Pressurised Liquid Extraction of Polycyclic Aromatic Hydrocarbons from Soil and Sediment Samples

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Summary

Pressurised liquid extraction (PLE) is essentially an analyte- and matrix-independent technique. It provides cleaner extracts than the time-consuming classical procedures. In this study, PLE was miniaturised and performed in a stainless-steel cell of 10 mm x 3 mm I.D. 50 mg amounts of the solid samples were packed in the holder. After being subjected to the PLE procedure, 50 out of 100-µl extracts were introduced into GC–MS using large-volume injection (LVI). The new device was applied to the determination of polycyclic aromatic hydrocarbons (PAHs) in soils and sediment. Evaluation of the pressure and temperature during extraction, and extraction solvent volume and nature (typical variables affecting the PLE efficiency) resulted in selection of 100 µl of toluene at 15 MPa for 10 min in a staticdynamic mode using not more than 50-mg samples. Clean-up or filtration of the extracts was not required.

Detection limits for the complete at-line PLE–LVI–GC–MS procedure were below 9 ng/g soil for the thirteen most volatile EPA PAHs in real soil samples. Repeatability (expressed as RSD values) was better than 15%. Comparison of PLE with Soxhlet or liquid-partitioning extraction showed that the efficiency of PLE is the same or better for both spiked and nonspiked samples.

1 Introduction

Classical methods for the determination of trace pollutants in environmental solid samples are usually laborious and time-consuming multi-step procedures. They usually require many manual sample handling steps [1,2]. At line or on-line coupling of these steps is one of the main goals of modern analytical chemistry. Several examples of on-line clean-up procedures can be found in the literature [3,4 and references therein]. However, the analyte extraction itself is usually regarded as the most difficult step when developing completely on-line and/or automated procedures for solid or semi-solid environmental samples.

Because of the low levels at which microcontaminants are generally present in the environment and the variety of the samples, the selected extraction technique should be essentially exhaustive [5] and, preferably, easy to standardise. This explains the general

preference for techniques such as Soxhlet or Soxtec extraction [6] rather than more selective, but also highly analyte- and/or matrix-dependent, techniques such as supercritical fluid extraction [7]. Microwave-assisted solvent extraction (MASE) and pressurised liquid extraction (PLE) are generally faster, and less analyte- and matrix-dependent and provide cleaner extracts than conventional methods involving heat treatment. These characteristics have caused both techniques, and specifically PLE, to be frequently used as extraction procedures for a variety of environmental applications. However, they are always carried out off-line. The at-line, or on-line, coupling of MASE or PLE with the separation-plus-detection part of the system would require miniaturisation of the extraction devices and, if at all possible, no additional clean-up step. Regarding the latter aspect, PLE has the advantage over MASE that no additional filtration step is required. The acceptation of PLE as an EPA method [8] can be taken as an additional stimulus to consider this procedure.

In this paper, a laboratory-made miniaturised device for PLE of microcontaminants from solid samples is described. It was used in a static-dynamic extraction procedure, which was optimised with regard to organic solvent choice, temperature and pressure. The performance of the novel set-up, which was combined at-line with gas chromatography–mass spectrometry (GC–MS), was evaluated. The complete procedure was applied to the determination of PAHs in soils and sediment. The results were compared with those of more conventional procedures.

2 Materials and Methods

2.1 Chemicals

The sixteen EPA PAHs [9,10] were selected as test compounds (see Table 1). Working standards, which were also used for spiking purposes, were prepared from individual PAH standards (Sigma-Aldrich, Zwijndrecht, The Netherlands and Supelco, Bellefonte, PA, USA) at 5 µg/ml of each analyte in toluene. One stock solution containing only naphthalene and pyrene was used for the initial PLE optimisation. A second stock solution contained all EPA PAHs, except phenanthrene, and was used once all the experimental PLE variables had been optimised. In all cases, phenanthrene was used as an internal standard (1 µg/ml in toluene) and phenanthrene-d10 (98%, MSD Isotopes, Merck Sharp & Dohme, Montreal, Canada) as external standard (1 µg/ml in toluene). The internal standard was added to the samples just before PLE, Soxhlet extraction or liquid-partitioning. The external standard was added to the final extracts just before the chromatographic analysis. Pro-analysis *n*-hexane and pesticideresidue-grade methanol and toluene were obtained from J.T. Baker (Deverter, The Netherlands). *n*-Hexane was glass-distilled prior to use.

