Chapter 7

THE DETERMINATION OF PAHS IN SOIL SAMPLES USING PRESSURISED LIQUID EXTRACTION AND GC/MS

INTRODUCTION

The extraction, matrix clean-up and pre-concentration of PAHs from the soil samples are important sample preparation steps, which are necessary before the extract can be submitted for a quantitative analysis using GC/MS. A critical requirement for the extraction method used is to have good recovery of analytes. Noordkamp and co-workers[40] 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[41] and Pressurised Liquid Extraction[42] have also been reported. The relatively new Pressurised Liquid Extraction (PLE) technique for the extraction of PAHs from soil and sludge samples that was discussed in **Chapter 2**, was investigated. The technique is also referred to as Accelerated Solvent Extraction (ASE). The main advantage of this extraction method above the others is automation and that the extraction process is more efficient at the elevated temperature and pressure. The GC/MS method used for the quantitative analysis of PAHs was based on the EPA method 8270. Modifications that were made to improve the overall results of the method included the redefining of the target analytes and internal standards, varying the sample mass according to expected contaminant levels (see **Table 7.1**), quantification of alkyl-PAH homologues and addition of a "keeper" solvent before evaporation. The results of this method were investigated for its applicability to the analysis of PAH contaminated soil samples and suitability for chemical fingerprinting. The sample purification and enrichment scheme is shown in **Figure 7.1.**

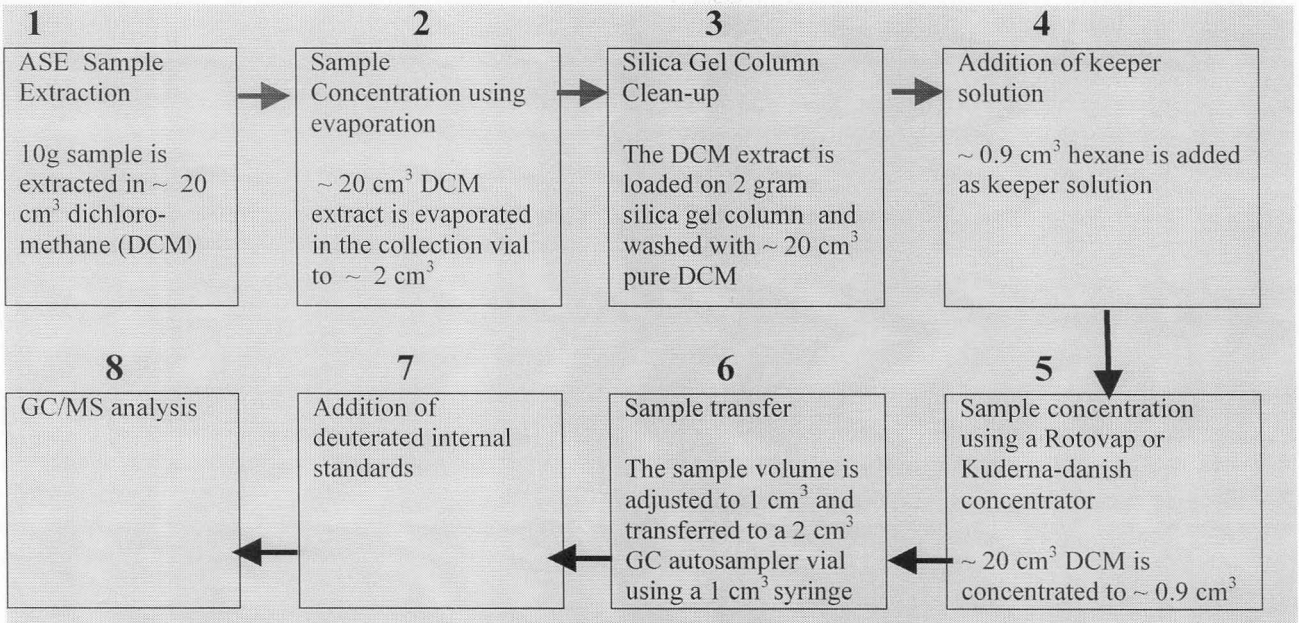

Figure 7.1: The sample purification and enrichment scheme for the analysis of soil samples

EXPERIMENTAL

Soil standards

Certified soil standard (SRS 100-103) was obtained from Resource Technology Corp. (Industrial Analytical).

Sampling and the preparation procedure for soil samples

Samples were dried before filling into the extraction cell. Samples that contained water (greater than 10%) were mixed in equal proportions with anhydrous sodium sulphate. Gummy, fibrous, or oily materials not amenable to grinding were cut, shredded, or otherwise separated to allow for mixing or maximum exposure of the sample surfaces for extraction. A cellulose disk was placed at the outlet end of the extraction cell. Approximately 0.1 - 30g (see **Table 7.1**) of each sample was weighed into a 11-cm^3 extraction cell or approximately 3 grams into a 32- cm^3 extraction cell (M_1). The extraction cells were placed into the autosampler tray and the collection tray loaded with the appropriate number (up to 24) of 40 cm^3, pre-cleaned, capped vials with septa.

