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Review

# Current use of pressurised liquid extraction and subcritical water extraction in environmental analysis

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**Abstract**

This review updates our knowledge about pressurised liquid extraction (PLE) and subcritical water extraction (SWE), two sample preparation techniques which are increasingly used for the extraction of moderately and non-volatile organic pollutants from a variety of solid and semi-solid environmental matrices. Parameters influencing the extraction yield and selectivity are discussed. The results deriving from the analysis of several different classes of compounds in a variety of matrices are compared with a reference method, e.g., Soxhlet extraction. PLE and SWE are both promising techniques due to the short extraction times and low solvent consumption. In addition, SWE offers a wide range of polarities by changing the temperature and can easily provide class-selective extraction by temperature programming and/or the addition of modifier(s). This indicates that, even though many applications have already been reported, more can be expected.


*Keywords:* Reviews; Pressurised liquid extraction; Subcritical water extraction; Environmental analysis; Extraction method

## Contents



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## 1. Introduction

As the knowledge about the fate and final consequences of organic pollutants in the environment increases, the number of trace pollutants that has to be monitored routinely in a wide variety of samples, increases dramatically. Simultaneously, there is a clear trend to reduce the maximum residue limits of these deleterious chemicals in different environmental matrices in an attempt to protect ecosystems and, especially, human health.

Classical methods for the determination of trace pollutants in environmental samples are usually multi-step procedures typically based on exhaustive extraction from the matrix and the subsequent removal of co-extracted material by successive clean-up steps prior to the actual analysis [1–3]. Such sample preparation involves a large amount of sample, sorbent(s) and high-quality organic solvents and requires much manual handling of the extracts. That is, these methods are expensive in terms of time and material consumption and sample throughput is too low to meet the challenges of modern environmental analysis. Developing faster, more cost-effective, and environmental-friendly procedures is, therefore, a pressing demand.

As an answer to such demands, several examples of automated clean-up procedures for the determination of microcontaminants in environmental samples can be found in the literature [4,5] (and Refs. therein). However, until recently complete on-line sample preparation methods have only been reported for aqueous samples [5,6]. The extraction step has been the critical part when developing similar approaches for solid and semi-solid samples. Because of the low levels at which the organic micro-contaminants are generally present and the variety of the matrices that have to be monitored, exhaustive [7] and easy-to-standardise extraction techniques are usually preferred. This explains the general preference for, e.g., Soxhlet and Soxtec extraction [8] over more selective and rapid, but also highly analyte- and/or matrix-dependent techniques like supercritical fluid extraction (SFE) [9]. In recent years, several novel extraction techniques have been developed in an attempt to overcome the main limitations of the conventional methods. In general, these alternative techniques allow a more efficient extraction of the analytes from the matrix by improving the contact of the target compound(s) with the extraction solvent which allows a reduction of both the extraction time and the organic solvent consumption and increases sample throughput. Enhanced extraction efficiency can be achieved by using microwave energy, as in the case of microwave-assisted Soxhlet extraction [10] or the more general microwave-assisted solvent extraction (MASE, also known as microwave solvent extraction, MAE) [11] (and Refs. therein), or by solvents at high pressures and temperatures, as in pressurised liquid extraction (PLE) or the closely related subcritical water extraction (SWE).

Many studies have demonstrated the feasibility of the new extraction techniques for the determination of different microcontaminants in a variety of (semi)-solid samples while fulfilling pressing demands such as fast and relatively analyte- and matrix-independent determinations and simplification of the subsequent clean-up steps by providing cleaner extracts than classical methods involving heat treatment. Regarding this latter aspect, PLE-based methods (including SWE) have the advantage over MASE that no additional filtration step is required which will be an additional benefit when considering automation and/or on-line coupling of the extraction and separation—plus—detection parts of the system.

The aim of this paper is to discuss the state of the art of PLE and SWE by reviewing the recent studies on these techniques for the analysis of organic trace pollutants in environmental samples. The basic set-ups and relevant experimental parameters affecting the extraction efficiency will be discussed. Special attention will be paid to recent trends in the application of the extraction techniques and their perspectives. Therefore, where several references were found to be available for similar studies, only the most recent one will be mentioned to avoid repetition and ensure complementarity to recent reviews by Camel [12] and Björklund et al. [13] for PLE of persistent organic pollutants (POPs) in environmental analysis. Finally, for obvious reasons, results related to endogenous pollutants were preferred to those corresponding to spiked compounds.

## 2. Basic experimental equipment and parameters

### *2.1. Pressurised liquid extraction*

The basic set-up for PLE, also known as pres-

surised fluid extraction (PFE), pressurised solvent extraction (PSE), accelerated solvent extraction (ASE) or enhanced solvent extraction [14], has previously been described in detail [13,15,16]. Briefly, it consists of a stainless-steel cell in which the sample is placed and kept at the selected temperature and pressure during the extraction, electronically controlled heaters and pumps for solvent delivery and a vial for the collection of the liquid extract. Fig. 1 shows a schematic of the basic PLE set-up. Most of the applications reported (ca. 70% of the references reviewed) were performed on a Dionex (Sunnyvale, CA, USA) ASE 200, until recently the only commercially available PLE system. With the Dionex ASE 200, one can reach temperatures up to 200 °C and pressures up to 21 MPa in extraction cells of 1, 5, 11, 22 or 33 ml. Up to 24 samples can be placed in the carrousel and the extracts collected in 26 vials of 40 or 60 ml, there being four extra vials for rinsing. For larger samples, the ASE 300 can be used. The same temperatures can be reached as with the Model 200 but only for pressures up to 10 MPa. Extraction cells of 34, 66 and 100 ml are available; 12 samples can be placed in the carrousel and there are 12 collection vials (plus one rinsing vial) of 250 ml. As an alternative to the Dionex systems, the so-called fast-pressurised solvent extraction (fast PSE) device from Applied Separations (Allentown, PA, USA) can be used. The system allows the parallel extraction of up to six samples in extraction cells of 11, 22 or 33 ml at temperatures ranging from 50 to 150 °C and pressures up to 15 MPa. In addition, some supercritical fluid extraction devices such as the SFX 3560DM (dual mode) from Isco (Lincoln, NE, USA) can be used for PLE. The maximum operating temperature in this system is 150 °C, but pressures of 52 or 70 MPa can be reached. The carrousel can hold 24 samples plus one blank, and extracts can be collected in 24, 20-ml vials with an additional four vials for washing and blank runs. Finally, it is noteworthy that other conventional supercritical fluid extractors have been used successfully for PLE of a variety of samples [14,17–19], and that only a few authors have built their own PLE systems [20,21]. Safety considerations related to the latter devices have been discussed elsewhere [16].

Since its introduction in 1995 [15,22], PLE has been shown to be a valuable, and in some cases superior [17,21], alternative to conventional methods such as Soxhlet, Soxtec or ultrasonic (USE) extraction for the isolation of micropollutants from (semi-)solid environmental matrices. The principle of PLE is simple. The sample placed in the extraction cell is extracted with an organic solvent at a temperature ranging from room temperature to 200 °C and a relatively high pressure (from 4 to 20 MPa) [23]. Raising the temperature increases the diffusion rates,

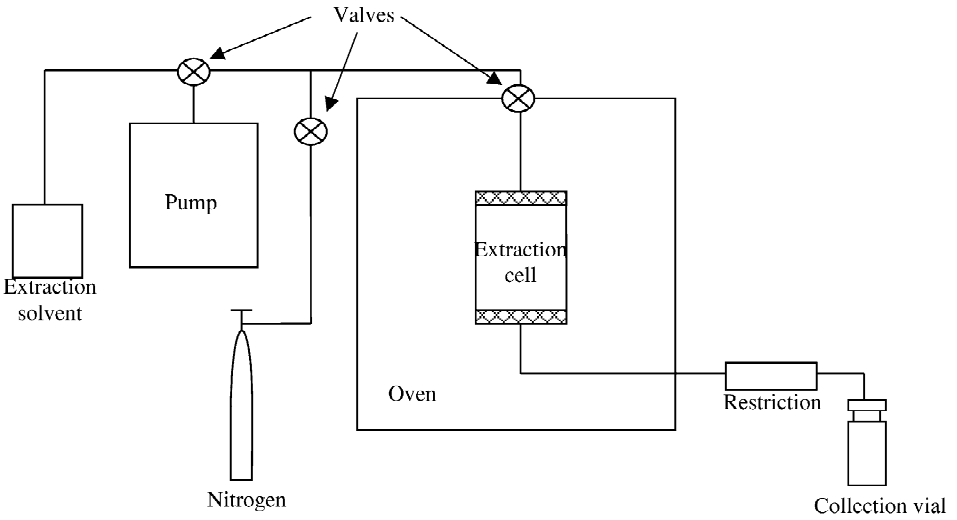


Fig. 1. Schematic of the basic set-up for PLE.

the solubility of the analytes and the mass transfer, and decreases the viscosity and surface tension of the solvents. These changes improve the contact of the analytes with the solvent and enhance the extraction, which can then be achieved more rapidly and with less solvent consumption compared with classical methods. On an average, 10–50 ml of the selected solvent and ca. 20 min are enough for quantitative PLE of POPs from soils and sediments, while 100–200 ml of solvent and 10–48 h are typically required for Soxhlet extraction. High pressure helps to force the solvent into the matrix pores and to keep the solvent in the liquid state at the operating temperature [20]. Of course, the thermal stability of the analytes of interest and, occasionally, the matrix can pose limitations on the experimental conditions.

PLE can be carried out in the static or the dynamic mode. So far, most of the PLE applications reported in the literature were performed in the static mode followed by a brief post-extraction dynamic flush with the organic solvent [14,17,21,24–27]. In this approach, the selected solvent is pumped to fill the cell containing the sample, which is kept for a specified time at the selected pressure and temperature. Next, the extraction solvent is transferred to a collection vial and the sample and the connective tubing are rinsed with a small volume of solvent at a preselected flow-rate. Including a final nitrogen purge (typically 1–2 min) to guarantee the complete removal of the solvent from the PLE system is current practice [25–30]. Dynamic PLE (also called dynamic high-pressure solvent extraction, DHPSE [20]) is usually carried out in SFE [18,19] or laboratory-made devices [20]. With this technique, the pressurised extraction solvent, which can be at room temperature [18–20] or be preheated to the selected temperature [31], is continuously pumped through the extraction cell at a constant flow-rate (typically 0.33–2.5 ml/min) for a specified period of time. According to Fick's law of diffusion, continuous contact between the sample and fresh solvent should accelerate the mass transfer. Consequently, the extraction efficiency should be enhanced and the extraction time reduced [20]. However, the results reported until now do not seem to support this conclusion. For example, Popp et al. used two consecutive 10-min static extractions with toluene at 14 MPa and 200 °C [8] for the determination of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) in fly ash, while Bautz et al. [20] proposed 30-min dynamic PLE with toluene–methanol (3:1, v/v) at 1 ml/min, at 15 MPa and 200 °C, while all other experimental conditions were rather similar in both cases. Despite the 10 more min used in the latter procedure, the PLE efficiency for the extraction of the 2,3,7,8-hepta- and octa-CDD/Fs was found to be 30–50% higher with the static PLE method. Similar results were found for the other PCCD/F congeners. On the other hand, Windal et al. [19] reported efficiencies for dynamic PLE of PCDD/Fs from this type of matrix with toluene at 5 MPa and 150 °C which were similar to those of Popp et al. [8], but provided the extraction time was increased to 120 min and 120 ml of solvent were used. It is important to add that, because of the strong adsorption of PCDD/Fs to the matrices used in these studies and the inherent complexity of the sample, a comparison of the performance of the two PLE modes should preferably be based on the direct comparison of sets of values systematically obtained by dynamic and static PLE of the same fly ash sample under identical experimental conditions.

The variables affecting the PLE process, such as the nature and temperature of the extraction solvent and the extraction time, can be derived from the principle of the technique. The nature of the extraction solvent and the temperature have, for obvious reasons, a profound effect on PLE efficiency. For PLE of organic trace pollutants from environmental samples, the same solvent can be used as for Soxhlet extraction [8,15,17,20,32]. As is also true for other extraction techniques used in environmental studies, mixtures of low- and high-polar solvents generally provide more efficient extractions of the analytes than single solvents, especially in the case of non-polar solvents such *n*-alkanes [13,33]. As an example, Fitzpatrick and Dean [33] reported an increase in the recoveries of bupirimate and ethirimol from aged soils ranging from 30 to 46% (values depending on the organic content of the sample; investigated range 3.2–83%) when using acetonitrile–dichloromethane (1:1, v/v) instead of iso-hexane as extraction solvent. Nevertheless, several studies show that more polar (and/or selective) solvents such as toluene should be preferred when extracting analytes from highly adsorptive matrices [8,19–21,25]. For example, the efficiency of toluene for the static PLE of naphthalene and pyrene freshly spiked to an organic soil

was reported to be 3 and 29% higher, respectively, than that obtained with *n*-hexane [21]. The effect became more pronounced when endogenous pollutants had to be determined. Bandh et al. [25] achieved an increase of the recoveries of endogenous polychlorinated biphenyls (PCBs) ranging from 5 to 28% when using toluene instead of *n*-hexane–acetone (1:1, v/v) for the PLE of sediments with high organic contents (>8.5%), although this less selective mixture provided quantitative recoveries of these micropollutants (83–113%) when extracting sediments with relatively low amounts of organics and soot carbon (<2.8%).