An organic and a sandy soil from the Amsterdam region (The Netherlands) and a Haringvliet river sediment (Den Bommel, The Netherlands) were used as samples. They were air-dried and sieved to 270 mesh. This fraction was used for subsequent studies. Properties of the soil and sediment fractions used were determined by adequate standard methods.

2.2 Instrumentation and Procedures

A cartridge holder previously used for the removal of water from solid-phase extraction (SPE) desorption solvents in on-line SPE–GC [12,13] was modified and adapted for the PLE experiments. The extraction cell was built-in in a heatable 10 mm x 3.0 mm I.D. stainlesssteel holder (Figure 1). It was sealed by a 5-µm stainless-steel frit (Sigma, Zwijndrecht, The Netherlands) at its upper end (in the direction of solvent flow) to prevent clogging of the exit tubing and valve by soil/sediment particles. This frit was never removed during the entire study. No clogging problems of either frit or tubing were observed during 3 months of constant use. Once the sample and the internal standard had been put into the cell, the lower part was sealed by a laboratory-made manually removable 5-µm stainless-steel screen. Two PTFE rings positioned at the top and bottom ends of the extraction cell allowed to fix it to two adapters for connection to standard Valco nuts and stainless-steel tubing. The two adapters and the cell were pressed together to achieve leak-tightness by tightening a large nut at the top of the cartridge. The extraction cell was surrounded by a stainless-steel ring to which a resistive wire and a thermocouple were attached for heating and temperature control,

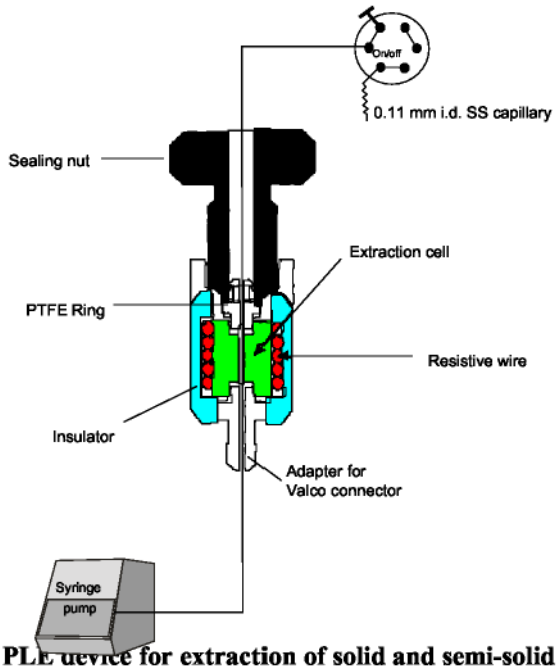

Figure 1. PLE device for extraction of solid and semi-solid samples.

respectively. Isolation was achieved by a ceramic ring around the stainless-steel ring [12]. The temperature was programmed by defining a start temperature, a temperature rate, a final temperature and a hold time in a controller. The temperature programme was manually started at the beginning experiment. A Phoenix 20 CU syringe pump Strumentazione, Italy) was used to deliver the extraction solvent. The extraction cell was placed between this pump and a 6-port automated Valco valve (Must HP6, Spark Holland, Emmem, The Netherlands) for direct control of the pressure in the cell via the pump. All tubing was of stainless-steel. Tubing connected to the extraction cell was 0.13 mm I.D. and tubing leading from the valve port to the vial for sample collection was 0.20 mm O.D. and 0.075 mm I.D. to improve heat dissipation before solvent collection.

In a typical experiment, 50 mg of a spiked sample were weighed into the extraction cell (85% of its total volume) already provided with the stainless-steel frit. The internal standard was added before closing the cell with the stainless-steel screen. Then, the cell was mounted in the device and the selected solvent was pumped to fill the cell and the lines from the pump to the valve. Next, the solvent was pressurised to the selected pressure using the constant pressure mode. Simultaneously, the temperature programme was started to heat both the sample and the extraction solvent. After a preselected static extraction time, the valve was switched to allow the extraction solvent to leave the cell. An additional volume of solvent was briefly then pumped through the cell and the lines (dynamic extraction step) to ensure proper purging of the sample and the lines. Blank samples (Soxhlet-cleaned silica) showed that no additional clean-up or reconditioning was required between consecutive extractions when using this combined static-dynamic extraction.

