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Micelle formation for improvement of continuous subcritical water extraction of polycyclic aromatic hydrocarbons in soil prior to high-performance liquid chromatography–fluorescence detection

V. Fernández-Pérez, M.D. Luque de Castro*

Analytical Chemistry Division, Anex C-3, Campus of Rabanales, University of Córdoba, E-14071 Córdoba, Spain

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Abstract

A new method for the extraction–individual separation–determination of polycyclic aromatic hydrocarbons (PAHs) in soil is reported. The method is based on the integration of three steps: continuous subcritical extraction, solid-phase clean-up/preconcentration, and HPLC separation with post-column fluorimetric determination. Sodium dodecyl sulfate (SDS) was added to the water for favouring the extractability of the low-polarity analytes. Soil samples spiked with the target PAHs were subjected to static–dynamic extraction with SDS–water at 50 bar, 150°C, for 15 min of static extraction and 10 min dynamic extraction at a flow-rate of 3 ml/min. Recoveries from 73.6 to 110.4% were obtained in the presence of SDS versus 30 to 80% obtained with water as extractant. The calibration graphs provided by HPLC–fluorimetric detection were run between 0.031 and 0.375 μg/ml for each analyte with regression coefficients between 0.917 and 0.999 and precision, expressed as RSD, between 1.2 and 11.5%. The method was applied to a certified reference material [CRM 524, BCR (Community Bureau of Reference), industrial soil/organic] for validation and the results obtained were in agreement with the certified values.

Keywords: Subcritical water extraction; Extraction methods; Soil; Polynuclear aromatic hydrocarbons

1. Introduction

The determination of polycyclic aromatic hydrocarbons (PAHs) in environmental samples represents an area of analysis where strict government controls now exists in order to regulate the production, usage and disposal of this group of materials [1,2] due to their mutagenic and carcinogenic characteristics. It is evident that the concentration levels of PAHs in natural, solid samples, if present, should be very low; so some extraction and preconcentration steps are usually required prior to their measurement.

The most common procedure for leaching PAHs from soils and sediments is conventional Soxhlet extraction which, whilst being efficient, usually requires extraction times in excess of 6 h and necessitates the use of large volumes of solvent. Techniques such as pressurised liquid extraction (PLE) are also widely used [3,4]. The main trends of present studies in this area are the use of auxiliary energies and fluids at suitable temperature and pressure. Auxiliary energies such as ultrasounds and microwaves have enabled one to shorten treatment

*Corresponding author. Tel./fax: +34-957-218-615.
E-mail address: qa1lucam@uco.es (M.D. Luque de Castro).

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steps such as digestion, fusion and leaching of solid samples [5,6].

In the last few years, a number of analytical chemists have tried to use supercritical fluids as leaching agents [7–9]. The vast majority of analytical supercritical fluid extraction (SFE) methods have been focused on the use of supercritical CO_2. The most important limitation in using CO_2 as an extraction solvent is that its polarity is often too low to obtain efficient extraction of organic pollutants from solid matrices [10–12].

Water is an environmentally acceptable solvent, but its dielectric constant (ϵ) at ambient temperature and pressure (ca. 80) [13] hinders efficient solvation of low-polarity organic pollutants such as fuel hydrocarbons, PAHs and PCBs (polychlorinated biphenyls). Increased temperatures have a lowering effect on the dielectric constant of water, which reaches a value between 5 and 15 above its critical point (378°C, 221 bar), thus allowing extraction of low-polarity and non-polar compounds [14–16]. Nevertheless, the corrosiveness of water increases with increased temperature; so, low-temperature extractions are desirable in order to decrease deterioration of the experimental set-up and also to decrease cost. In the last years some authors have investigated the use of subcritical water for the extraction of organic pollutants from natural samples [17–19].

On the other hand, the cloud-point extraction methodology [20] has been applied to the extraction of a wide range of analytes including PAHs, porphyrins, vitamin A, vitamin E, β-estradiol, estriol, estrogen, progesterone and proteins [21–26] from aqueous solutions. The analytical interest of cloud point is a consequence of the (a) ability to concentrate a variety of analytes; (b) safety and cost benefits; (c) easy disposal of the surfactant; (d) compatibility of the surfactant-rich phase with micellar liquid chromatography; and (e) preclusion of the analytes losses during the evaporation of the solvent used in traditional liquid–liquid extraction.

The choice of a fluorimetric technique for on-line detection of PAHs after chromatographic separation is supported on the highest selectivity and sensitivity of this technique as compared with other such as molecular absorption. The selectivity could also be increased by wavelength selection.

The aim of this paper has been to develop a method linking subcritical water extraction and micelle-based methodologies for the leaching of low-polarity organic compounds from solid matrices, thus overcoming the high polarity of the extractant.