As quoted above, except for the limitations associated with the analysis of thermolabile pollutants such as explosives [32,34], and/or matrices, e.g., some synthetic polymers and plastics which will melt above a certain temperature [35,36], in general, higher extraction temperatures will cause enhanced sample wetting and better penetration of the extraction solvent and also higher diffusion and desorption rates of the analytes from the matrix to the solvent, i.e., an increase of the PLE efficiency. With *n*-hexane, the yield of naphthalene, freshly spiked to an organic soil, increased from 8 to 15%, when the temperature increased from 70 to 80 °C. No further improvement was found at 90 °C [21]. Actually, a temperature of 100 °C is often selected as *default value* and used for the PLE of POPs from a variety of matrices with different solvents [8,16,25,29,37], while mixtures containing toluene often require temperatures close to 200 °C to provide levelled off recoveries. For the latter solvent, Hubert et al. [23] reported a 2–3-fold increase for endogenous HCH isomers, DDT, DDE, DDD (which will be denoted as DDXs throughout the paper), hexachlorobenzene (Cl-Bz), PCBs and polycyclic aromatic hydrocarbons (PAHs) upon increasing the temperature from 100 to 140 °C. As an alternative approach to the use of high-temperatures, Yang et al. [38] reported an average increase of 15% of the PLE recoveries of a limited number of spiked PCBs and PCDD/Fs extracted from a fly ash at 100 °C by increasing the polarity of the extraction solvent by adding 5% of isopropanol to the toluene. Finally, extraction times used for PLE of microcontaminants typically range from 5 to 10 min and, not unexpectedly, better results are achieved by subjecting the matrix to several short consecutive static extractions than to a single longer static extraction. According to Björklund et al. [39], a second static step of 5 min increased the recoveries of some PCBs as much as 14%.

As regards other variables, pressure has been reported to play no role other than to keep the extraction solvent liquid at the high-temperatures used [15,16,21,31,35]. However, in applications involving wet samples [12,16] or highly adsorptive matrices [20], a high pressure can help to enhance the PLE efficiency by forcing the organic solvent into the matrix pores. This may explain why little effect of the pressure was observed during PLE of herbicides from dry soils, while in the case of moistened soils, increasing the pressure from 4 to 10 MPa was beneficial [40]. A similar trend was observed by Obana et al. [41] when extracting methamidophos and acephate from spiked orange juice dispersed in Extrelux as drying agent.

The flow-rate at which the extraction solvent is eluted in dynamic PLE has been found to have little effect in the range of 0.1–2.0 ml/min used in most of the applications [21,36].

The procedure used to pack the extraction cell may well influence the static PLE efficiency for semi-solid or heterogeneous samples. In the former case, a uniform distribution of the sample over an inert solid support such as sand prior to packing and (complete) filling of the extraction cell with the mixture to prevent separation of the sample from the support can be recommended [36]. For heterogeneous samples, grinding—typically to a 63–150-μm particle size [42]—will help to improve the homogeneity and, also, to shorten the diffusion pathways inside the matrix and increase the surface area. Filters or glass wool plugs should be inserted at both ends of the extraction cell to prevent blocking of the connective tubing by small particles. Finally, the possibility of swelling of the matrix upon introduction of the solvent, as can be the case for synthetic polymers and plastics [35,36], should be considered.

### *2.2. Subcritical water extraction*

Subcritical water extraction (SWE), also called hot water extraction, pressurised (hot) water extraction, high-temperature water extraction, superheated water extraction or hot liquid water extraction, is an

emerging technique based on the use of water as extraction solvent at temperatures between 100 and 374 °C (critical point of water, 374 °C and 22 MPa) and at a pressure which is high enough to keep it in the liquid state. Under these conditions, the dielectric constant of water, $\varepsilon$, i.e., its polarity, can easily (and dramatically) be lowered by increasing the temperature. Pure water at ambient temperature and pressure has $\varepsilon=79$, while increasing the temperature to 250 °C at a pressure of 5 MPa (necessary to maintain the liquid state) yields a significant reduction to about 27 [43]. This value is similar to that of ethanol at 25 °C and 0.1 MPa and consequently, low enough to dissolve many compounds of intermediate or low polarity. As explained above for PLE, increasing the temperature at moderate pressure also reduces the surface tension and viscosity of water, which results in an enhanced solubility of the analytes in this solvent. Therefore, while satisfactory recoveries (>90%) were reported for polar POPs such as phenols in water at temperatures below 100 °C [44], temperatures of about 200 °C are required for the quantitative extraction of more apolar compounds such as some pesticides [45,46] and low-molecular masses PAHs [47]. Temperatures of 250–300 °C were required for the extraction of PCBs [48] and high-molecular-mass PAHs [47,49] from soils and sediments. *n*-Alkanes were only extracted at temperatures higher than 300 °C [44,47,49].

Pressure has a limited influence on the solvent characteristics of water as long as it remains in the liquid state; for example, increasing the pressure from 0.1 to 10 MPa yields an increase of $\varepsilon$ of only 0.37 [43]. This means that it is possible to increase the pressure to avoid the formation of steam at the high-temperatures used in SWE without compromising the achieved decrease of polarity. Although changing the water from liquid to steam by decreasing the pressure at temperatures above 100 °C causes a reduction of $\varepsilon$ (e.g., from 27 to 1.1 when lowering the pressure from 50 to 2.5 MPa at 250 °C) [43], steam is corrosive and can degrade the analytes. Nevertheless, Yang et al. [48] reported a substantial reduction of the extraction time (from 15 to 5 min) required for the quantitative extraction of selected PCBs from soils when using steam conditions instead of SWE. Steam conditions were also necessary for the quantitative extraction of other highly hydrophobic pollutants such as PCDFs and polychlorinated naphthalenes (PCNs) from naturally contaminated soils [50].

To the best of our knowledge, up to now there is no specific device commercially available for SWE. That is, all published results were obtained using home-made devices by adapting a gas chromatographic oven [45,49–52], designing a new type of oven [53], in an SFE system [47,54] or in a commercially available PLE device [55,56]. Fig. 2 shows the basic arrangement typically used for continuous SWE. It consist of two pumps, one for deoxygenated water and one for the selected organic solvent, an oven containing a stainless-steel heating coil and the extraction cell, a stainless-steel cooling coil, and a vial for collection of the extracts. After filling the extraction cell with the sample and placing it in the oven, an experiment typically starts with pumping both the water and the organic solvent at their selected flow-rates until the pressure selected for SWE is reached. The actual extraction starts once the oven reaches the temperature selected for the SWE experiments. The water is heated up by passing it through a heating coil before reaching the stainless-steel extraction cell and is constantly pumped through the sample during the extraction in a way similar to that described for dynamic PLE, i.e., from bottom to top. The hot water containing the analytes is mixed with the organic solvent via a T-piece placed in the oven at the outlet of the cell. Before collection in a vial, the mixture is passed through a cooling coil (typically immersed in an ice bath) where the temperature decreases rapidly, water becomes a polar solvent and the less polar analytes previously dissolved in the SWE are partitioned to the less polar solvent preventing their adsorption to the tubing. After separation of both phases, the organic layer is removed and concentrated before further clean-up and analysis. More recently, in an attempt to minimise the dilution of the analytes in the liquid extract derived from this approach, solvent trapping was replaced by sorbent trapping on solid-phase extraction (SPE) disks or cartridges placed in-line [45,57] or on-line with the cell [58], or on solid-phase microextraction (SPME) fibers [52,55]. Although using internal standards can always be recommended in environmental analysis, the several partition processes involved in an SWE plus SPME

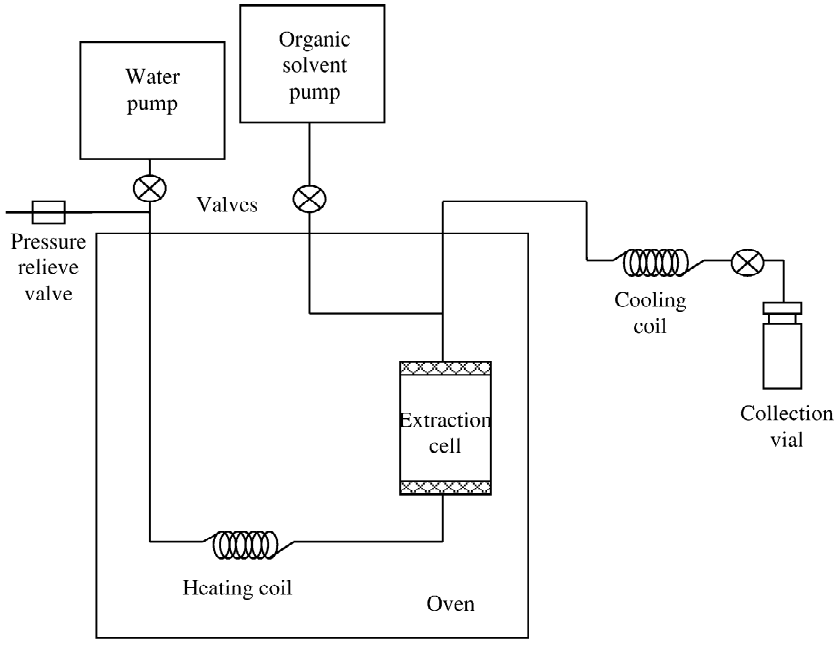


Fig. 2. Schematic of the basic set-up for SWE.

procedure makes their use mandatory to achieve proper quantification [52,59].

As can easily be concluded from the previous considerations, in addition to the static SWE approach [45,52,55,59,60], which is similar to that described for PLE but with water as extraction solvent, two types of continuous SWE are possible, regular extraction, in which the analytes are eluted at a selected temperature and pressure, and sequential extraction. In the latter approach, programming the temperature may lead to selective sequential extraction of compound classes of different polarity. Hawthorne et al. [47,49] investigated the feasibility of this type of approach for obtaining (relatively) matrix-free PAH extracts form urban air particulates under ''milder'' conditions, i.e., 250 °C and 5 MPa. Under these conditions, none of the straight-chain and branched alkanes extracted when using either Soxhlet extraction with acetone–dichloromethane (1:1, v/v), PLE with the same solvent mixture at 100 °C and 7 MPa, or pure $CO_2$ at 15 °C and 40 MPa, were extracted (Fig. 3). In other words, the 17 EPA PAHs investigated were selectively (but not quantitatively) extracted with SWE versus the bulk of the organic matrix. It is important to add that raising the temperature to the 300 °C required for the quantitative extraction of the PAHs caused an increase of the co-extracted alkane mass of only 13% compared to that leached by Soxhlet extraction of the same amount of sample. The authors concluded that, considering the wide range of polarities that can be generated by changing the temperature of the subcritical water, SWE looks to have a greater potential than SFE with $CO_2$ for selective analyte extraction.

## 3. PLE of organic pollutants from environmental samples

In the next sections, the experimental conditions for PLE of organic microcontaminants from a variety of environmental samples will be reviewed and the results obtained by various methods will be compared. Non-fatty and fatty samples are treated separately; the latter category will include biological matrices and food. In an attempt to simplify the comparison of the performance of various proce-