The suitability of PLE for PAH extraction was evaluated by analysing organic soil samples spiked at six concentration levels of 10-250 ng/g soil. Spiked samples were prepared by adding the proper amount of the PAHs dissolved in methanol to a soil or sediment sample (1:1, w/v). The mixture was homogenised by 2 min shaking and the methanol allowed to evaporate in a fume hood. The analyses were performed 24 h after spiking the samples.

Because of an intended comparison of the different extraction methods assayed, the analytical conditions in these experiments were initially kept as identical as possible to those used in PLE. Therefore, the finally selected PLE extraction solvent was used in all cases. In the case of Soxhlet extraction, 0.5-g aliquots of the spiked soil in the 10 x 50 mm thimble were spiked with an amount of internal standard to provide a final concentration per gram of soil or sediment similar to that used in PLE. The sample was then extracted for 6 h with 40 ml of the selected solvent. With liquid-partitioning, 100-mg aliquots of the spiked soil were also spiked with the internal standard to provide a final concentration per gram of soil similar to that used in PLE, and extracted by 10 min shaking with the selected solvent.

All experiments were carried out in triplicate. Extracts from the PLE experiments were coloured but transparent, i.e. they were not cloudy and no precipitate was found in the solutions. They were therefore analysed without any additional clean-up. Because of the intended comparison of the different extraction methodologies, Soxhlet and liquidpartitioning extracts were also analysed without any additional purification.

2.3 LVI–GC–MS

PAHs determination in the collected extracts was carried out by capillary gas chromatography (HP 6890 Series, Hewlett Packard, Palo Alto, CA, USA) with MS (HP 6890 Series) detection in the selected ion monitoring (SIM) mode. 50-µl amounts of the extract were injected in the at-once large volume injection (LVI) mode on a programmed temperature vaporising (PTV) injector (Optic 2, Ai Cambridge, Cambridge, UK) provided with a packed ‘A’ type liner. GC separation was performed on a Restek XTI-5 capillary column (30 m x 0.25 mm I.D., 0.25

µm film thickness). Helium was used as the carrier gas at a column head pressure of 97 KPa. The split flow was 120 ml/min. After solvent elimination, the PTV was heated at 7°C/s from 80°C to 300°C. The splitless time was 1.5 min. The column temperature was programmed from 103°C (4.5 min) to 280°C at 12°C/min. The final temperature was held for 12 min.

Identification of the target compounds was based on the simultaneous detection, at the appropriate retention time, of the chromatographic signals corresponding to the two *m/z* values selected for each congener (see Table 1 below), and on their ratios being within +15% of the previously calculated theoretical ratio. Quantification was based on the individual peak areas and the response factor of the individual compounds related to the selected external standard. Recovery of the internal standard (in all cases above 82%) was taken as a control parameter for the efficiency of the proposed extraction procedures. The PAH levels reported were not corrected for the recovery of the internal standard.

3 Results and Discussion

3.1 PTV Injection and GC–MS Analysis

The PTV injector was packed with so-called ´A´ type adsorbent, because this material is known to be inert for the present set of target compounds [13,14]. Optimisation of the injection procedure was performed according to a published procedure [15] with special attention for the maximum volume of solvent that can be rapidly injected without flooding the liner and the solvent elimination time.

Since non-volatile matrix constituents remain in the liner, GC (pre)column contamination is prevented [15-17]. When matrix components remain in the liner, analyte response can change [18,19] and quantification based on calibration plots obtained using a matrix similar to the sample is recommended [15]. In this study, differences in analyte response were also observed after the analysis of some real-life samples, although all invariably within the range of experimental errors (RSDs of less than 10%). That is, deactivation of the liner due to adsorption of non-volatile matrix components did not really affect the results when using the response-factor-based quantification procedure. In addition, no memory effects were observed when analysing pure solvent after a real-sample run. As regards the inertness of the packing material of the liner, it is important to add that over 230 analyses were carried out -with about 100 of these being analyses of real samples- with the same liner. The only problem encountered was some peak tailing for the most volatile PAHs eluting prior to phenanthrene in the final twenty analyses.