ASE 200 Conditions

System pressure:	14 MPa (2000psi)
Oven Temperature:	100 °C
Sample size:	0.1 - 10 grams
Oven Heat-up time:	5 minutes
Static time:	5 minutes
Solvent:	Dichloromethane
Flush volume:	60% of extraction cell volume
Nitrogen purge:	1 MPa (150 psi) for 60 seconds

Preparation of extracts for GC/MS analysis

- The extraction vial was opened and the excess DCM extract obtained from the ASE evaporated under a stream of air to obtain a final volume of about 2 cm^3.
- A glass column fitted with a porous disk was filled with about 2 grams of stationary phase (chromatographic quality silica gel or neutral alumina). The column dimensions was 10 mm x 300 mm. The height of the stationary phase in the column was be about 50 mm.
- The stationary phase was equilibrated with DCM and air bubbles removed by shaking.
- The concentrated extract was transferred to the top of the stationary phase in the column by using a 1 cm^3 syringe. The flow rate was between 1 and 5 cm^3/minute.
- The extract was passed through the column and the eluent collected in a clean 250 cm^3 round bottom flask. The stationary phase was washed with an additional 20 cm^3 of pure DCM. Hexane (0.9 cm^3) keeper solvent was then added to the round bottom flask.
- The DCM was evaporated using a rotary evaporator to obtain a final volume of just less than 1 cm^3.
- The hexane concentrate was withdrawn from the round bottom flask using a 1 cm^3 syringe and small quantities of toluene added to the flask until the syringe was filled to the 1 cm^3 mark.
- The syringe contents were transferred to a 2 cm^3 GC autosampler screwcap vial and sealed with a teflon-coated septum.
- The appropriate amount of internal standard was added to each standard and sample, to obtain a concentration of 20 $\mu g/cm^3$.

Conditions, calibration procedure, quality control and quantitative analysis

Extracts obtained in the above way were analysed by GC/MS using the gas chromatographic and mass spectrometer conditions as described in **Chapter 3**. A 2µl aliquot of the sample was injected into the GC, equipped with a high resolution J&W DB-5 fused-silica column.

Table 7.1: Sample mass and final volume for the determination of PAHs in soil samples

Expected PAH concentration in the soil (mg/kg)	Mass in grams (M_1)	Dilution volume in cm^3 (V_1)
< 1	30g	0.25
1 – 10	10g	1
10 – 100	10g	10
100 – 500	10g	50
500 –1000	5g	50
1000 – 5000	1g	50
5000 – 10000	0.5	50
>10000	0.1	50

The temperature program of the GC oven is based on the conditions of EPA method 8270, which were developed to achieve near baseline separation of the 16 priority PAHs. The same list of target analytes, quantitation ions and internal standards, as discussed in **Chapter 5** (**Table 5.1**) were used. Before sample analysis, a five point initial calibration based on 16 parent PAHs was established, demonstrating the linear range of the analysis. Check standards were analysed with every ten samples to validate the integrity of the initial calibration. The method of internal standards, using peak areas and relative response factors (RF) generated from the linear initial calibration, was used to quantify parent PAHs. Peaks of alkyl-PAH homologues were manually integrated and their concentrations determined using the selected ion current of the primary ion (m/z), and the RF of the respective unsubstituted parent PAH compound. That is, in the absence of standards for the alkyl-PAHs, equal response is assumed between the primary ions of these compounds and the corresponding parent PAHs.

RESULTS AND DISCUSSION

Method Validation

This investigation mainly deals with the determination of PAHs in industrial soils and sediments, which have been polluted by coal tar, mineral oil, lubricating oil or similar PAH sources. Some of the PAHs, particularly the 4- to 6-ring structures, are relatively resistant to degradation, and can be used for source identification. Accurate analytical data for PAHs is required, as the toxicity of certain PAHs (see **Table 3.1**) is a concern. Maximum concentration levels are normally specified the sum of the 16 USEPA priority PAHs. The Dutch soil standard specifies a maximum total concentration of 40 mg/kg.

The interpretative objective of this method was to detect PAHs originating from anthropogenic sources relative to the background. Samples collected from unpolluted areas were analysed to determine typical background levels. The chemical data obtained from selected areas were analysed to determine the typical contaminant levels and the method sensitivity for the specific alkyl-PAH isomers that are normally used for ratio calculations. The selection criteria for the integration and reporting of each alkylated isomer were based primarily on retention time, pattern recognition relative to the soil CRM, and on the presence of selected confirmation ions. Non-zero results for each PAH were reported when the concentration is above the practical quantification limit (see **Table 7.3**). The presence of petroleum hydrocarbons (n-alkanes) in samples were also investigated to determine the contribution of petrogenic sources to the overall pollution and the

influence thereof on the PAH determinations, such as peak overlap. The performance characteristics of the method were measured against the data quality objectives that are listed in **Table 3.3**. Only the method detection limits (MDLs) of parent PAH compounds were determined, but the MDLs for isomer groups, such as C_2-naphthalenes, would generally be higher than the MDL for parent compounds, because the instrument response for each series is spread over multiple peaks. To optimise the sensitivity, data were collected only when the signal-to-noise ratio was greater than 3:1. The selectivity of the method was evaluated for its ability to detect trace levels of PAHs in complex matrixes.

Recovery and repeatability

The recoveries of PAHs from a soil matrix using PLE were determined using a certified SRS-103 soil standard with a PAH content over a wide concentration range, namely 10 – 1500 mg/kg. For this determination, a 2 gram sample was concentrated to 20 cm^3, i.e. a dilution factor of 10. The recoveries obtained are shown in **Table 7.2**.