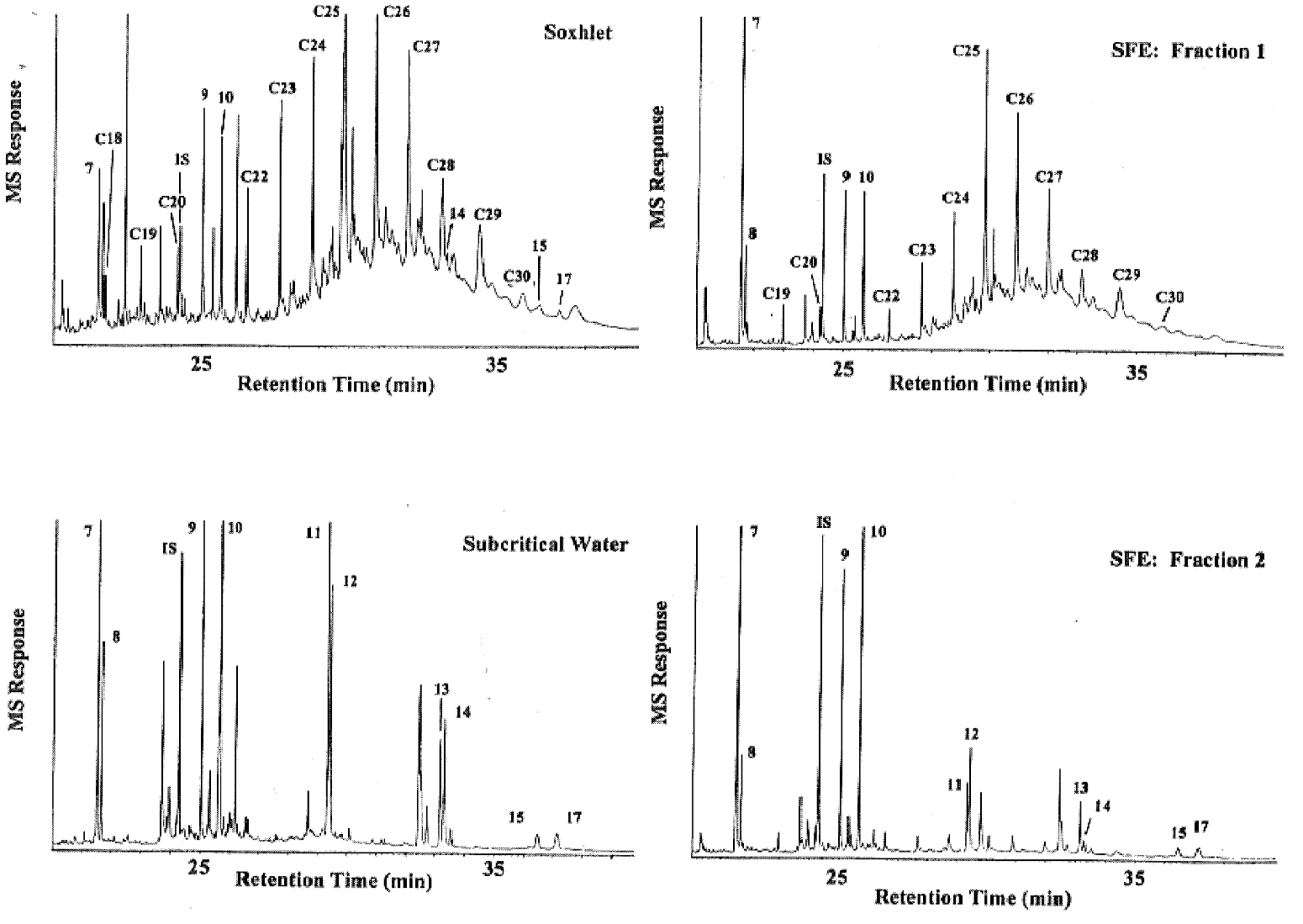


Fig. 3. Comparison of the selectivity of SWE, SFE with pure $CO_2$ and Soxhlet extraction for endogenous alkanes and PAHs from urban air particulate matter. For selected $m/z$ values for the analytes and experimental details of GC–MS, see [49]. Peak identification: major *n*-alkanes in Soxhlet and first SFE fraction are denoted by their chain length (e.g., $C_{18}$ for *n*-octadecane), (7) phenanthrene, (8) anthrancene, (9) fluoranthene, (10) pyrene, (11) benzo[*a*]anthracene, (12) chrysene, (13) benzo[*e*]pyrene (14) benzo[*a*]pyrene, (15) indeno[1,2,3-*c,d*]pyrene, (17) benzo[*g,h,i*]perylene.

dures, the PLE recoveries reported in each study were normalised against those found with the reference procedure chosen by the authors, typically Soxhlet extraction with the same solvent as used for PLE. Results, presented as the ratio, $f$= (concentration determined by PLE/concentration determined by the reference method), were calculated by us for the individual analytes, and are presented as a range of values in Tables 1 and 2 below.

### 3.1. PLE of non-fatty environmental samples

Table 1 summarises relevant analytical data on selected PLE procedures for the determination of organic microcontaminants in a variety of non-fatty samples: these include (i) dust and fly ash, (ii) soil and sediments and (iii) sludge. Up to now, most of the PLE applications dealing with the analysis of these types of samples were devoted to the determination of POPs, a heterogeneous group of chemicals including ubiquitous compounds such as organochlorinated pesticides (OCPs), PAHs, PCBs and PCDD/Fs.

Contrary to what might be expected from the complexity of these samples, most of the methods included no pretreatment of the matrix but drying, homogenisation (usually by grinding) and, in some cases, sieving. As quoted above, reducing the particle size can contribute to enhancing the PLE efficiency by providing a better contact of the solvent with the sample particles. However, the need for grinding the matrix to obtain a representative sample is mainly determined by the sample size used in the experiments. As an average, 1–2 g of dust and fly ash are typically used for PLE of the target compounds and 1–5 g for soil and sediment analysis. However, procedures involving much higher (10–15 g [14,23,26]) or smaller (0.05–0.2 g [21,42,62]) amounts were also published. Satisfactory PLE recoveries were reported for the 16 (endogenous) EPA PAHs from soil and sediment samples as small as 0.05 g, i.e., with $f$ in the range of 0.9–1.1 for a sandy soil, 0.9–1.5 for an organic soil and 0.9–1.1 for a sediment after with 6-h Soxhlet extraction with toluene as the reference procedure [21]. Despite the small amount of a very heterogeneous sample, the RSDs were still satisfactory, 0.5–22%. Although careful homogenisation of the matrix before PLE was mandatory in this particular application, it is important to note that these RSD values were in the range of those typically reported for PLE methods irrespective of the type of sample used and the nature and concentration level of the analytes investigated.

Only a few procedures involving more drastic pretreatment procedures are found in the literature and they are usually related to the PLE of recalcitrant chemicals, e.g., PCDD/Fs, from highly adsorptive matrices such as fly ash [8,19,20]. In these analyses, treatment of the fly ash with concentrated HCl followed by neutralisation of the acid and drying of the sample according to classical procedures for this type of analyses were found to be key factors for the final PLE efficiency. Bautz et al. [20] reported an average increase in the PLE recoveries of the endogenous 2,3,7,8-PCDD/Fs from a fly ash of 8% just by introducing the acid pretreatment. (Values obtained in both sets of experiments were compared with those obtained by classical 24-h Soxhlet extraction of the sample pretreated with HCl and toluene; Table 1.) Although some alternative procedures to this time-consuming acid treatment have been attempted (e.g., toluene–glacial acetic acid (95:5, v/v) [20]), the results can be questioned. The data of this ''on-line acid treatment'' do not fully agree with those obtained by the final method, i.e., off-line acid pretreatment plus PLE with toluene, with $f$=0.8–1.1 for PCDD/Fs; although most PCDD/Fs were extracted more efficiently ($f$=1.0–1.1), 4–21% lower concentrations were found for tetra- to hexa-CDDs.

The acceptance of PLE as an EPA method [65] for the determination of POPs in a variety of environmental samples has convinced many authors to use the specified experimental conditions in their work, viz. 5 min of static PLE with *n*-hexane–acetone (1:1, v/v) at 100 °C and 14 MPa followed by a brief dynamic PLE step. Although in many applications PLE provided similar [20,26,28,37], or even better [18,19,23,27], results than the reference method—typically Soxhlet extraction with the same or a more efficient extraction solvent—some criticism arose in recent years and the ''universality'' of the conditions proposed in the EPA 3545 method start to be questioned [25,29]. Popp et al. [8] found that two

Table 1
PLE procedures for the analysis of moderately volatile organic pollutants in non-fatty environmental samples

| Matrix | Analyte | Analyte level (μg/g) | Pre-treatment | PLE | | | | Post-treatment | Instrum. anal. | *f*[PLE]/[Ref.] | Reference method | Refs. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | p (MPa) | *T* (°C) | Solvent[a] | Extract. time[b] (min) | | | | | |
| *Dust and fly ash* | | | | | | | | | | | | |
| Dust slurry | PAHs | NQ[c] – 209 | – | 14 | 175–200 | Tol | 2×5 | USE + $SiO_2$ | LC–Fluoresc | 0.9–1.5 | Soxhlet[d] | [8] |
| Urban dust (CRM)[e] | PAHs | 0.32–6.7 | Not required | 13 | 100 | DCM | 5+1×5 | Cu + $SiO_2$ + Cc[f] | GC–MS | 0.9–1.1 | Soxhlet | [37] |
| Urban dust (CRM) | PAHs | $(1–7)\times10^{-3}$ | Not required | 13 | 100 | DCM:Acet (1:1) | 5+1×5 | – | LC–Fluoresc | 0.8–1.1 | Soxhlet | [16] |
| Urban dust (CRM) | PCB, POPs | $(5.7–210)\times10^{-3}$ | Not required | 13 | 100 | DCM | 5+1×5 | Cu + $SiO_2$ + Cc | GC–ECD | 0.9–1.1 | Soxhlet | [37] |
| Diesel partic. matter (CRM) | PAHs | ND[g]–0.07 | Not required | 13 | 100 | Tol:MeOH (1:1) | 5+1×5 | Aminopropyl-$SiO_2$ + Cc | GC–MS | 0.7–1.9 | Soxhlet | |
| Polyurethane foam[h] | PCBs | 1–0.05 (μg/ml) | Not required | 10 | 90–100 | $C_6$ | 5+1×5 | $Na_2SO_4$ + Cc | GC–ECD | 1.0 | – | [28] |
| Polyurethane foam[h] | Aroclor 1248 | $10^{-2}$ (μg/ml) | Not required | 10 | 90–100 | $C_6$ | 5+1×5 | $Na_2SO_4$ + Cc | GC–ECD | 0.8 | Soxhlet | |
| Dust particles | PCDD/Fs | $(60–410)\times10^{-3}$ | Grind + homog | 15 | 200 | Tol:MeOH (3:1) | 1×50 | $SiO_2$–Ag + $SiO_2$–$HSO_4$ + $SiO_2$ + $Al_2O_3$ | GC–HRMS | – | Soxhlet | [20] |
| Fly ash (1.6–8.4% OM) | PCDD/Fs (homologues) | $(2.5–78)\times10^{-3}$ | HCH (stir, 24 h) + centrif + wash with $H_2O$(×3) | 5 | 150 | Tol | 120 | NS | GC–LRMS | 1.3–1.8 | Soxhlet | [19] |
| Fly ash | PCDD/Fs | $(0.25–170)\times10^{-3}$ | HCl + neutralize + dry | 15 | 200 | Tol:MeOH (3:1) | 1×30 | $SiO_2$–Ag + $SiO_2$–$HSO_4$ + $SiO_2$ + $Al_2O_3$ | GC–HRMS | 0.8–1.1 | Soxhlet | [20] |
| Fly ash | 2,3,7,8-PCDD/Fs | $(0.8–3000)\times10^{-3}$ | HCl + neutralize + dry | 14 | 200 | Tol | 2×10 | [Cc + $SiO_2$ + $Al_2O_3$ + $SiO_2$–Ag] + $H_2SO_4$ | GC–HRMS | 0.8–1.5 | Soxhlet | [8] |
| Fly ash (1.6–8.4% OM) | 2,3,7,8-PCDD/Fs | $(0.05–160)\times10^{-3}$ | HCl (stir, 24 h) + centrif + wash with $H_2O$(×3) | 5 | 150 | Tol | 60 | – | GC–HRMS | 1.0–1.6 | Soxhlet | [19] |
| Fly ash | 2 PCB, 5 PCDDs | 0.5 | Dry | 13 | 100 | Tol:MeOH (95:5) | 5+1×5 | $SiO_2$ | LC–UV | 0.8–0.9 | – | [38] |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Soils and sediments* | | | | | | | | | | | | |
| Agricultural soil[h] | s-Triazines + chloroacetanilides | 0.25–2.0 | Air-dry + sieve | 10 | 125 | MeOH | 1×10 | Cc | GC–NPD/MS | 1.0–1.2 | Soxhlet | [61] |
| Agricultural soil | s-Triazines + chloroacetanilides | 0.07–0.51 | Air-dry + sieve | 10 | 125 | MeOH | 1×10 | Cc | GC–NPD/MS | 0.7–0.9 | Soxhlet | |
| Sea sand | 15 pesticides | 20–40 | – | 24 | 150 | MeOH:$H_2O$ (80:20) | 1×5 | $H_2O$ + SPE-RP-$C_{18}$ | GC–MS | 0.9–1.2 | SLP, MeOH: $H_2O$ (80:20), (30 min) | [14] |
| Contaminated soil (4% OM) | Pesticides | 0.1–1.2 | Sieve | 24 | 150 | MeOH:$H_2O$ (80:20) | 1×5 | $H_2O$ + SPE-RP-$C_{18}$ | GC–MS | 0.89 (average) | SLP, MeOH: $H_2O$ (80:20), (30 min) | |
| Soil (4.4% OM) (24 h aged) | Polar acidic pesticides | 50 | Air-dry | 10 | 100 | Acet + 30% PFBBr[i] | 1×30 | – | GC–MS | 0.9 | Soxhlet (EtAc) | [30] |
| Soil (4.4% OM) (24 h aged) | Polar acidic pesticides | 05 | Air-dry | 10 | 100 | Acet + 30% PFBBr | 1×30 | – | GC–MS | 0.7 | Soxhlet (EtAc) | |
| Aged soil | Pyrimidine pesticides | 20 | – | 14 | 100 | ACN:DCM (1:1) | 3×5 | derivatizn + I.S.[j] | GC–MS | 0.7–0.8 | – | [33] |
| Soil (7%, OM) (4 weeks aged) | Phenols and Chlorophenols | – | Air-dry | 14 | 120 | Tol:acetic anhydride: pyridine (100:1:0.5) | 1×20 | not required | GC–MS | 1.0–1.1 | Soxhlet | [62] |
| Clay, loam and sandy soils (CRM) | DROs[k] WOOs[l] TPHs[m] | 250–3000 | Mixt. with diatomae | 10 | 175 | DCM:Acet (1:1) | 8 + 1×5 | LLE + $Na_2SO_4$ + $SiO_2$ + Cc | GC–FID | 0.8–1.0 0.8–0.9 0.8–1.0 | – | [26] |
| Contaminated soil | POPs | 0.9–2.2 | Air-dry | 10–14 | 100 | Acet:$C_6$ (1:1) | 2×5 | Cc | GC–ECD | 0.9–1.1 | Soxhtec | [8] |
| Contaminated soil | PAHs | 0.1–2.0 | Air-dry | 14 | 175–200 | Tol | 1×8 | not required | LC–Fluoresc | 0.8–1.1 | Soxhlet | |
| Heap mat. copper mine | PAHs | 0.01–4.4 | – | 14 | 175–200 | Tol | 2×5 | USE + $SiO_2$ | LC–Fluoresc | 0.9–1.5 | Soxhlet | |
| Contaminated soil (CRM) | PAHs | 14–1900 | $Na_2SO_4$ | 13 | 150 | Acet:$C_6$ (1:1) | 2×5 + 11 ml | Cc + $SiO_2$ + $Na_2SO_4$ | GC–MS | 0.9–1.4 | – | [24] |
| Sandy soil | 16 EPA PAHs | – | Air-dry + sieve | 15 | 200 | Tol | 1×10 | PTV ATAS ''A'' sorbent | LVI–GC–MS | 0.9–1.1 | Soxhlet | [21] |