Analyte loss due to co-evaporation in the solvent elimination step was only observed for naphthalene, which gave a 59% (RSD=8% at 30 ng/ml level; n=4) response of that obtained by cold splitless injection. Other rather volatile PAHs gave satisfactory responses (acenaphthylene (83%), acenaphthene (111%), fluorene (106%) and phenanthrene (102%); the RSDs were 4-7% (n=4)) as well as the less volatile PAHs (94-108%; RSDs of 1-6% (n=4)).

Because of the complexity and the small size of the samples, and, moreover, the absence of a clean-up step, extracts were analysed using MS detection in the SIM mode, which allowed proper analyte recognition as well as quantification.

3.2 Optimisation of the PLE Parameters

Preliminary experiments were carried out to optimise the main parameters affecting the PLE efficiency. For this study, an organic soil spiked at 75 ng/g soil with naphthalene and pyrene was used.

The functionality of the extraction cell design was evaluated by measuring the actual temperature of the soil particles during heating. After being filled and placed in the holder, a thermocouple manufactured in-house was placed in the centre of the cell. The maximum temperature of the soil particles was found to be 240°C at a set value of 250°C. More importantly, the device allowed temperatures of 100°C and 150°C typically used in PLE experiments [8,20-22] to be reached within 4 and 6 min, respectively. In other words, the heater was well suited for the present study.

As regards the preferred mode of PLE extraction, a smaller volume of organic solvent may be expected to be required for a static as compared with a dynamic extraction. The solvent volume required for transfer of the extract into the collection vial and rinsing the cell and connecting tubing was carefully optimised to keep the total volume amount to a minimum. Preliminary experiments carried out by extracting the organic spiked soil with *n*-hexane at 80°C and 15 MPa for 5 min showed that 75 µl of solvent extracted some 90% of both naphthalene and pyrene. An additional volume of 25 µl was added as a safety margin. Further increase of the total volume indeed led to higher recoveries (about 95% for 200 µl), while the final extract became more diluted. Therefore, a total solvent volume of 100 µl for the static-plus-dynamic extraction was selected for subsequent experiments.

As earlier papers on ASE™ (PLE as commercialised by Dionex) [20-22] or laboratory-made PLE [1,23] indicated, the influence of pressure was not impressive. As an example, results obtained for soil spiked with naphthalene and pyrene after being extracted under various pressures with toluene for 10 min at 180°C are shown in Figure 2A. Differences observed in the investigated pressure range were within the experimental error. A pressure of 15 MPa was selected for further work because it allowed the use of a standard switching valve and good control of the elution flow rate at 100 µl/min from the extraction cell after the dynamic extraction. Because the elution flow rate has an insignificant effect on the extraction yield [23], it was not separately optimised. The flow rate of 100 µl/min was used in further experiments. Besides, this flow rate allowed accurate collection of the 100-µl extracts in an autosampler vial for the subsequent LVI–GC–MS analysis.

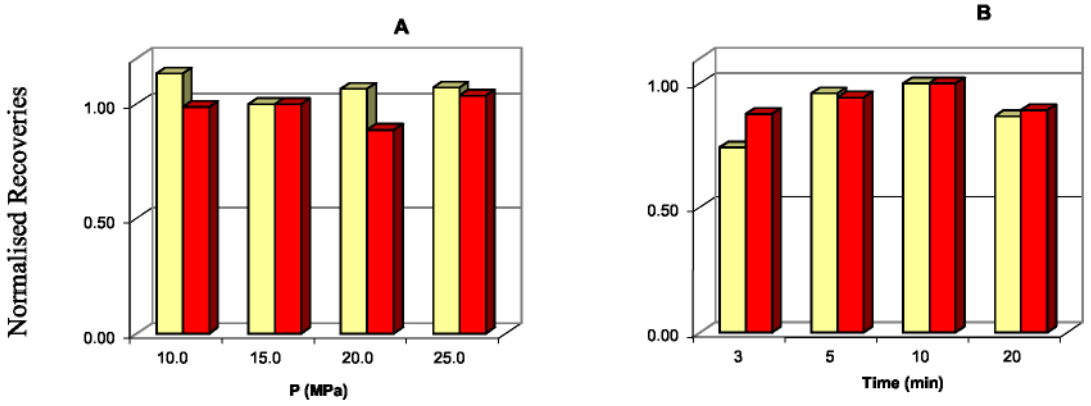

Figure 2. Influence of (A) extraction pressure and (B) extraction time on the recoveries of naphthalene (■) and pyrene (■)spiked to an organic soil at the 75 ng/g level. The recoveries were normalised against the yields found when the soil was extracted with toluene for 10 min (A) at 180°C and 15 MPa, and (B) at 200°C and 15 MPa.