Table 7.2: Recovery of PAHs from contaminated soil Calibration and analytical results

Compound	Recovery SRS-103 (mg/kg)	Certified Value (mg/kg)	Recovery SRS-103 as %
Naphthalene	36.4	34.8	105
Acenaphthylene	18.4	16.5	112
Acenaphthene	633	627	101
Fluorene	356	443	80
Phenanthrene	2087	1925	108
Anthracene	541	431	126
Fluoranthene	1475	1425	104
Pyrene	1237	1075	115
Benzo[a]anthracene	273	264	103
Chrysene	335	316	106
Benzo[k,b]fluoranthene	160	182	88
Benzo[a]pyrene	69	96	72
Benzo[g,h,i]perylene	29	14.2	204
Indeno[1,2,3-cd]pyrene	20	25	80

The average percentage recoveries of all PAHs were required to fall between 80 and 120%. The recoveries compared well with the certified values and except for anthracene (126%) and benzo[g,h,i]-perylene (204%). It must, however, be kept in mind that the extraction was optimised for the high concentration phenanthrene, fluorene and pyrene (dilution factor of 10) with a resulting low concentration in solution for the 5- and 6-ring compounds. They were measured at the lower end of the calibration curve with expected high %RSDs.

The average repeatability for a mid-range verification standard (40 mg/kg) was determined by using the average of twelve independent results. The RSDs ranged between 6.1% (naphthalene) and 26.8% (benzo[a]anthracene) that were all lower than the data quality objective of 30%. The highest RSDs were obtained for the 5- and 6-ring compounds. The repeatability was found to be suitable for its intended use.

Calibration

A straight-line calibration curve was constructed for each PAH to validate the linearity of the calibration over the range of 20 $\mu g/cm^3$ to 160 $\mu g/cm^3$. The values are summarised in **Table 7.3.** The 2- and 3- ring compounds showed good linearity in almost all cases and were characterised by correlation coefficients of better than 0.99. The laboratory found that fluctuations in response factors were mainly caused by injection discrimination. The GC inject speed, inlet pressure and split ratio were found to have a large influence on mass discrimination. The RSDs of the relative response factors were monitored over the longer period and showed a %RSD of smaller than 30% over the linear range of the calibration, which conforms to the data quality objectives in **Table 3.3**.

Table 7.3: Calibration and analytical results

		5-level CALIBRATION			ACCURACY AND PRECISION OF VERIFICATION STANDARD			SENSITIVITY			REPRESEN-TATIVINESS (n=19)
Compound	Internal Std	Average RF	Average Regression Coefficients (R^2)	Average %RSD	Value found for a 40 ng/cm^3 spiked sample	% Recovery	%RSD for a 40 ng/cm^3 Standard (n=10)	Signal to Noise (S/N) At 40 ng/cm^3	Quant. Limit [(a)] mg/kg	Detection limit [(b)] mg/kg	Procedural Blank Values mg/kg
Naphthalene	A	0.98	0.998	6.4	40.0	100	6.1	3484	0.004	0.001	0.000
Acenaphthylene	B	1.58	0.996	4.9	39.5	99	7.7	1613	0.008	0.002	0.000
Acenaphthene	B	1.20	0.996	6.1	38.9	97	8.2	4360	0.004	0.001	0.000
Fluorene	C	0.64	0.993	8.5	39.6	99	16.3	2260	0.008	0.002	0.000
Phenanthrene	C	0.95	0.995	8.8	40.3	101	11.0	1394	0.010	0.003	0.093
Anthracene	C	0.85	0.979	15.2	40.4	101	14.2	602	0.022	0.007	0.016
Fluoranthene	C	1.50	0.999	3.2	37.4	94	16.3	4332	0.003	0.001	0.015
Pyrene	C	1.71	0.999	3.8	36.4	91	16.1	4711	0.003	0.001	0.014
Benzo[a]anthracene	D	2.71	0.991	22.0	36.4	91	26.8	1679	0.008	0.002	0.012
Chrysene	D	2.84	0.990	13.7	37.2	93	25.6	1609	0.008	0.002	0.023
Benzo[k]fluoranthene	D	3.42	0.992	11.1	35.0	88	23.2	1660	0.008	0.002	0.000
Benzo[a]pyrene	D	3.15	0.990	15.0	40.3	101	25.2	759	0.017	0.006	0.000
Benzo[g,h,I]perylene	E	2.82	0.999	0.3	42.9	107	24.4	244	0.054	0.016	0.019
Dibenz[a,h]anthracene	E	3.06	0.996	9.4	38.6	97	26.4	279	0.054	0.016	0.000
Indeno[1,2,3-cd]pyrene	E	2.86	0.996	5.9	41.4	104	20.0	253	0.054	0.016	0.000

(a) - Signal to noise = 10, and based on a 30x concentration factor
(b) - Signal to noise = 3, and based on a 30x concentration factor
(c) - Maximum concentration level, US Environmental Protection Agency.