Table 1 (contd.)

| Matrix | Analyte | Analyte level (μg/g) | Pre-treatment | PLE | | | | Post-treatment | Instrum. anal. | *f*[PLE]/[Ref.] | Reference method | Refs. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | p (MPa) | *T* (°C) | Solvent[a] | Extract. time[b] (min) | | | | | |
| Organic soil | 16 EPA PAHs | – | Air-dry + sieve | 15 | 200 | Tol | 1×10 | PTV ATAS "A" sorbent | LVI–GC–MS | 0.9–1.5 | Soxhlet | |
| Contaminated top soil | PAHs | 1.1 | Air-dry + [Flor[n] + $Al_2O_3$ (2:1)] | 15 | 140 | Tol | 8+3×10 | Cc + Flor + Cc + (3×) diethyl ether + Cc | GC–MS | 1.1–9.1 | Soxhlet | [23] |
| Contaminated soil | PAHs | 5–490 | Sieve | 7 | 100 | DCM:Acet (1:1) | 50 | not required | GC–FID | 0.9–1.2 | Soxhlet | [49] |
| Contaminated soil | 3 keto-PAHs | 8.2–18 | Air-dry + grind + sieve + homog | 15 | 100 | DCN:MeOH (1:1) | 5+2×5 | not required | GC–MS | 1.0–1.1 | Soxhlet | [27] |
| Contaminated top soil | PCBs | $3\times10^{-3}$ | Air-dry + [Flor + $Al_2O_3$ (2:1)] | 15 | 140 | Tol | 8+3×10 | Cc + Flor + Cc + (3×) diethyl ether + Cc | GC–MS | 3.5–4.5 | Soxhlet | [23] |
| Soil | PCDD/Fs | $(2.3–1000)\times10^{-3}$ | Grind + homog | 15 | 200 | Tol:MeOH (3:1) | 1×50 | $SiO_2$–Ag + $SiO_2$–$HSO_4$ + $SiO_2$ + $Al_2O_3$ | GC–HRMS | 1.0–1.4 | Soxhlet | [20] |
| Contaminated top soil | HCHs | 0.04 | Air-dry + [Flor + $Al_2O_3$ (2:1)] | 15 | 140 | Tol | 8+3×10 | Cc + Flor + Cc + (3×) diethyl ether + Cc | GC–MS | 1.9–2.4 | Soxhlet | [23] |
| Contaminated top soil | DDXs | 0.04 | Air-dry + [Flor + $Al_2O_3$ (2:1)] | 15 | 140 | Tol | 8+3×10 | Cc + Flor + Cc + (3×) diethyl ether + Cc | GC–MS | 3.5–20 | Soxhlet | |
| Contaminated top soil | Cl-$B_7$ | 0.09 | Air-dry + [Flor + $Al_2O_3$ (2:1)] | 15 | 140 | Tol | 8+3×10 | Cc + Flor + Cc + (3×) diethyl ether + Cc | GC–MS | 2.4–13 | Soxhlet | |
| Soil[h] | Linear benzosulfonates | 5 | Air-dry + grind + sieve + 10%$H_2O$ + Cu | 15 | 100 | MeOH | 1×10+5 | Cc + MeOH + USE + filtr | LC–Fluoresc | 0.9–1.3 | – | [18] |
| Soil (4 months aged) | Linear benzosulfonates | 5 | Air-dry + grind + sieve + 10%$H_2O$ + Cu | 15 | 100 | MeOH | 1×10+5 | Cc + MeOH + USE + filtr | LC–Fluoresc | 1.1–1.7 | – | |
| Soil[h] | Alkylphenol ethoxylates + degrad. products | 5–10 | Air dry + grind + sieve + 10%$H_2O$ + Cu | 46 | 100 | $CO_2$ + 27.5% MeOH (1 ml/min) | 30 | Cc + MeOH + USE + filtr | LC–post-derivatizn –Fluoresc | 1.1–1.4 | – | |
| Soil (4 months aged) | Alkylphenol ethoxylates + degrad. prodts | 5–10 | Air-dry + grind + sieve + 10%$H_2O$ + Cu | 46 | 100 | $CO_2$ + 27.5% MeOH (1 ml/min) | 30 | Cc + MeOH + USE + filtr | LC–post-derivatizn –Fluoresc | 1.8–2.2 | – | |
| Aged soil | Thiodiglycol | 10 | Dry | 10 | 150 | MeOH:$H_2O$ (9:1) | 2×(7+15) | filtr + Cc | GC–FPD | 0.1–1.2 | – | [34] |
| Contaminated Sediment | RDX[o]<br>HMX[p] | $1.6\times10^{4}$<br>$1.0\times10^{4}$ | Dry + grind + sieve | 14 | 120 | ACN | 1×10 | filtr | LC–UV | 1.3<br>1.3 | Soxhlet | [63] |
| Coal waste water sediment | Phenols | – | Air-dry + sieve + hydromatrix | 12 | 120 | Tol + acetic acid anhydride (2%) | 1×15 | – | GC–MS | 1.0 | PLE (Acet) | [42] |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sediment[h] | PAHs | ND–9.01 | Not required | 14 | 100 | DCM | 5+1×5 | Cu+$SiO_2$+Cc | GC–MS | 0.9–1.2 | Soxhlet | [37] |
| Marine Sediment | PAHs | (0.30–85) $\times 10^{-3}$ | Not required | 13 | 100 | DCM:Acet (1:1) | 5+1×5 | Cu+Cc | GC–MS | 0.3–1.3 | Soxhlet | [16] |
| River Sediment | PAHs | 1.5–190 | Air-dry+sieve+hydromatrix | 13 | 120 | Tol | 2×15 | – | GC–MS | 1.1–1.7 | Soxhlet | [42] |
| Sediment | 16 EPA PAHs | – | Air-dry+sieve | 15 | 200 | Tol | 1×10 | PTV ATAS "A" sorbent | LVI–GC–MS | 0.9–1.1 | Soxhlet | [21] |
| Sediment (CRM) | PCBs, POPs | (0.6–140) $\times 10^{-3}$ | Not required | 14 | 100 | DCM | 5+1×5 | Cu+$SiO_2$+Cc | GC–ECD | 0.8–1.1 | Soxhlet | [37] |
| Sediment (LRM)[q] | PCBs, POPs | 0.06–4.3 | Air-dry+grind | 14 | 150 | Acet:$C_6$ (1:1) | 2×10 | $SiO_2$ | GC–MS | 0.9–1.6 | Soxhlet | [64] |
| Sediment (3% OM) | 15 monitoring PCBs | (0.01–1.0) $\times 10^{-3}$ | Air-dry+grind+hydromatrix | 14 | 100 | Acet:$C_6$ (1:1) | 5+1×5 | $SiO_2$+Cu+Cc+NP–$SiO_2$[r]+Cc+[$SiO_2$+$SiO_2$–KOH+$SiO_2$–$HSO_4$]+Cc | GC–MS | 0.8–1.2 | Soxhlet (Tol) | [25] |
| Sediment (8% OM) | 15 monitoring PCBs | (0.3–70) $\times 10^{-3}$ | Air-dry+grind+hydromatrix | 14 | 100 | Acet:$C_6$ (1:1) | 5+1×5 | $SiO_2$+Cu+Cc+NP-$SiO_2$+Cc+[$SiO_2$+$SiO_2$–KOH+$SiO_2$–$HSO_4$]+Cc | GC–MS | 0.5–0.9 | Soxhlet (Tol) | |
| Sediment (8% OM) | 15 monitoring PCBs | (0.3–70) $\times 10^{-3}$ | Air-dry+grind+hydromatrix | 20 | 160 | Tol | 5+1×5 | $SiO_2$+Cu+Cc+NP–$SiO_2$+Cc+[$SiO_2$+$SiO_2$–KOH+$SiO_2$–$HSO_4$]+Cc | GC–MS | 0.7–1.0 | Soxhlet (Tol) | |
| Sediment[h] | 4-Nonylphenol | 20 | Freeze-dry+grind+sieve | 10 | 100 | MeOH | 1×15+10 | $Al_2O_3$+Cc | LVI–GC–MS | 0.9 | Soxhlet | [17] |
| Sediment (24 h aged) | 4-Nonylphenol | 20 | Freeze-dry+grind+sieve | 10 | 100 | MeOH | 1×15+10 | $Al_2O_3$+Cc | LVI–GC–MS | 0.9 | Soxhlet | |
| Sediment | 4-Nonylphenol | 18 | Freeze-dry+grind+sieve | 10 | 100 | MeOH | 1×15+10 | $Al_2O_3$+Cc | LVI–GC–MS | 1.6 | Soxhlet | |
| Sediments | 4-Nonylphenol +4-NPE | 0.3–11 | Homog+freeze-dry | 10 | 100 | MeOH | 1×5 | $Al_2O_3$+Cc+filtr | LC–Fluoresc | 0.7–1.9 | Soxhlet | [32] |
| *Sludge* | | | | | | | | | | | | |
| Sewage sludge (CRM) | PCBs | 0.16–0.20 | Dry+grind+sieve | 13 | 100 | Acet:$C_6$ (1:1) | 5+1×5 | $SiO_2$–Ag+$SiO_2$–$HSO_4$+Cc | GC–ECD | 0.6–0.9 | Soxhlet | [16] |

[a] Acet, acetone; ACN, acetonitrile; $C_6$, *n*-hexane; DCM, dichloromethane; EtAc, ethyl acetate; MeOH, methanol; TOL, toluene. [b] Total extraction time. When possible, times involved in the different steps were mentioned according to: equilibration time+no. of static PLE cycles×static PLE time per cycle+dynamic PLE time. [c] Not quantified. [d] Unless specified, same solvent as for PLE; extraction time in the range 6–48 h. [e] Certified Reference Material. [f] Concentration step. [g] Not detected. [h] Freshly spiked sample. [i] Pentafluorobenzylbromide. [j] Addition of internal standard. [k] Diesel range organics. [l] Waste oil organics. [m] Total petroleum hydrocarbons. [n] Florisil. [o] Hexahydro-1,3,5-trinitro-*s*-triazine. [p] Octahydro-1,3,5,7-tetrazocine. [q] Laboratory Reference Material. [r] Nitropropylphenyl-silica column.

Table 2
PLE procedures for the analysis of moderately volatile organic pollutants in fatty environmental samples[a]

| Matrix | Compound | Analyte level (μg/g) | Pre-treatment | PLE | | | | Post-treatment | Instrum. anal. | *f* [PLE]/[Ref.] | Reference method | Refs. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | *p* (MPa) | *T* (°C) | Solvent | Extract. time (min) | | | | | |
| *Vegetal samples* | | | | | | | | | | | | |
| Mosses | HCH, DDX, Cl–Bz | (0.15–6.5) $\times 10^{-3}$ | Dry till 80 wt% $H_2O$ | 15 | 120 | $C_6$ | 5+3×10+2 | Cc+Flor[a] (4% $H_2O$)+Flor (180 °C)+diethyl ether (×3)+Cc+Tol | GC–MS | – | USE (3×100 ml $C_6$) | [29] |
| Mosses | 5 PAHs | (5–70)$\times 10^{-3}$ | Dry till 80 wt% $H_2O$ | 15 | 120 | $C_6$ | 5+3×10+2 | Cc+Flor (4% $H_2O$)+Flor (180 °C)+diethyl ether (×3)+Cc+Tol | GC–MS | – | USE (3×100 ml $C_6$) | |
| Mosses | 6 monitoring PCBs | (0.02–1.5) $\times 10^{-3}$ | Dry till 80 wt% $H_2O$ | 15 | 40 | $C_6$ | 5+3×10+2 | Cc+Flor (4% $H_2O$)+Flor (180 °C)+diethyl ether (×3)+Cc+Tol | GC–MS | – | USE (3×100 ml $C_6$) | |
| Pine needles (inner part) | PCBs+[HCHs+DDTs+Cl-Bz+PAHs] | ND–0.12 | Dry till 55–60 wt% $H_2O$+USE (isolate inner part+wax layer) | 15 | 40;120 | $C_6$ | 5+3×10+2 | Cc+Flor (4% $H_2O$)+Flor (180 °C)+diethyl ether (×3)+Cc+Tol | GC–MS | 0.2–500 | USE (3×100 ml $C_6$) | |
| Pine needles (wax layer) | PCBs+[HCHs+DDTs+chloro-benz+PAHs] | ND–0.03 | Dry till 55–60 wt% $H_2O$+USE (isolate inner part+wax layer) | 15 | 40;120 | $C_6$ | 5+3×10+2 | Cc+Flor (4% $H_2O$)+Flor (180 °C)+diethyl ether (×3)+Cc+Tol | GC–MS | 0.5–85 | USE (3×100 ml $C_6$) | |
| Fruits | organo-P pesticides | 0.03–0.22 | Exterlux | 17 | 100 | EtAc | 5+1×5 | SEC[b], Cc | GC–FPD | 0.6–1.0 | LLE ($C_6$) | [41] |
| Cereal-based foodstuff | Basic drugs | 5000 | Not required | 17 | 70 | Methanol | 2 ml/min | Not required | LC–UV | 1.0–1.1 | SFE | [66] |
| Cereal-based foodstuff | 7 indicator PCB | 0.02 (fat basis) | Sand+$Na_2SO_4$ (1:1, w/w) | 10 | 100 | $C_6$ | 5+2×1 | Not required | GC–MS | 0.9–1.0 | LLE ($H_2SO_4$) | [67] |
| *Animal samples* | | | | | | | | | | | | |
| Mussel (CRM) | PAHs | (2.4–57) $\times 10^{-3}$ | Freeze-dry | 14 | 100 | DCM | 5+1×5 | SEC+Cc | GC–MS | 0.9–1.2 | Soxhlet | [37] |
| Fish (CRM) | PCBs, OCPs | (2.1–200) $\times 10^{-3}$ | $Na_2SO_4$ | 14 | 100 | DCM | 5+1×5 | SEC+Cc | GC–MS | 0.9–1.1 | Soxhlet | |
| Oyster (CRM) | PCBs | 0.05–0.15 | Diatomae (1:1) | 13 | 100 | Isooct[c] | 5+1×5 | Not required | GC–ECD | 1.1–1.6 | Soxhlet | [16] |
| Cod-liver oil (CRM) | 6 indicator PCB | 0.7–1.0 (fat basis) | Sand+$Na_2SO_4$ (1:1, w/w) | 10 | 100 | $C_6$ | 5+2×5 | Not required | GC–MS | 1.0 | – | [67] |
| Milk powder (CRM) | 4 indicator PCB | (1–19)$\times 10^{-3}$ (fat basis) | Sand+$Na_2SO_4$ (1:1, w/w) | 10 | 100 | $C_6$ | 5+2×5 | Not required | GC–MS | 1.0–1.2 | – | |
| Mussel (CRM) | | (5.5–150) $\times 10^{-3}$ | Freeze-dry+grind+sieve+Flor | 14 | 40 | DCM:$C_5$ (15:85) | 2×10 | Not required | GC–MS | 1.0 | Soxhlet (Acet:$C_5$, 1:2) | [68] |
| Egg | | (7.6–600) $\times 10^{-3}$ | Freeze-dry+grind+sieve+Flor | 14 | 40 | DCM:$C_5$ (15:85) | 2×10 | Not required | GC–MS | 0.9–1.1 | Soxhlet (Acet:$C_5$, 1:2) | |