The natures of the extraction solvent and the temperature have, for obvious reasons, a profound effect on PLE efficiency [1,21-23]. In this study, *n*-hexane and toluene were tested, which were selected on the basis of their frequent use as extraction solvents for PAH from environmental analysis [22,24,25]. Temperature was evaluated in the ranges 70–90°C and 175–200°C for *n*-hexane and toluene, respectively (pressure, 15 MPa; static extraction time of 10 min). In general, increasing the extraction temperature results in higher recovery independent of the solvent. Not unexpectedly, the recoveries for PAHs were higher for toluene extraction than for *n*-hexane extraction. The highest recoveries were observed at 90°C for *n*-hexane; no further improvement was observed at higher temperatures. In the case of toluene, best conditions were found at 200°C. Consequently, toluene at 200°C was selected as extraction solvent for subsequent experiments.

As regards the static extraction time, Figure 2B summarises data for the same analytes in the range 3–20 min. The normalised values show that for both compounds, the recoveries distinctly increased with time from 3 to 10 min, while no further improvement appeared at 20 min. A static extraction time of 10 min was selected for subsequent experiments.

Finally, it should be added that, in the present set-up, no additional cooling of the transfer lines connecting the extraction cell and the microvials was provided. Obviously, heat exchange of the heated and pressurised extraction solvent with the surrounding air via the 0.20 mm O.D. outlet tubing is rather rapid. No differences in naphthalene and pyrene yields were observed in experiments when the extraction solvent was collected directly in the microvial or in a small-volume solvent trap. This is a distinct advantage of our miniaturised PLE compared with other (large scale) devices, with which cooling of the extraction solvent or collection in a sealed vial was mandatory [1,20-22].

3.3 Analytical Data

LVI–GC–MS of standard solutions resulted in linear calibration plots for all sixteen PAHs. For naphthalene, acenaphthylene and acenaphthene the tested range of 0.5-100 ng/ml led to regression coefficients better than 0.96 (n=7). Other PAHs had regression coefficients 0.994–0.999 (n=10) in the concentration range 0.05–500 ng/ml. The repeatability, which was determined by analysing a solution at the 0.5 ng/ml level, was satisfactory with relative standard deviations (RSD) of 1-10%. The experimentally determined limits of detection (LOD) were 0.3-0.5 ng/ml for the 3 early eluting PAHs, and substantially better, i.e. 0.04–0.1 ng/ml, for most other analytes. These results, which have been summarised in Table 1, clearly demonstrated that reliable quantification should be possible for PAHs at levels as are typically encountered in soil and sediments [15,21,22,24,26] even if only 50 mg of sample are used for an extraction.

The analytical performance of the at-line PLE plus LVI–GC–MS procedure for real-life samples was evaluated by analysing an organic soil spiked at six different levels (10-250 ng/g soil of each PAH). Three PAHs, benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(a)pyrene, were spiked at 10-fold higher levels to evaluate simultaneously if the proposed PLE procedure can also be used for heavily contaminated soils without any further modification. Three separate analyses were carried out for each of the six spiking levels, 24 h after spiking. Relevant analytical data are shown in Table 2. The total procedure showed good linearity over the whole test range for all target compounds with regression coefficients ranging from 0.95 to 0.99 (n=6). The experiments demonstrate that the present procedure is also suitable if individual PAH concentrations are in the 1-2 µg/g range. The repeatability of the whole analytical procedure was evaluated by analysing non-spiked (cf. footnote to Table 2) organic soil as well as soil spiked at the 150 ng/g level. The RSD data, which were essentially the same irrespective of the PAH concentration level, were 10% or better for all PAHs. This result is similar to or better than data reported for similar analyses using ASE and involving larger amounts of sample and solvent [2,22,26]. One may conclude that the proposed PLE plus LVI–GC–MS methodology shows fully satisfactory performance under conditions typically encountered in environmental PAH analysis.

TABLE 1. Analytical data for the LVI-GC-MS analysis of standard solutions.