Internal standards: A = Naphthalene–d8 B = Acenaphthene-d10 C = Phenanthrene-d10 D = Chrysene-d12 E = Perylene-d12

Method Detection limits

Estimated MDLs are based on a sample mass of 30 grams and a final volume of 1 cm^3, i.e. a concentration factor of 30. Under these conditions individual parent PAHs can be determined with the lowest quantifiable limit ranging from 0.004 mg/kg for naphthalene and 0.054 mg/kg for the 6-ring compounds. These practical quantification limits are well below the regulatory requirement of a total of 40 mg/kg, as specified in the Dutch soil standards. The MDLs ranged from 0.001 to 0.016 mg/kg, which was lower than the 0.066 mg/kg specified by the USEPA for individual PAHs and in most cases, lower than the 0.010 mg/kg required for chemical fingerprinting studies. The ASE-GC/MS method was found to be suitable for the application to hazard and advanced chemical fingerprinting.

Representativeness

The average PAH content of procedural blanks was obtained from values that were acquired over a period of one year. These values ranged between 0.000 and 0.093 mg/kg, which were all within the limit of 10 x MDL, except for phenanthrene, which was 31 x MDL.

Selectivity

A typical chromatogram for a PAH contaminated soil sample (SRM-103-100) is shown in **Figure 7.2**. This sample was chosen because it contains large quantities of a full range of pollutants and because this sample was contaminated by a petrogenic source, presenting large quantities of alkyl-PAHs and aliphatic hydrocarbons. Excellent separation is achieved between the large variety of contaminants and the separation between phenanthrene (8) and anthracene (9) is shown in the figure. This example illustrates the selectivity of the method to separate the target analytes from co-extracted compounds.

Specificity for alkyl substituted isomers

A high degree of specificity is required to be able to differentiate among various isomers, which is used to calculate source or weathering ratios. The selected ion chromatograms of isomers that are normally used for this purpose (naphthalenes, phenanthrenes and dibenzothiophenes) are shown in **Figures 7.3, 7.4 and 7.5**. The figure shows data obtained for two samples, namely the crude oil contaminated reference standard SRM 103-100 and a typical coal tar contaminated soil sample. The results in **Figures 7.3 – 7.5** illustrates the following:

- most isomers are well separated from co-extracted compounds and each other which allow the analyst to differentiate among most isomers
- the sensitivity of alkyl substituted isomers decrease with an increase in the degree of alkylation due to the pyrogenic profile of coal tar contaminated samples.

In the case of this specific coal tar contaminated sample the C_2-substituted isomer peak intensities were characterised by a very low signal to noise ratio. In samples with a low degree of contamination C_2-P, C_1-D and C_2-D isomers peaks could not be detected at all. The conclusion is that the calculation of reliable source and weathering ratios, e.g. C_2-P/C_2-D and C3-N/C2-P respectively, are only possible in samples with a high degree of contamination.

The analyses of typical soil and sediment samples

Various soil and sediment samples obtained from different industrial areas were analysed for this purpose using PLE and GC/MS analysis. Sediment samples were obtained in a wastewater channel flowing from an industrial site. The site history of the sampling points revealed that coal tar spills occurred at these sites over the last few years and were

contaminated with PAHs. The drill-core samples were collected at intervals of one meter, i.e. (a) is taken 1 meter below the surface, (b) is taken 2 meters below the surface etc. The results for the 16 priority PAHs found in these samples are given in **Table 7.4**. The concentrations of individual PAHs found in the samples varied from 0.05 to 396 mg/kg. Different trends were observed for the three different boreholes, No 1 - 3. In the case of Sample No 1 contamination was mainly present in the top layer of the soil, with a gradual decrease in PAH concentration deeper down. The trend in borehole No 2 was exactly the opposite, namely a relative low concentration of PAHs on the surface, with an increase in PAH concentration with an increase of depth. In bore hole No 3 there was first an increase and then a decrease in PAH concentrations with an increase of depth. PAHs were also found in certain sediment samples. The concentration of PAHs in the sediment samples was relatively low and the heavy PAHs were found to be more abundant. The results are in agreement with the theory that heavy PAHs have a high fugacity in water and will tend to partition onto sediments.