Table 2. (contd.)

| Matrix | Compound | Analyte level (μg/g) | Pre-treatment | PLE | | | | Post-treatment | Instrum. anal. | *f* [PLE]/[Ref.] | Reference method | Refs. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | *p* (MPa) | *T* (°C) | Solvent | Extract. time (min) | | | | | |
| Milk powder (CRM) | PCDD/Fs | (0.05–1.8) $\times 10^{-6}$ | Freeze-dry + $Na_2SO_4$ | 10 | – | $C_6$ | 2×5 | Acid + basic + neutral silica | GC–HRMS | 1.0–1.2 | – | [69] |
| Liver | Corticosteroids | (1–4)$\times 10^{-3}$ | Diatomae | 10 | 50 | $C_6$:EtAc (1:1) | 1×5 | Cc | LC–MS | 0.8–0.9 | – | [70] |
| Freshwater fish muscle | Polycyclic musk | (4–80)$\times 10^{-3}$ | Hydromatrix | 10 | 80 | $C_6$:EtAc (5:1) | 5+2×5 | Not required | GC–MS | 0.7–1.1 | – | [71] |
| Fish muscle | $C_{14}$–$C_{17}$ PCAs[d] | (0.2–780) $\times 10^{-3}$ | $Na_2SO_4$ | 14 | 100 | $C_6$:DCM (1:1) | 5+1×10 | SEC + Flor | GC–ECNI-MS | 0.8–1.0 | spiked mPAC-53 | [72] |

[a] For acronyms, see Table 1.
[b] Size exclusion chromatography.
[c] Isooctane.
[d] Polychloroalkanes.

5-min static PLEs are preferred for the quantitative extraction of the endogenous PAHs from a complex sample such as dust. Similarly, Björklund et al. [39] reported recoveries of up to 14% in the extract obtained by a second 5-min PLE step. Some criticism exists also as regards the extraction mixture proposed in the EPA method and toluene is instead indicated as the solvent of choice when extracting POPs from dust and fly ash [8,19,20,37] (Fig. 4). Toluene allowed a much more efficient extraction of 15 endogenous monitoring PCBs from sediments with high organic content (>8.5%), with recoveries up to 3-fold higher than with *n*-hexane–acetone [25] ($f$=0.7–1.0 vs. $f$=0.5–0.9, respectively; reference: 24-h Soxhlet with toluene). For less complex (or adsorptive) samples, PLE usually provides rather similar efficiencies irrespective of the extraction solvent selected [13,25]. However, this is not always true for highly contaminated soils. Hubert et al. [23] reported a 2-fold (HCHs) and 4-fold (PAHs) increase during PLE of a highly contaminated sandy soil when using toluene instead of the EPA mixture. Obviously the nature of the matrix and its degree of contamination are key factors to be considered during PLE solvent selection. On the other hand, the suitability of different solvent mixtures has been tested in an attempt to achieve more selective extractions which will contribute to simplify the subsequent clean-up steps [8,29].

An interesting alternative to the studies already mentioned is to include an in-cell pre-clean-up of the sample. Such treatment consists of blending the sample, typically a soil or sediment, with either a sorbent or chemicals used for subsequent purification of the extracts in classical procedures. The mixture is then packed in the extraction cell and PLE performed as usual. With this approach satisfactory recoveries were obtained for a variety of POPs [23], such as DDXs, PCBs, HCH isomers, Cl-Bz and PAHs, from a sandy soil ($f$=1.1–13 with 24-h Soxhlet with toluene as reference). In this study, a 10-g subsample of the soil was placed in a 33-ml extraction cell and the remaining volume was filled with 10 g of a mixture of Florisil–$Al_3O_2$ (2:1, w/w) for in-cell pre-clean-up. The different groups of pollutants investigated were then sequentially extracted with toluene at their corresponding optimal temperature, the former two classes at 80 °C and the latter three at 140 °C. The only additional clean-up required was the elimination of the co-extracted lipophilic material in a 3.5-g column of activated Florisil. In a rather similar approach, Kreisselmeier et al. [18] prevented the extraction of elementary sulphur, which could obstruct the whole PLE system, by adding 0.75 g of copper powder per g of soil. In this study a combined three-step PLE procedure was proposed for the simultaneous extraction of anionic (linear alkylbezenesulphonates, LASs) and non-ionic surfactants (alkylphenolethoxylates, APEOs, and their degradation products, alkylphenols, APs) from sediments. In the first one, the spiked LASs were quantitatively recovered ($f$=0.9–1.3) by 10-min static PLE with methanol at 100 °C and 15 MPa. After 10-min dynamic PLE under similar experimen-

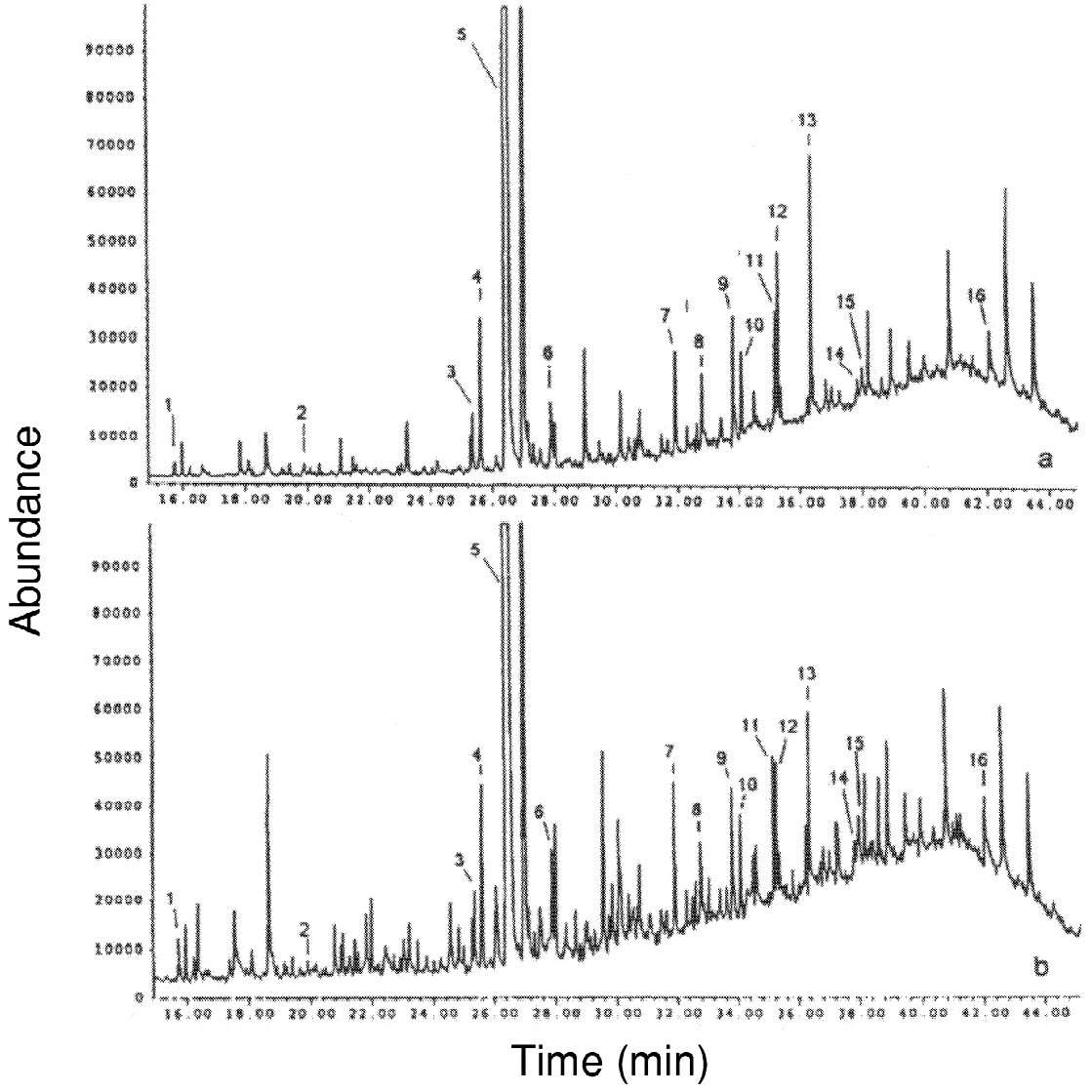


Fig. 4. GC–MS chromatograms showing the importance of PLE solvent selection for the analysis of contaminated soil: (a) acetone–hexane and (b) toluene; for experimental details, see Ref. [8]. Peak identification: (1) 2-methylnaphthalene, (2) acenaphthylene, (3) α-HCH, (4) HCB, (5) β-HCH, (6) δ-HCH, (7) fluoranthene, (8) pyrene, (9) *p,p′*-DDE, (10) *o,p′*-DDD, (11) *p,p′*-DDD, (12) *o,p′*-DDT, (14) benz[*a*]anthracene, (15) chrysene, (16) benzo[*a*]pyrene.

tal conditions, the APEOs and APs were extracted by a further 10-min dynamic PLE with $CO_2$ modified with 27.5% (v/v) methanol at 1 ml/min, 100 °C and 45 MPa ($f$=1.1–1.4). Application of the method to samples aged for 4 months proved that ageing did not affect the recoveries of the LASs due to the weak interaction of these compounds with the matrix. However, the recovery of NPEO and OPEO was reduced by ca. 40 and 20%, respectively.

Typical clean-up procedures applied to the collected PLE extracts are, except in the examples quoted above, rather similar to those used in classical procedures for the determination of micropollutants in environmental samples. Nevertheless, some at-

tempts to simplify these time-consuming multi-step methodologies have been reported. Addition of derivatisation agents such as acetic acid anhydride–trimethylamine [42] or acetic acid anhydride–pyridine [62] to the extraction solvent for in-cell derivatisation of phenols and chlorophenols was reported to yield the same efficiency as post-extraction treatment without affecting the PLE recoveries ($f$=1.1–1.7 and 1.0–1.1; Soxhlet with toluene as reference). The simplification of the post-PLE treatment of the extracts and the reduction of the total analysis time were clearly evident. According to the authors [42], the addition of the derivatisation agents to the extraction cell helps to improve the PLE efficiency by reducing the strong interaction between the polar analytes and the matrix and by preventing re-adsorption or re-absorption of the target compounds by covering active sites. This allows the use of less polar solvents for the extraction and, thus, yields cleaner extracts than obtained with polar solvents such as methanol or acetone, without affecting the performance of the method ($f$=1, PLE with acetone as reference, Table 1). Similarly, David et al. [30] substantially simplified the classical derivatisation procedures for the determination of polar acid herbicides by gas chromatography with mass spectrometric detection (GC–MS) in soil by developing an in-cell derivatisation PLE method with pentafluorobenzyl bromide (PFBBr), which was added directly to the top of the extraction cell together with 0.7 ml of a 10% aqueous solution of $K_2CO_3$ to effect quantitative derivatisation. The efficiency of in-cell derivatisation was proven to be better than that obtained by the out-of-cell procedure, as the authors were not able to recover more than 5% of any of the six herbicides studied in the latter approach as against 75% for triclopyr, silvex and bentazone and 54–61% for dicamba, 2,4-D and 2,4,5-T (soil spiked at 0.5 mg/kg and aged for 24 h). Preliminary results suggested that these yields could be improved by adding $Na_4EDTA$ to the extraction vessel.