Compound	Peak no.	tr (min)	m/z [1]	Regres. coeff. [2]	RSD [3] (%)	LOD [4] (ng/ml)
Naphthalene	1	4.14	128/102	0.96	8	0.5
Acenaphthylene	2	7.87	153/152	0.97	6	0.4
Acenaphthene	3	8.30	153/152	0.97	8	0.5
Fluorene	4	9.45	165/166	0.994	1	0.3
Phenanthrene (I.S.) [5]	5	11.51	178/176	0.995	5	0.1
Anthracene	6	11.61	178/176	0.998	8	0.1
Fluoranthene	7	14.04	202/101	0.999	2	0.05
Pyrene	8	14.49	202/101	0.999	2	0.06
Benzo(a)anthracene	9	17.03	228/226	0.999	10	0.09
Chrysene	10	17.11	228/226	0.999	10	0.07
Benzo(b)fluoranthene	11	19.20	252/250	0.999	2	0.09
Benzo(k)fluoranthene	12	19.25	252/250	0.998	2	0.04
Benzo(a)pyrene	13	20.05	252/250	0.999	8	0.1
Indeno(1,2,3-cd)pyrene	14	23.61	278/276	0.999	9	0.2
Benzo(ghi)perylene	15	23.77	278/276	0.999	6	0.3
Dibenzo(a,h)anthracene	16	24.60	278/276	0.998	2	0.3
Phenanthrene-d10 (E.S.)[6]	5	11.50	188/ 94	-	-	-

[1] Two most abundant ions; [2] Regression coefficient of response vs. area plot (see text for range); [3] n=3 at 0.5 ng/ml; [4] Experimentally determined limit of detection (S/N, 3:1); 50 µl injected; [5] Internal standard; 6 External standard

3.4 Different Matrices

To further illustrate the potential of the proposed method, the new set-up was used to extract PAHs from three samples with widely different physicochemical characteristics, an organic soil, a sandy soil and a sediment. The soils and sediment were analysed both without spiking and with spiking at a realistic level of 75 ng/g soil. In all cases, the performance of the PLE-based procedure was compared with results obtained by liquid-partitioning and Soxhlet extraction of the samples. According to expectations, essentially the same results were obtained with the non-spiked and spiked samples. As an example, Figure 3 summarises the results for the former set of samples. The mean concentrations of each PAH as calculated by three separate analyses of each soil or sediment are shown for the liquid-partitioning, PLE and Soxhlet extraction procedures. Not unexpectedly, closely similar results were found for the target compounds with all three extraction methods when extracting the spiked sandy soil. However, for more complex samples, i.e. with higher organic content, liquid-partitioning was generally found to be less efficient than Soxhlet or PLE for the extraction of the PAHs. The stronger adsorption of the investigated PAHs to the organic matter of the organic soil and the sediment can be regarded to be responsible for the relatively low liquid-partitioning yields in these cases. On the other hand, the PLE extraction efficiency was found to be similar, or even better (least volatile analytes) than that of Soxhlet extraction with these samples. Similar