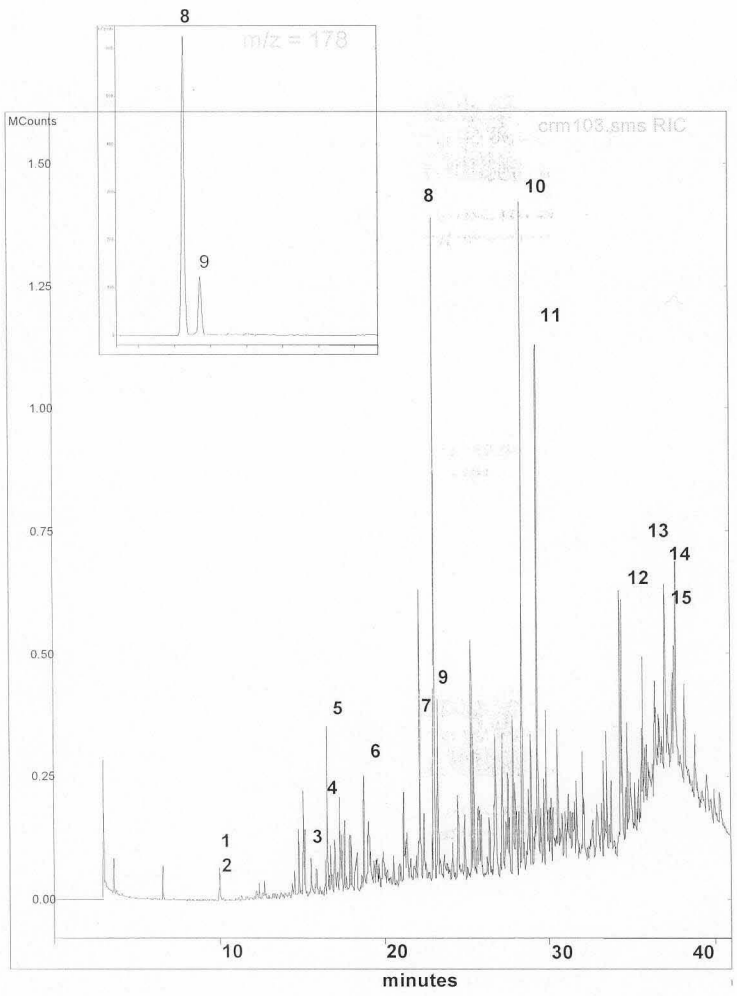

Figure 7.2: Total ion chromatogram of a contaminated soil extract – SRM 103-100: : (1)d10-naphthalene (2) naphthalene (3) d8-acenaphthene (4) acenaphthene (5) acenaphthylene (6) fluorene (7) d10-phenenthrene (8)phenenthrene (9) anthracene (10) fluoranthene (11) pyrene (12) d12-chrysene (13) chrysene (14) d12-perylene (15) benzo[a]pyrene. Selected ion current (m/z = 178) for phenanthrene and anthracene shown in the window at the top to illustrate the spesificity.

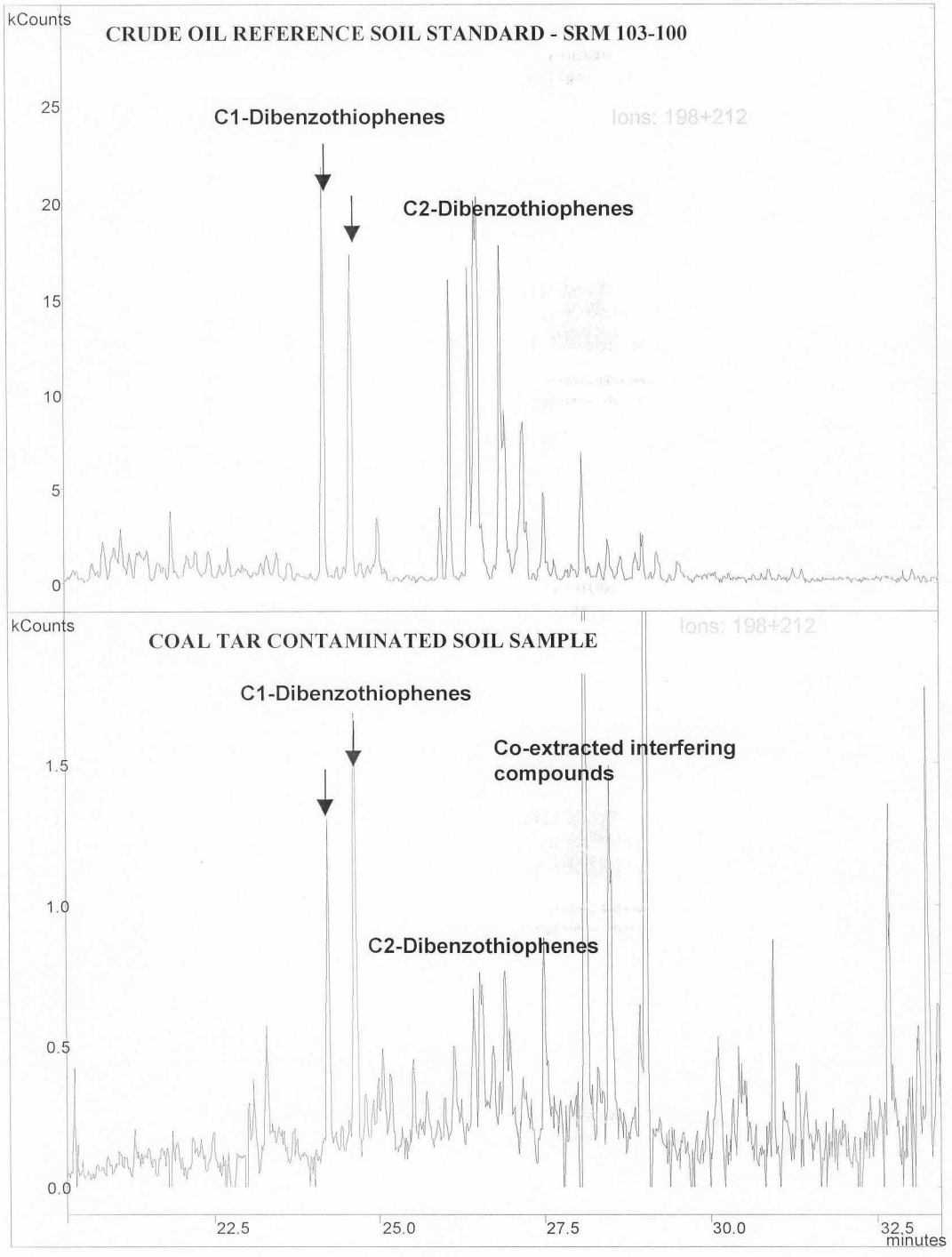

Figure 7.3
: Selected Ion Current plots for alkyl substituted dibenzothiophene isomers

