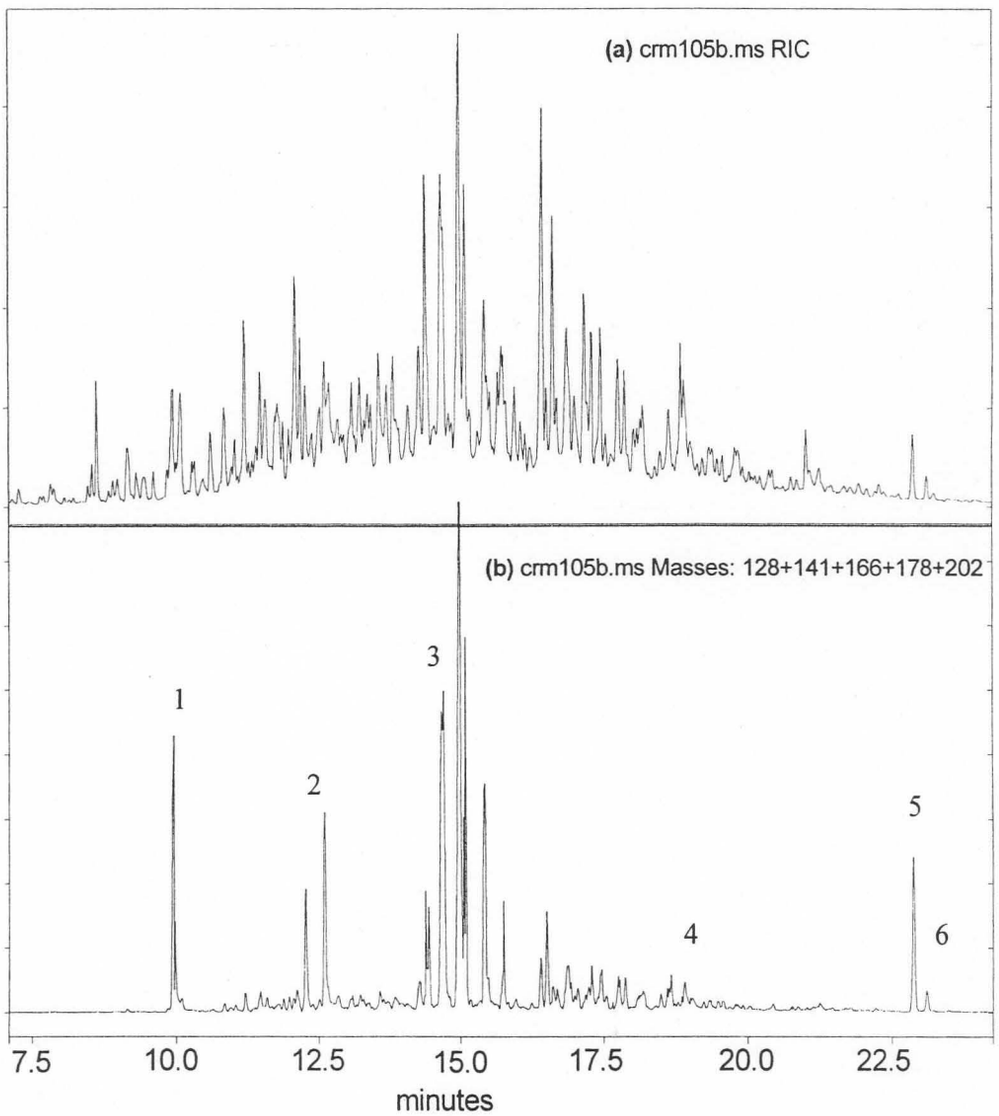

Fig. 7. Chromatograms of CRM-105–100. Sample selected to illustrate the identification of data in a complex matrix. (a) Reconstructed total ion current, (b) selected ion current of (1) naphthalene, (2) C_1-naphthalenes, (3) C_2-naphthalenes, (4) fluorene, (5) phenanthrene, (6) anthracene.

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