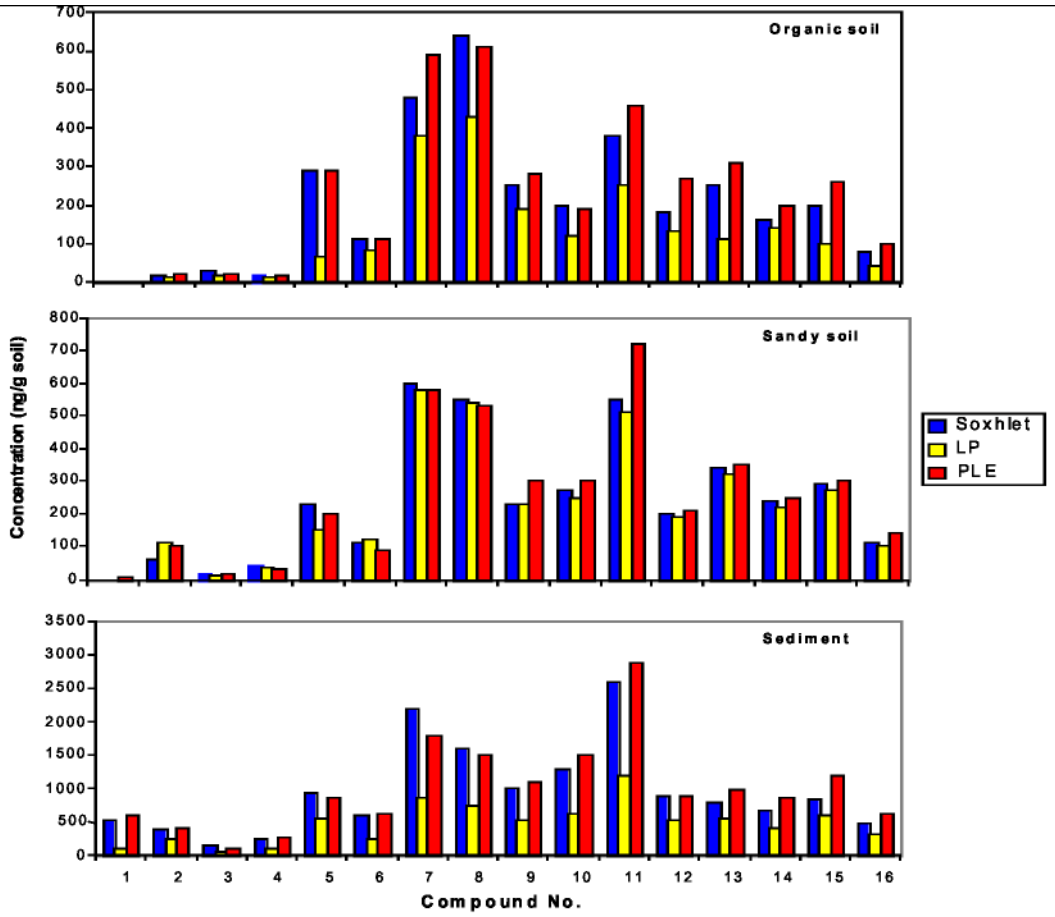

Figure 3. PAH concentrations determined by LVI–GC–MS in three samples after Soxhlet or liquid-partitioning. The concentrations were calculated from three separate analyses of each sample. See Table 1 for peak identification.

results were previously reported for spiked and contaminated soils [2,23] and certified sediments [21,22]. However, the differences observed in the present study were larger than those found in the literature with 20-30% improved results for the least volatile PAHs. This demonstrates the practicality of the miniaturised PLE device. This was also apparent from the RSD data recorded for the organic soil, which were substantially better for PLE (2-15%; n=3) than for liquid-partitioning and Soxhlet extraction (3-35% and 5-27%, respectively).

As an illustration of the GC–MS data obtained, Figure 4 shows the merged fragmentograms traces obtained for a standard PAH solution, and for the non-spiked organic soil. The typical quantitative results obtained for all samples can be read from Figure 4. In all instances fluoranthene, pyrene, benzo(b)fluoranthene and benzo(k)fluoranthene, were present in the highest concentrations. The limits of detection in the real-life samples, which are included in Table 2, were less than 9 ng/ g soil for all but the three late eluting PAHs for which values of above 30 ng/g soil were found. Again, this demonstrates that 50 mg of sample is amply sufficient.