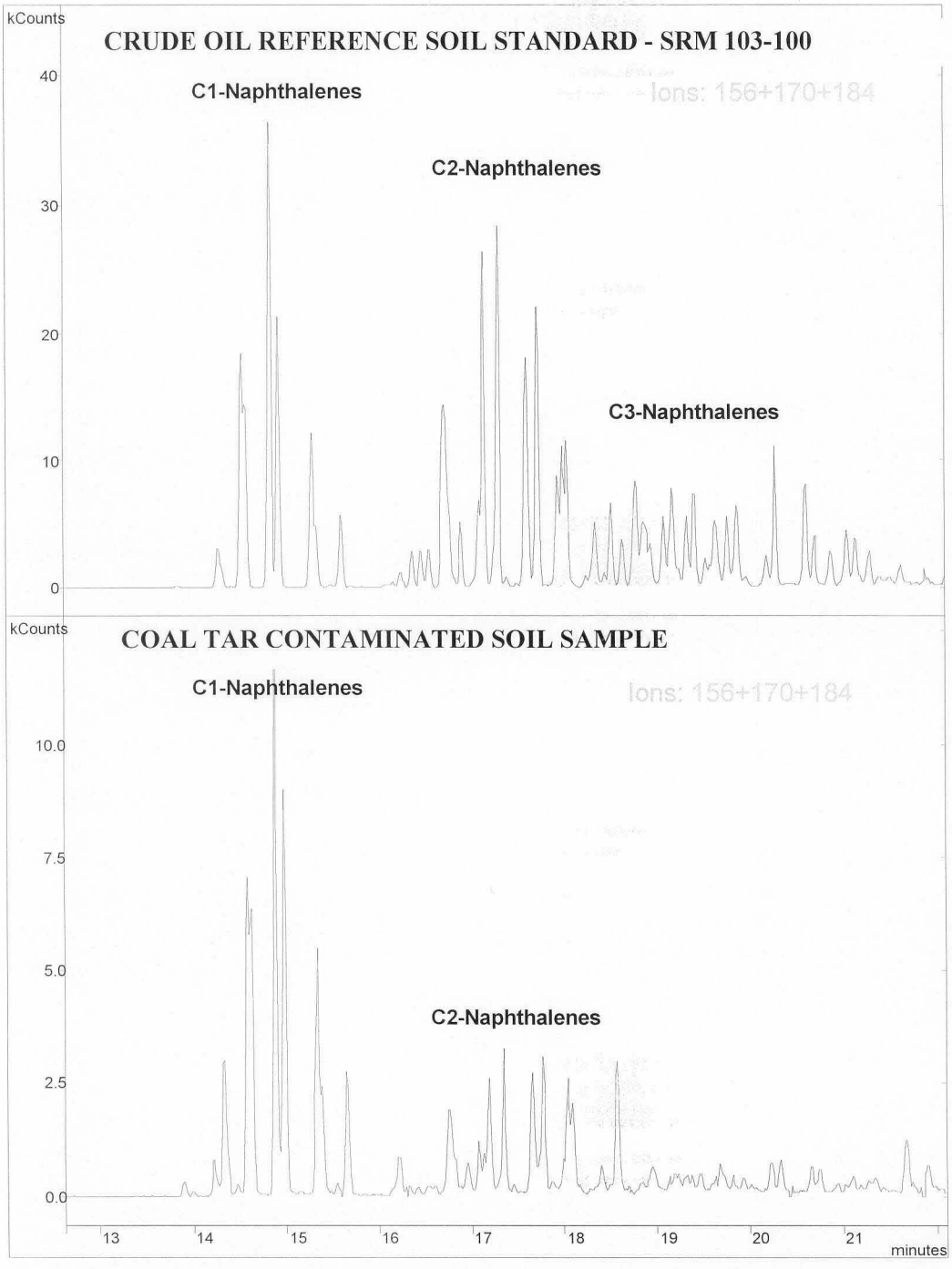

Figure 7.4: Selected ion current plots for the alkyl substituted naphthalene isomers