A rather different approach which, nevertheless, also provides satisfactory results for the determination of PAHs in soils and sediments, consists of the purification of the PLE extract by direct large-volume injection (LVI) in a programmed temperature vaporiser (PTV) equipped with a liner packed with an appropriate sorbent, here the ATAS ''A'' [21]. The reported PLE efficiencies compared well with those obtained by 6-h Soxhlet extraction of a variety of soils with toluene ($f$=0.9–1.5) and the RSDs of 0.5–22% agreed with those reported for more conventional PLE procedures [17,20,27,30,33,37,42]. Although the sorbent had to be exchanged occasionally, the benefits due to the complete elimination of the laborious clean-up steps previous to the final GC determination and the fact that the volume of the PLE extract was only 100 μl, shows the approach to be particularly interesting for routine analysis and complete automation. As an example, Fig. 5 shows an LVI–GC–MS trace obtained after PLE of 50 mg of a naturally contaminated organic soil.

It is always recommended to use an internal standard, but the addition of the internal standard should be given serious attention. Lundstedt et al. [24] found that if the internal standard is added on top of the sample in the extraction cell, its elution is not representative for the extraction process as it is more a chromatographic elution than an extraction. When [$^2H_{12}$]chrysene and [$^2H_{10}$]acenaphthene were both added on top of the sample in the cell, the peak area of [$^2H_{12}$]chrysene decreased relative to that of [$^2H_{10}$]acenaphthene when the sample amount increased (Fig. 6). It is therefore recommended to thoroughly mix the internal standard with the sample matrix prior to extraction, or alternatively, add it to the extract immediately after extraction.

### *3.2. PLE of fatty biological samples and food*

Up to now, the feasibility of PLE for the determination of organic pollutants in biological samples and food or foodstuff has been tested in a rather limited number of papers. Table 2 summarises relevant analytical data related to some of these studies which have been organised in two categories, (i) vegetal samples, and (ii) animal samples. In agreement with what was observed for non-fatty samples, no pre-treatment but drying and homogenisation of the matrix is usually carried out before PLE of biological samples. In general, the range of temperatures and pressures is similar to those used for PLE of non-fatty matrices. However, single solvents are usually preferred as extraction solvent as they provide similar PLE efficiency but cleaner

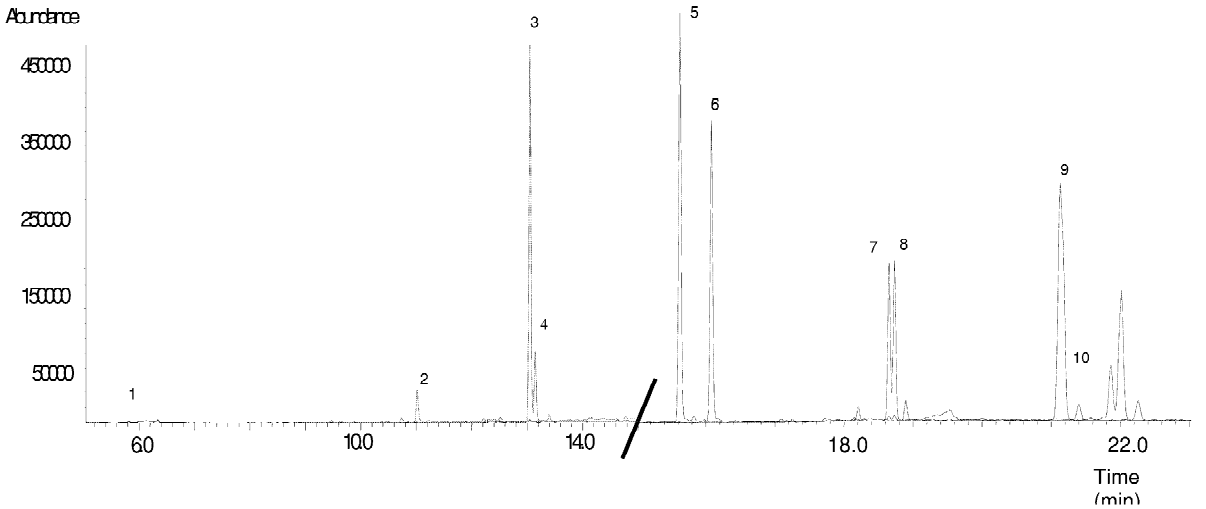


Fig. 5. Fifty-μl LVI–GC–MS (SIM) fragmentograms of endogenous PAHs extracted from 50 mg of an organic soil with a miniaturised PLE using 100 μl of toluene at 200 °C and 15 MPa. For selected $m/z$ values and other experimental details (see Ref. [21]). Peak identification: (1) naphthalene, (2) fluorene, (3) phenanthrene, (4) anthrancene, (5) fluoranthene, (6) pyrene, (7) benzo[*a*]anthracene, (8) chrysene, (9) benzo[*b*]fluoranthene + benzo[*k*]fluoranthene, (10) benzo[*a*]pyrene. Slash in the *x*-axis indicates change in the ions monitored.

extracts than mixtures containing solvents of different polarity. After testing the practicality of several mixtures involving *n*-hexane, acetone and dichloromethane, Wenzel et al. [29] chose *n*-hexane as the most convenient solvent for PLE of a variety of POPs, including HCH, DDXs, Cl-Bz, PAHs and PCBs, from wet mosses (ca. 80% water content). Although these solvents provided similar recoveries

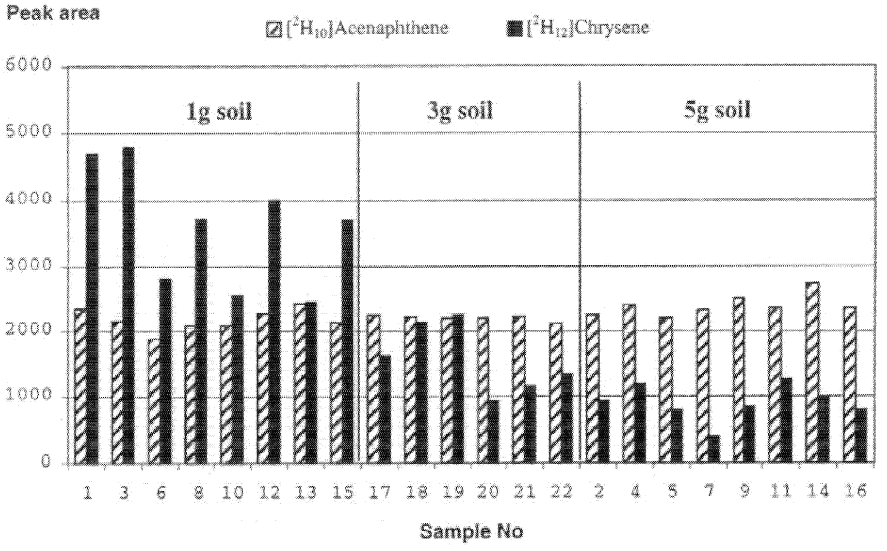


Fig. 6. Peak areas of high ([$^2H_{12}$]chrysene) and low ([$^2H_{10}$]acenaphthene) molecular mass compounds added as internal standard on top of the soil sample in the extraction cell. It is shown that the elution of the I.S. is more a chromatographic process than an extraction and that different elution times are needed for compounds of different size [24].

of the target compounds, a large amount of polar substances was extracted when increasing the polarity of the extraction solvent(s). This influenced the subsequent clean-up and final determination of the analytes. The authors also preferred *n*-hexane to toluene because more matrix-interfering components were extracted at the high-temperature required for the latter solvent without any further improvement in the recoveries of the POPs. The different extraction temperature used for the PLE of the classes of compounds investigated allowed their selective sequential extraction at two different temperatures, 40 and 120 °C, from the wax layer and the inner part of pine needles with satisfactory recoveries in all the cases ($f$=0.5–85 and 0.2–500, respectively; ultrasonic extraction with *n*-hexane as reference). Including an in-cell clean-up of the fraction corresponding to the inner part of the pine needles by dispersion on a mixture of Florisil and $Al_2O_3$ did not change the efficiency of the PLE process, but simplified the subsequent clean-up of the extracts.

Much more variable results have been reported for the PLE of polar compounds from non-fatty food. Obona et al. [41] reported a satisfactory PLE of organo-P pesticides spiked to flour, grapefruit, broccoli, and orange fruit when the samples were dried for 2 h by dispersion on Exterlux and a water-soluble solvent such as ethyl acetate was used as extraction solvent (average recoveries, 79–90%). However, the proposed method showed a somewhat lower efficiency when analysing the endogenous levels of these pesticides in different fruits ($f$=0.6–1.0 with solid–liquid partitioning with *n*-hexane as reference). Williams et al. [66] also encountered problems when developing a general method for the dynamic PLE of basic drugs from cereal-based food. Even though the recoveries of most analytes with the final PLE procedure were higher than those of the SFE reference method ($f$=1.0–1.1), it is important to note that the absolute recoveries ranged from 79 to 92% at a spiking level as high as 5 mg/g. Rather surprisingly, the authors also reported a decrease in the absolute recoveries of the target compounds as the flow-rate of the extraction solvent, methanol, decreased.

In most of the reported applications for PLE of lipophilic compounds from fat-containing matrices both analytes and fat are simultaneously extracted. This makes an exhaustive clean-up of the extracts prior to injection in the chromatographic system necessary [16,37,41]. In an attempt to eliminate this time-consuming step and reduce sample handling to a minimum, Muller et al. [67] proposed in-cell fat removal by packing the sample dispersed in a sand–$Na_2SO_4$ mixture (1:1, w/w) on top of a multilayer column containing acid silica and neutral silica in the bottom part to remove sulphuric acid traces from the *n*-hexane eluate. The method gave satisfactory recoveries of the indicator PCBs for spiked samples with a relatively low fat content such as cereal-based foodstuff (3% fat, $f$=0.9–1.0; classical off-line sulphuric treatment as reference), but also for complex fatty certified reference materials such as cod-liver oil ($f$=1.0) and milk powder ($f$=1.0–1.2) whenever the fat–acid silica ratio was lower than 0.025. Despite the limitations that this requirement represents when analysing compounds at the trace level, the methodology efficiently contributed to reduce sample manipulation and solvent consumption, and the total time required for sample preparation while increasing the possibilities of automation. In a rather similar approach, Draisci et al. [71] proposed the use of 5 g of activated alumina for the quantitative in-cell removal of the lipids extracted by PLE with *n*-hexane–ethyl acetate (1:1, v/v) at 80 °C of 3 g of fish muscle dispersed in 5 g of Hydromatrix. Polycyclic musk compounds were determined by GC–MS of the collected extracts without any further purification.

PLE has also proven to be efficient for the quantitative extraction of pollutants such as PCDD/Fs from high-fat-content foodstuff although a much larger amount of sample is required for this type of analyses. For example, Focant et al. [69] reported some detection problems for TeCDF and PeCDF homologues in 5 g of a certified milk powder (ca. 1 g of fat), although satisfactory results were found for the other PCDD/F homologues ($f$=1.0–1.2). An alternative procedure for in-cell defatting of animal samples based on the control of the selectivity of the extraction solvent was recently proposed by Draisci et al. [70]. They proposed two-step PLE which allows the preliminary selective removal of the fat from bovine liver dispersed in diatomaceous earth by 3×5-min static PLE with *n*-hexane at 60 °C and, then, the quantitative extraction of the spiked dexamethasone and β-epimer betamethasone by one

5-min cycle with *n*-hexane–ethyl acetate (1:1, v/v) at 50 °C (recoveries, 75–77% at spiking levels of 1–4 ng/g; RSDs, 3–7%). Sample preparation took 35 min and only 35 ml of solvent, and no further treatment was required but concentration of the final extract.

## 4. SWE of organic pollutants from environmental samples

### *4.1. SWE of non-fatty environmental samples*

Table 3 summarises relevant analytical data of selected SWE methods for the determination of organic micropollutants in a variety of environmental samples, including (i) urban dust, (ii) soils and sediments, and (iii) foodstuff. As was also observed for PLE, most samples were not subjected to any pre-treatment other than homogenisation (or grinding) and, occasionally, sieving before SWE. For obvious reasons, drying of the matrix is not required with this type of extraction. The sample size and the water flow-rates typically required for continuous SWE are rather similar to those used for PLE of the same type of sample (i.e., 1–5 g and about 1 ml/min). Nevertheless, examples of quantitative SWE of polar compounds from complex samples using smaller amounts of sample and faster flow-rates have also been reported. Jiménez-Carmona et al. [53] observed an increase of 21% in the recovery of trichloropyridinol from 0.1 g of a freshly spiked soil by 15 min of SWE at 250 °C and 20 MPa per 1 ml/min increase in the flow-rate and proposed 4 ml/min as the optimum value (average recovery, 98%; RSD, 2% at spiking levels of 0.005–5 μg/g). This result clearly shows that, in this particular application, the extraction process was limited by the solubility of the analyte in the subcritical water. Because of the same reason, the extraction was also improved by reducing the sample size. This solubility-controlled step can always be expected to some degree in SWE for polar and less retained (i.e., sorbed) analytes. However, for moderately or non-polar and strongly (chemi-)sorbed analytes, it may be expected that the extraction process is controlled by the desorption kinetics of the analyte from the matrix, and independent of the solvent–mass sample ratio, i.e., independent of the sample size and the flow-rate [47].