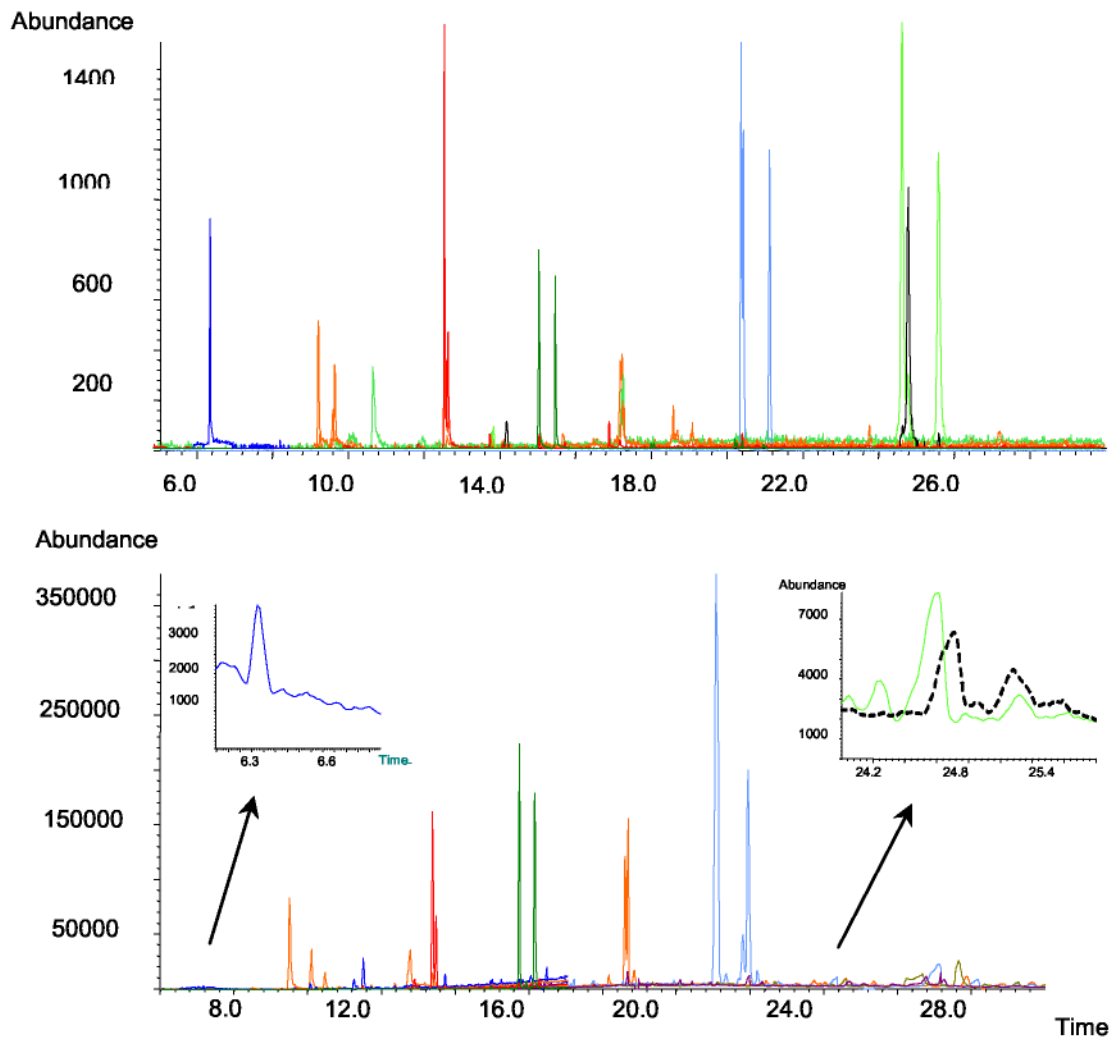

Figure 4. LVI–GC–MS of (A) standard solution of PAHs (concentration, 5ng/ml) and (B) PLE extract of the non-spiked organic soil. For selected *m/z* values and other experimental details, see Table 1 and text.

4 Conclusions

The practicality of a new miniaturised PLE combined at-line with LVI–GC–MS was demonstrated for the trace-level determination of PAHs in soils and sediment. The favourable conditions inherent to a PLE extraction (closed extraction vessel and extraction solvent at high pressure and temperature), explain the good extraction efficiencies compared with Soxhlet extraction and, much more so, liquid-partitioning. Compared with conventional PLE procedures, the present approach reduces sample volumes to about 50 mg, and solvent consumption to 100 µl rather than 20-200 ml. The reduced solvent volume, together with the use of LVI, allowed the at-line coupling of the extraction and separation-plus-detection steps since no concentration step is necessary prior to GC analysis. Even so, the detection limits for a large majority of the target analytes were 1-9 ng/g soil, and analytical performance was fully satisfactory (RSD below 15%).

As regards the maintenance of the PLE device, no clogging of either frit or tubing were observed during three months of constant use. However, due to the relatively high pressures used during extraction, the stainless-steel screen placed on the bottom part of the extraction cell was replaced every 3-4 extractions. The screen at the top of the extraction cell was never replaced. Memory effects were absent because of the so-called dynamic step which consisted of a brief flush of the cell and capillaries with a 25 µl of the extraction solvent. Leaking was detected -or, at least, suspected- when using extraction times of some 20 min which were much longer than conventionally required. Finally, the simple design of the miniaturised PLE device allowed the use of open microvials rather than large sealed vials for collecting the extractant.

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