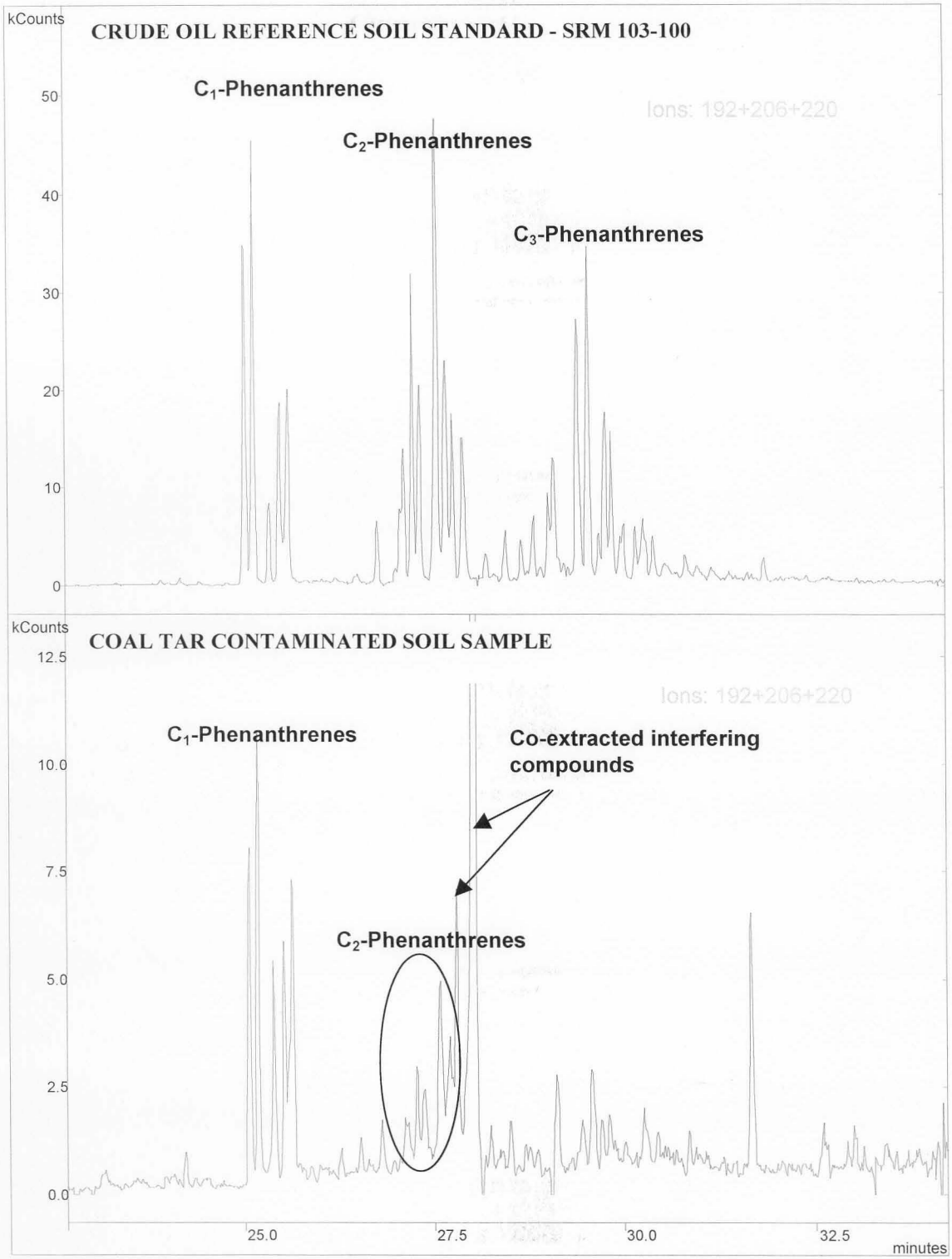

Figure 7.5: Selected Ion Current plots for alkyl substituted phenanthrene isomers

As coal tar is the suspected source of contamination, a relatively high abundance of FL and PY were found. The results for soil samples that were collected in an unpolluted area but close to an industrial site, indicate that background levels of PAHs in the area are generally < 0.08 mg/kg. These values are low enough to allow the detection and characterisation of coal tar pollution.

Critical stages in the analysis procedure

Sampling and sample pretreatment

The most critical factors affecting the stability of PAHs in soils is vaporization and photo-degradation. Transportation and storage precautions must include cooling to below 5 °C and light must be exclude to avoid photo-degradation.

Sample purification and enrichment

It is critical to remove the polar organic substances from the DCM extract to limit matrix interference and ensure high quality results

Sample extraction

As contamination is always a factor in trace analysis, the extraction cells and glassware should be thoroughly cleaned before use and glassware must be treated in a muffle furnace at 450 °C to remove any traces of contamination from the glass surface. Only solvents of a high analytical purity should be used, as the extraction step is followed by an evaporation step. The solvent purity and equipment contamination was checked by performing a procedural blank in parallel with samples.

Sample clean-up

Adsorbents that are used for sample clean-up, such as silica gel, must be purified from contaminants by washing with pure solvent. The quality of the adsorbent is also important, as it may alter the selectivity of the clean-up step.

Standards

The storage of certified reference soil standards is critical. These standards must be stored in a refrigerator below 5 °C to prevent evaporation.

CONCLUSIONS

The PLE extraction method followed by GC/MS was validated during this investigation and found to be suitable for the determination of PAHs in soil samples in µg/kg to mg/kg range. The detection limits of the method were well below the soil standards specified by the USEPA. Based on the detection limits, selectivity and specificity, the method was also found to be suitable for advanced chemical fingerprinting. In most of the soil samples that were investigated during this study it was possible to distinguish between petrogenic and pyrogenic profiles, even at low levels of contamination (< 1 mg/kg). The detection of isomers of C_2- to C_4-alkyl-PAHs was, however, very limited due to the low abundance of these compounds found in the coal tar polluted soil samples. Due to a lack of data for the higher degree of alkyl-PAHs in slightly contaminated samples, reliable source and weathering ratios could not be determined.

For advanced chemical fingerprinting, where lower detection limits are required, the method detection limits can be improved by:

- increasing the sample size to 30 grams
- reducing the final volume to 250 µl
- acquiring the MS spectra in the SIS mode.

Implementing these changes will decrease the detection limit quoted in **Table 7.2** by a factor of between 200 and 600, but with the disadvantage of also increasing the spectral noise.