As a consequence of the above, generally speaking, two types of SWE approach can be distinguished, based on the polarity of the target compounds and, to some extent, on the nature of the sample(s). With polar compounds, relatively low temperatures (up to 100–150 °C) can be used (almost) irrespectively of the matrix characteristics [45] and the problem of extracting the analytes from a solid matrix is, in a way, shifted to that of extracting them from water. With moderately and low-polar analytes, the high-temperatures required for SWE, typically 200–300 °C, can cause degradation of the solutes and application is therefore restricted to analytes that are stable at high-temperatures, such as POPs.

As regards the first type of applications, transformation products of a variety of pesticides were satisfactorily extracted at temperatures ranging from 50 [57] to 250 °C [53], depending on the stability of the target compounds, and selectively preconcentrated by in-cell strong anion-exchange (SAX) disk extraction and immunoassay with monoclonal antibodies, respectively. In a rather similar approach, Crescenzi et al. [58] proposed the preconcentration of the analytes by Carbograph 4 SPE outside the oven but connected on-line with the extraction cell for multiresidue herbicide analysis in aged soils. In this case, the eluate was not cooled before elution through the SPE cartridge, which was subsequently disconnected from the extraction system for sequential selective elution of the basic–neutral herbicides and the acidic herbicides. The procedure compared favourably with conventional procedures such as Soxhlet extraction and sonication with organic solvents for most test compounds. Field et al. [57] proposed an alternative rapid, but rather expensive, approach for the sequential extraction of dacthal and its mono- and di-acid metabolites from soil. After achieving a rapid quantitative extraction of the pesticide from 2 g of dried sample placed in the extraction cell on top of a SAX disk with supercritical $CO_2$ at 150 °C and 40 MPa and collection of the eluate in 5 ml of acetonitrile (recovery, >95%; RSD, <9.7% at 0.1–0.9 μg/g level), the residue remaining in the extraction cell was subjected to 10-min SWE at 50 °C and 20 MPa for simultaneous extraction and

Table 3
SWE procedures for the analysis of moderately volatile organic pollutants in environmental samples[a]

| Matrix | Analyte | Analyte level (μg/g) | Pre-treatment | SWE | | | | Post-treatment | Instrum. anal. | *f* [PLE]/[Ref.] | Reference method | Refs. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | *p* (MPa) | *T* (°C) | Solvent | Extract. time (min) | | | | | |
| *Urban dust* | | | | | | | | | | | | |
| Air particulates (CRM) | PAHs | 2.9–8.2 | – | 5 | 250 | $H_2O$ | 15 | LLE (chloroform) | GC–MS | 0.6–110 | Soxhlet, DCM:Acet (1:1) | [47] |
| Air particulates (CRM) | PAHs | 2.2–6.5 | – | – | 250 | $H_2O$ | 60 | SPME | GC–MS | 0.8–1.6 | Soxhlet, DCM:Acet (1:1) | [52] |
| Air particulates (CRM) | 11 EPA PAHs | $(0.7–9.1)\times10^3$ | Dry+homog | <4 | 250 | $H_2O$ | 60 | In-cell SPE disk+constant mixing | GC–MS | 1.1–2.9 | – | [60] |
| *Soils and sediments* | | | | | | | | | | | | |
| Soils | Metabolites of dacthal | 1.0–4.1 | Dry+homog+ieve+SFE of dacthal | 20 | 50 | $H_2O$ | 10 | Desorption from SAX disk at 100 °C +ethyl iodide | GC–ECD | 0.8–1.3 | SLP, 0.4 *M* HCl: Acet (20:80) | [57] |
| Soil[b] | Trichloropyridinol | 0.005–5 | Dry+homog+sieve | 20 | 250 | $H_2O$ | 15 | Immunoassay | ELISA | 1.0 | SFE-$CO_2$+MeOH+ion-par reagent | [53] |
| Aged soils (40 days) | Chlorinated acid herbicides and esters | 1.0 | – | – | 100 | $H_2O$ | NS | In-cell SAX disk+off-line derivatizn | GC–ECD/MS | 0.5–1.4 | EPA method 8151 | [45] |
| Aged soils | Basic, neutral and acidic herbicides | 0.01–0.1 | Dry+homog+sieve | – | 90 | $H_2O$ | 5 | SPE | LC–ES/MS | Nonacidic herb., 1.0–1.7 acidic herb. 0.8–2.1 | nonacidic herb., Soxhlet (MeOH) acidic. herb., USE (ACN: $H_2O$:acetic acid, 2 h) | [58] |
| Sand[b] | Chloromethyl-anilines | 0.12–23 | – | 5 | 100 | $H_2O$ | 9 | On-line LC | LC–UV | 0.9–1.1 | – | [73] |
| Aged soils | High and medium polar pesticides | 0.04–0.44 | Dry+sieve | – | 90; 130 | 0.5 M phosphate buffer | 32 | On-line SPE $C_{18}$ | LC–ES/MS | 1.0–1.8 | Soxhlet (MeOH) | [46] |
| Soils[b] | Imidazolinone | 0.01 | Dry+homog+sieve | – | 90 | 0.1 *M* KCl | 5 | Not required | LC–ISI/MS | 0.8–1.0 | – | [51] |
| Sand[b] | Chlorophenols | 0.12–11 | – | 5 | 100 | $H_2O$ | 9 | On-line LC | LC–UV | 0.9–1.1 | – | [73] |
| Contaminated soils | Cholorphenols | 0.01–12 | Dry+homog+sieve | 10 | 125 | $H_2O$:ACN (94:5) | $3\times10$ | Acidification (pH 2), SPME | GC–MS | 1.0–3.0 | EPA method 3545 | [55] |
| Industrial soil | Alkylbenzenes, chloroanilines | 0.18–6.0 | Dry+homog+sieve | – | 250 | $H_2O$ | 60 | SPME | GC–MS | 0.6–0.9 | Sonication, DCM: Acet (1:1), (18 h) Soxhlet (DCM) | [52] |
| Sand[b] | Nitrotoluenes | 2.0 | – | 5 | 200 | $H_2O$ | 8.3 | On-line LC | LC–UV | 0.9–1.1 | – | [73] |
| Contaminated soil (CRM) | PAHs | 16–1500 | dry+sieve | 5 | 250 | $H_2O$ | 15 | LLE (chloroform) | GC–FID | 0.8–1.5 | Soxhlet, DCM:Acet (1:1) | [47] |
| Highly contaminated soil (CRM) | 17 EPA PAHs | 5.0–490 | sieve | 5 | 300 | $H_2O$:Tol. (3:1) | 30 | On-line LLE (Tol) | GC–MS | 0.8–1.7 | Soxhlet, DCM:Acet, (1:1) | [49] |
| | | | | | | | | | | 0.8–2.0 | SFE-$CO_2$, 1 ml/min, (60 min) | |
| | | | | | | | | | | 0.6–1.3 | PLE, DCM:Acet (1:1), (30 min) | |
| Contaminated soil (CRM) | PCBs | 0.3–140 | Dry+sieve | 5 | 250 | $H_2O$ | 15 | LLE (DCM) | GC–ECD | 0.7–1.0 | Sonication, DCM: Acet (1:1), (16 h) | [48] |
| Contaminated soil (CRM) | PCBs | 0.3–140 | Dry+sieve | 5 | 300 | $H_2O$ (steam) | 5 | LLE (DCM) | GC–ECD | 0.9–1.0 | Sonication, DCM: Acet (1:1), (16 h) | |

Table 3. (contd.)

| Matrix | Analyte | Analyte level (μg/g) | Pre-treatment | SWE | | | | Post-treatment | Instrum. anal. | *f* [PLE]/ [Ref.] | Reference method | Refs. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | *p* (MPa) | *T* (°C) | Solvent | Extract. time (min) | | | | | |
| Contaminated sediment (CRM) | PCBs | ND–4.5 | Dry+sieve | 5 | 250 | $H_2O$ | 15 | LLE (DCM) | GC–ECD | 0.7–1.1 | Sonication, DCM: Acet, (1:1), (16 h) | |
| Contaminated soil | PCBs | 0.02–0.75 | Dry+sieve | <4 | 250 | $H_2O$ | 60 | SPME | GC–ECD | 0.8–1.4 | Soxhlet, $C_6$:Acet (1:1), (18 h) | [59] |
| Contaminated soil | PCDFs | $(7.0–24)\times10^{-3}$ | Dry+homog+ sieve | 5 | 300 | $H_2O$ | 30 | Cc+$Na_2SO_4$ | GC–MS | 0.3–1.1 | Consensus value in interlaboratory comparison | [50] |
| Sand[b] | PCBs | 50 | Dry | 25 | 250 | $H_2O$ | 30 | On-line Tenax TA | GC–ECD | 0.9 | – | [54] |
| Contaminated soil | PCNs | 0.62–2.9 | Dry+homog+ sieve | 5 | 300 | $H_2O$ | 30 | Cc+$Na_2SO_4$ | GC–MS | 0.9–1.4 | Soxhlet,(Tol) | [50] |
| Sediment | 13 EPA PAHs | 0.07–0.70 | Dry+homog+ sieve | 12 | 250 | $H_2O$ | 30 | On-line Tenax TA | LVI–GC–FID | 0.3–8.8 | SFE ($CO_2$+MeOH, 150 °C, 36 MPa, 10 min static+20 dynamic) | [74] |
| Marine sediment (CRM) | 11 EPA PAHs | $(3.0–9.4)\times10^{3}$ | Dry+homog | <4 | 250 | $H_2O$ | 60 | In-cell SPE disk+ constant mixing | GC–MS | 0.8–1.9 | – | [60] |
| Contaminated sediment | PCBs | 0.13–4.2 | Dry+sieve | <4 | 250 | $H_2O$ | 60 | SPME | GC–ECD | 0.5–1.9 | Soxhlet, $C_6$:Acet (1:1), (18 h) | [59] |
| Sediments | Brominated flame retardants | 0.01–0.13 | Dry+homog+ sieve | 12 | 325 | $H_2O$ | 40 | On-line Tenax | LVI–GC–FID | 2.8–5.6 | Soxhlet, $C_6$:Acet (1:1), (24 h) | [75] |
| *Foodstuff* | | | | | | | | | | | | |
| Fruits and vegetables | Organochlorine pesticides+ chlorobenzenes | 0.05 | Chopped+ homog +grind | 10 | 120 | $H_2O$:Acet. (9:1) | 2×10 | SPME or SBSE | GC–MS | – | – | [56] |
| Fruits and vegetables | Thiabendazole+ carbendazim | 0.01–0.80 | Homog+dispersion on sorbent | 5 | 75 | $H_2O$ | 20 | pH adjusted+LLE (EtAc)+Cc | GC–MS | 1.0–1.8 | Second laboratory | [76] |

[a] For acronyms, see Table 1.
[b] Freshly spiked sample.

preconcentration of the polar metabolites on the SAX disk. The disk was then transferred to the vial containing the pesticide in acetonitrile and heated for 1 h at 100 °C in the presence of ethyl iodide to convert the metabolites into volatile esters. The three target compounds were determined by GC–ECD without further clean-up. This two-step method compared favourably with the reference procedure, conventional solid–liquid partitioning (SLP) with two times 100 ml of 0.4 *M* HCl–acetone (20:80, v/v) for total dacthal determination in a variety of naturally contaminated soils ($f$=0.8–1.3), but required only 25 min and a total solvent consumption of 5 ml of acetonitrile. In a rather similar approach, Hawthorne et al. [60] proposed the preconcentration of PAHs from soils, sediments and air particulate matter on styrene–divinylbenzene extraction disks cut in pieces and packed in-cell using static SWE at 250 °C. After extraction, the sorbent disks can be stored in autosampler vials, which provides a useful method of shipping samples from the field to the analytical laboratory.