Table 7.4. Results for the 16 priority PAHs from various borehole samples, expressed as mg/kg

		N	AC	AE	F	P	A	FL	PY	BA	C	BK	BeP	BP	IP
INDUSTRIAL SOIL SAMPLES															
	Depth														
No 1(a)	1 m	3.69	114	87	39.5	726	149	768	641	--	353	181	256	234	188
No 1(b)	2 m	1.20	9.2	24.2	8.1	180	23.5	121	93	--	52	72	41	30	24
No 1(c)	3 m	0.61	0.60	1.07	0.87	10.9	0.64	6.07	4.09	2.06	1.89	2.42	1.54	0.00	0.00
No 1(d)	4 m	0.00	0.00	0.00	0.00	1.44	0.00	1.00	0.78	0.00	0.00	0.00	0.00	0.00	0.00
No 1(e)	5 m	0.00	0.00	0.00	0.00	0.83	0.00	0.78	0.69	0.00	0.00	0.00	0.00	0.00	0.00
No 1(f)	6 m	0.00	0.00	0.00	0.00	0.61	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 2(a)	1 m	1.91	2.44	0.78	0.00	4.30	1.22	5.84	4.88	2.56	2.78	6.00	3.94	3.47	3.01
No 2(b)	2 m	2.90	9.20	1.28	0.00	9.51	4.94	27.5	24.7	6.81	16.5	19.7	9.10	6.60	5.20
No 2(c)	4 m	2.90	10.9	4.93	0.00	46.7	9.00	43.8	33.0	18.9	19.8	7.33	11.4	8.70	7.20
No 2(d)	5 m	23.0	5.43	46.4	10.9	193	31.6	62.6	37.5	7.73	8.06	5.60	3.99	2.56	2.24
No 2(e)	6 m	56.2	4.21	72.2	45.0	164	30.5	37.6	21.1	2.30	3.34	2.75	1.64	1.63	1.48
No 3(a)	1 m	2.29	6.04	0.97	0.00	14.6	3.49	25.8	20.6	11.2	13.4	18.5	12.0	9.62	7.75
No 3(b)	2 m	4.17	7.10	1.33	0.00	8.65	0.00	14.1	11.5	6.95	8.36	9.81	9.42	5.73	5.13
No 3(c)	3 m	1.35	3.80	0.44	0.00	5.51	0.00	8.08	6.68	3.71	4.75	8.67	3.87	0.00	3.07
No 3(d)	4 m	4.80	7.18	2.37	0.00	8.71	2.60	14.7	12.6	7.80	9.70	14.3	9.99	8.51	6.70
No 3(e)	5 m	4.30	29.9	2.32	0.00	27.1	14.8	86.1	71.7	44.0	51.0	57.8	44.1	31.3	22.2
No 3(f)	6 m	7.20	62.8	23.8	8.55	91.8	42.8	225	195	91.4	101	97.6	66.2	42.8	31.0
No 3(g)	7 m	5.73	84.8	63.5	0.00	181	74.2	352	293	109	113	110	64.3	58.4	40.0
No 3(h)	8 m	11.9	84.6	79.1	0.00	250	85.6	396	329	130	130	41.4	71.0	59.6	42.5
No 3(i)	9 m	6.30	36.8	28.8	8.30	117	34.4	156	121	56.8	62.5	67.3	45.2	28.7	21.0
No 3(j)	10 m	8.30	37.8	24.1	0.00	114	33.2	158	126	57.9	65.3	24.4	43.9	30.9	21.5
No 3(k)	11 m	6.50	15.0	9.08	4.03	41.7	11.5	63.3	50.3	26.2	29.5	35.6	21.6	14.7	10.8
No 3(l)	12 m	4.11	17.1	14.6	5.97	52.9	16.1	87.2	66.3	27.6	31.1	32.3	21.0	15.4	11.0
SEDIMENT SAMPLES															
No 4(a)		0.00	0.07	0.05	0.00	0.00	0.00	1.67	0.77	0.93	1.00	1.81	2.00	0.00	0.00
No 4(b)		0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.19	0.15	0.00	0.00
No 4(c)		0.00	0.17	0.19	0.00	1.15	0.00	4.76	3.26	1.27	2.98	4.50	5.65	0.00	0.00
No 4(d)		1.49	0.54	0.96	0.32	4.89	1.42	14.6	11.5	9.12	9.80	12.9	17.1	0.00	0.00
No 4(e)		2.44	0.56	2.78	2.30	22.5	5.98	52.4	39.2	21.2	22.5	30.1	3.85	0.00	0.00
No 4(f)		0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.04	0.00	0.00	0.00	0.00	0.00	0.00
No 4(g)		0.74	0.00	0.00	0.00	0.00	0.12	1.57	0.91	0.14	0.13	0.18	0.10	0.00	0.00
SAMPLES FROM UNPOLLUTED AREAS															
No 5(a)		0.02	0.00	0.08	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 5(b)		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 5(c)		0.02	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 5(d)		0.01	0.00	0.00	0.00	0.00	0.01	0.03	0.03	0.00	0.00	0.00	0.00	0.00	0.00
No 5(e)		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 5(f)		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No 5(g)		0.03	0.00	0.00	0.00	0.03	0.00	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00
No 5(h)		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 7.5: Summary of ASE-GC/MS analytical method performance

Performance Criteria	Poor	Not acceptable	Acceptable	Excellent
Accuracy			x	
Repeatability			x	
Sensitivity (DL and QL) as required by USEPA				x
Sensitivity (DL and QL) as required for Advanced chemical fingerprinting		x (for slightly contaminated samples)	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	
Suitability for Chemical and Hazard Characterisation			x	