On-line preconcentration can also be done by solid-phase microextraction (SPME). As Fig. 7 shows, Hawthorne et al. demonstrated the higher selectivity of SWE–SPME, even after storing the SWE water for 24 h, compared to Soxhlet [59]. The chromatograms from the different PCB extractions are similar, except that the SWE–SPME chromatograms show somewhat higher peaks for the early

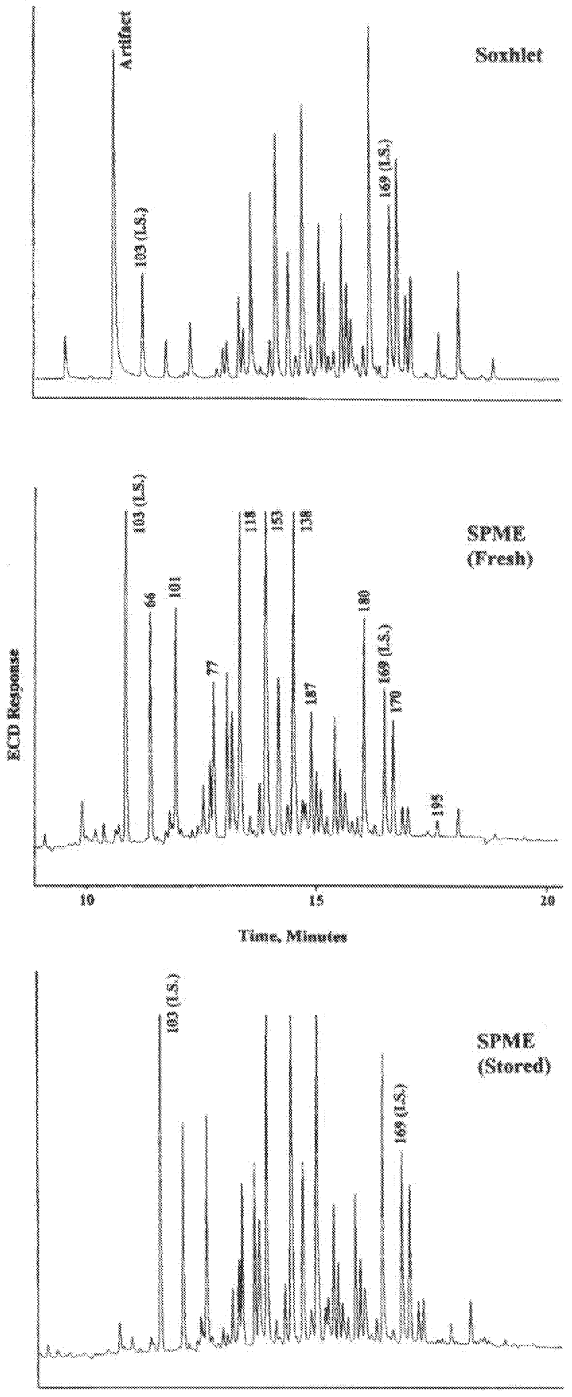


Fig. 7. Comparison of 18-h Soxhlet with a 20-fold preconcentration prior to analysis and 60-min, 250 °C SWE–SPME for the extraction of PCBs from soil and analysis by GC–ECD; see Ref. [59] for experimental details.

eluting congeners and the Soxhlet extract has a large artefact peak at the beginning of the chromatogram, which is not present with the SWE–SPME method.

Despite the obvious advantages of sorbent trapping versus solvent trapping of the analytes extracted with subcritical water, sorbent trapping and subsequent desorption is still a rather time-consuming approach: it usually requires concentration of the extracts before final analysis of an aliquot of the total initial sample. Coupling of SWE with LC has led to the development of solvent-free methods and has contributed to (virtual) elimination of most of these drawbacks. Li et al. [73] proposed the use of an LC guard column packed with $C_{18}$-bonded silica placed in an ice bath as solid trap to preconcentrate the analytes extracted by SWE. The method gave satisfactory recoveries for the SWE of pollutants of different polarity from a spiked clean sand, e.g., chlorophenols, 89–108%, chloro- and methylanilines, 94–108%, nitrotoluenes, 88–108%, and PCBs, 87–102%, with only some peak broadening and loss of the most polar compounds by breakthrough as the main shortcomings. However, no results on naturally contaminated (or aged) complex soils were presented. The feasibility of this approach for the extraction of endogenous pesticides with high and intermediate polarity from a variety of soils was reported by Crescenzi et al. [46]. The authors carried out a two-step extraction with phosphate-buffered water at 0.5 ml/min and 90 and 130 °C, respectively. Only 16 ml of buffered water were used. The analytes were on-line preconcentrated on a $C_{18}$ sorbent trap and then transferred to the LC analytical column via a loop to allow mixing with the internal standards. The authors reported that the organic matter content of the soils had no influence on the performance of the system or peak broadening because of the on-line coupling of the sorbent trap and the LC system and proved that the addition of phosphate enhanced the efficiency of the SWE process ($f$=1.0–1.8, SWE with pure water at 90 °C as reference). Complete analysis was accomplished within 1 h with satisfactory recoveries ($f$=1.0–1.8; 16-h Soxhlet extraction as reference) and precision (RSDs, 8–15%).

Much higher temperatures are required for the quantitative extraction of hydrophobic pollutants such as PCBs, PAHs and PCDD/Fs (Table 3).

Hawthorne et al. [49] compared the efficiencies of SWE and PLE with those of Soxhlet extraction and SFE with pure $CO_2$ for the extraction of 17 (endogenous) EPA PAHs from a highly contaminated soil. Although rather similar recoveries were obtained with all techniques, SWE provided better results for the high-molecular mass PAHs ($f$=0.8–1.5, 0.8–1.7 and 0.8–1.5: Soxhlet, PLE and SFE with pure $CO_2$ as reference methods, respectively). The authors theorized that this result is possibly due to the higher swelling of the clay particles with the subcritical water compared with the organic solvents and fluids. This would make the analytes more available for extraction in the former case. Nevertheless, the quantitative extraction of pollutants as apolar as PCDD/Fs and PCNs can be accomplished only by using steam conditions. Using water at 1 ml/min, 300 °C and 5 MPa, Van Bavel et al. [50] reported rather satisfactory results when determining the levels of endogenous PCDFs ($f$=0.7–1.1, except for OCDF; consensus value in interlaboratory comparison as reference) and PCNs ($f$=0.9–1.4; 12-h Soxhlet extraction with toluene as reference) from naturally contaminated soils. Increasing the extraction temperature to 350 °C while maintaining the pressure at 5 MPa caused increased PCDF recoveries, which could not be explained by the changing characteristics of water. According to the authors, the enhanced thermal desorption and vapour pressure of the analytes may explain the faster kinetics of extraction. However, the simultaneous rapid increase of the extracted amount of matrix components adversely affected the results and temperatures up to 300 °C were the recommended range for this kind of analysis.

Hyötyläinen et al. [74] also found a better efficiency for the extraction of the EPA PAHs from a river sediment with steam at 300 °C and 12 MPa than with liquid water. However, some back-pressure problems prevented them from using as high a temperature as they proposed for on-line SWE–LC–GC of solid environmental samples. Fig. 8 shows a schematic of a set-up for SWE–LC–GC which allows the entire sample preparation and analysis to be performed in a closed system. Briefly, the solid sample, in this case 10 mg of a sediment, was subjected to continuous SWE at 1 ml/min, and the extract preconcentrated on a Tenax TA trap which simultaneously acted as an analytical LC column to separate the target compounds, i.e., PAHs, from the

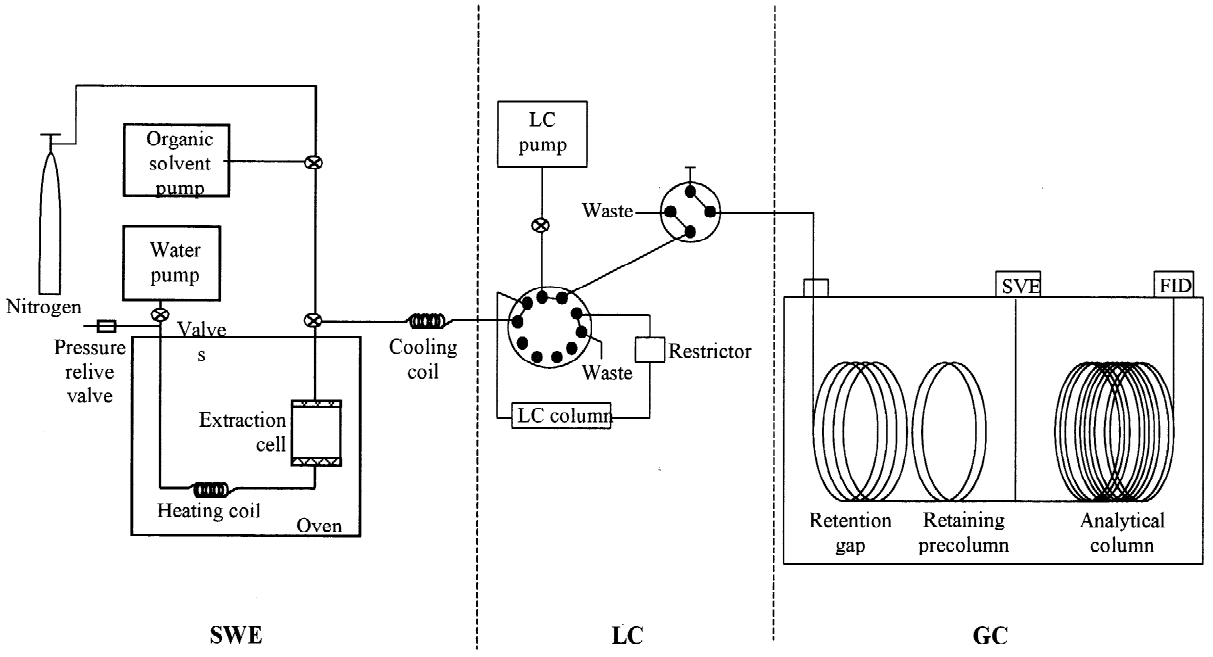


Fig. 8. Schematic of the basic set-up for SWE–LC–GC.

co-extracted material. After purification, a 780-μl fraction containing the analytes was transferred to a GC–FID system equipped with a retention gap and a retaining precolumn. Elimination of the solvent was achieved by partially concurrent solvent evaporation via a solvent vapour exit (SVE). Because of the use of a closed system, the amount of analytes injected in the GC is much higher than in off-line systems. This caused a 400-fold increase of the sensitivity of the analysis compared with traditional methods. Satisfactory recoveries were obtained for all PAHs ($f$=1.0–3.1; SFE with $CO_2$+MeOH at 150 °C, 36 MPa, 10 min static+20 min dynamic as reference), except for benzo[*a*]pyrene. As expected for a closed system, the method provided high relative recoveries for the most volatile analyte, naphthalene ($f$=8.8) and RSDs better than 28%. The limits of quantification (LOQ) were below 10 ng/g for all PAHs. The set-up was recently used for the determination of brominated flame retardants [75]. Here, 100 mg of a sediment were mixed with 1 g of sand and extracted for 40 min at 1 ml/min with steam at 325 °C and 12 MPa. A larger Tenax trap was used to avoid breakthrough of the analytes. The on-line procedure was much more efficient than the Soxhlet reference method ($f$=2.8–5.6) and gave LOQs below 12 ng/g.

### *4.2. SWE of foodstuff*

Until now, only a few examples of SWE of residues in foodstuff have been published [56,76]. Pawlowski et al. [76] evaluated the feasibility of two consecutive 10-min static SWEs, at 100 °C and 5 MPa for pesticide residue determination in a variety of fruits and vegetables, including lemon, orange, banana, mushrooms and rice. Because of the different characteristics of the samples, the authors proposed dispersion of the samples on glass beads to achieve uniform flow-rates of the solvent during the final dynamic SWE and, more importantly, to ensure the homogeneous extraction of the samples under the proposed experimental conditions. Satisfactory results were obtained for thiabendazole ($f$=1.0–1.8; results obtained by independent laboratory using traditional procedures as reference). However, carbendazim could not be detected when using SWE (0.08 μg/g were detected with the classical method) even if acids were added as modifiers.

## 5. Conclusions

PLE is a technique which allows the efficient extraction of micropollutants from a variety of environmental samples in less time than is required in classical procedures and with less solvent consumption. As not too many parameters affect the PLE process, optimisation is relatively easy. The main parameters to be considered are the extraction solvent, and the extraction temperature. As a general strategy, the solvent used for a specific analysis in classical extraction procedures involving heat treatment can also be used for PLE at a temperature above the solvent boiling point and a pressure high enough to keep it as a liquid at that temperature; the limitation is that the conditions should not cause degradation of thermolabile analytes and matrices. The nature of the matrix (water content, organic content) and its physical characteristics (homogeneity, porosity, particle size) should also be considered. For instance, the efficiency of PLE for analytes that have to be isolated from wet or highly adsorptive samples can be significantly improved by increasing the pressure and by using mixtures containing a more polar or selective solvent, respectively. Proper solvent selection can help to eliminate the influence of the matrix properties on the PLE recoveries. Once the optimal solvent has been selected, experiments should be carried out to determine the time required for the quantitative extraction of the target compounds. The selectivity of the PLE process can also be improved by adding an appropriate sorbent to the extraction cell for simultaneous clean-up. Such an approach increases the speed of the sample preparation by virtually eliminating the need for any subsequent clean-up of the extracts and reduces the total solvent consumption.

In summary, PLE combines good recoveries and adequate precision with rapid and rather selective extraction, while the sample handling is less time-consuming than with classical procedures. The high initial investment costs, some practical problems associated with the homogeneous and reproducible packing of heterogeneous samples in the smaller-size PLE extraction cells, and the limited possibility of carrying out selective extractions of organic compounds from complex samples are the main drawbacks of the technique.

SWE can be considered a PLE-type procedure in which water is used as the extraction solvent. Water is a non-toxic and inexpensive solvent but, from a practical point of view, the main advantage of SWE over PLE is that, as pressure has little effect, only one variable, i.e., the temperature, has to be optimised. This helps to simplify the optimisation of procedures. Furthermore, because the polarity of water can easily be modified by changing the temperature, the technique looks to have a wider range of applications than PLE or SFE with carbon dioxide, where the available polarity range is more narrow and polar compounds cannot easily be included. Class-selective extraction by means of temperature programming is an interesting option in SWE. Although dilution of the extracts is, in principle, a main drawback of SWE, the recent combination with SPE, LC and SPME has opened new routes and, consequently, a wide range of applications may well be expected, e.g., in the area of residue analysis in foodstuff or for the evaluation of the bioavailability of micropollutants which can be sequentially extracted from the sample matrix.

Finally, it is worth mentioning that for both PLE and SWE, the use of internal standards is strongly recommended, especially when small amounts of complex samples have to be analysed. As with all other preparation procedures for (semi-)solid samples, due care should always be taken to ensure a proper sorption of the spiked compounds in the matrix to avoid erroneous calculation of the concentrations of endogenous compounds if their extraction is not quantitative.

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