2. Experimental

2.1. Instrumentation

Subcritical water extraction was performed using the prototype extractor shown in Fig. 1 designed by Salvador and Merchán [27]. It consists of a stainless steel cylindrical extraction chamber (8×3 mm I.D.) (Keystone Scientific, Bellefonte, PA, USA), closed with screws at either end, that permits the circulation of the leaching fluid through them. Both screw caps contain stainless steel filter plates (2 μm in thickness and 1/4 in. I.D.; 1 in.=2.54 cm) to ensure that the sample remains in the extraction chamber. This chamber, together with a stainless steel preheater, is located in an oven, designed to work up to 300°C. This variable was controlled using a Toho TC-22 temperature controller. A Shimadzu (Tokyo, Japan) LC10AD pump with digital flow-rate and pressure readouts was used to impel the extractant through the

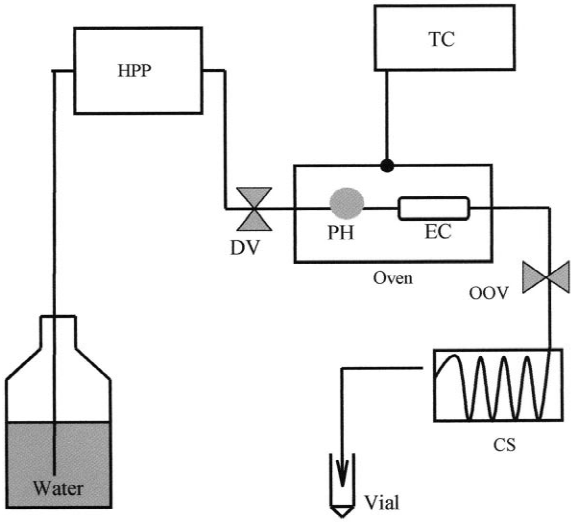

Fig. 1. Schematic diagram of the subcritical water extractor. HPP=High-pressure pump; PH=preheater; CS=cooler system; EC=extraction cell; TC=temperature controller; DV=diverting valve; OOV=on–off valve.

system. A cooler system (consisting of a loop made from 1 m length stainless steel tubing and cooled with water at room temperature) was used to cool the extract from the oven to a temperature close to 25°C.

A Vac Elut sps 24 (Varian) vacuum station incorporated to an Eyel4 A-3S evaporator (Tokyo, Japan) was used, too.

The individual separation and quantification of the analytes in the extract was performed by a HP 1100 liquid chromatograph (Hewlett-Packard, Avondale, PA, USA) consisting of a G1311A high-pressure quaternary pump, a G1322A vacuum degasser, a Rheodyne 7725 high-pressure manual injector valve (20 μl injection loop) and a G1315A diode array detection (DAD) system (Cotati, CA, USA). An ultrabase C_{18} column (250×4.6 mm I.D.) packed with 5 μm particles and supplied by Scharlau Science (Barcelona, Spain) was used for the chromatographic separation. A Hitachi (Model F-1050) chromatographic spectrofluorimeter (Hitachi, Tokyo, Japan) equipped with a high-pressure flow cell of 12 μl inner volume and a D-2500 integrator (Hitachi), was in series coupled to the DAD system for more selective and sensitive determination of the analytes.

2.2. Materials

Ultrapure water obtained from a Milli-Q system (Millipore, Bedford, MA, USA) was used throughout. Sodium dodecyl sulfate (SDS) (Aldrich, Milwaukee, WI, USA) was used as micelle former. The PAHs {namely pyrene (pyr), benzo[*a*]pyrene [b(a)pyr], benzo[*a*]anthracene [b(a)ant], benzo[*e*]acenaphtene [b(e)ace], benzo[*k*]fluoranthene [b(k)flu] and benzo[*ghi*]perylene [b(ghi)per]} were obtained from Sigma (St. Quentin, Fallavier, France), Aldrich (Milwaukee, WI, USA) and Fluka (Buchs, Switzerland). These compounds were used for preparing the stock solutions (350 μg/g of each) in HPLC-grade acetonitrile (Merck, Darmstadt, Germany).

The solid-phase extraction was performed using either C_{18} or silica gel, C_{Si} (500 mg, 3.0 ml) bonded phases obtained from Bond Elut cartridges (Varian, Harbor City, CA, USA); methanol and hexane (Merck) were used as eluents. An N_2 stream (Carburos Metálicos, Barcelona, Spain) was used for removal of hexane. All solvents were of HPLC-grade (Merck).

2.3. Sample preparation

A 500-g amount of air-dried clay soil was sieved to a size smaller than 1 mm. Samples spiked with PAHs (0.3 μg/g of each) were prepared by adding to the soil 200 ml of diethyl ether (Panreac, Barcelona, Spain) containing the necessary volume of stock standard solution of the PAHs. Then, the slurry was shaken for 72 h and, after evaporation of the solvent, the soil was completely dried under an N_2 stream. Finally, the sample was stored at −20°C until use.

2.4. Procedure

2.4.1. Continuous extraction with surfactant-modified subcritical water

A 0.2-g amount of sample and 1 ml of $5 \cdot 10^{-2}$ *M* SDS were placed in the extraction cell in Fig. 1. After connecting the cell to the system, this was pressurised with ~50 bar by opening the inlet valve from the pump and closing the outlet valve, in this way the sample was saturated with the extractant. Then, the oven was brought up to the working temperature (150°C) and the static extraction was developed for 15 min. Both the inlet and the outlet valves were then opened, the water was pumped through the oven at a flow-rate of 3 ml/min and the extract was collected in a vial after being cooled in the cooler system at ca. 25°C.

For kinetic experiments, the extraction was performed under optimum conditions and replacing the vial at preset intervals of 3 min.

2.4.2. Solid-phase extraction

After the extraction was complete, a known volume of approximately 50 ml of the collected effluent was passed through a C_{Si} bonded column where the micellar phase was retained and the waste discarded.

A hexane volume of 5 ml was passed through the cartridge for eluting the PAHs. The eluate was reduced to dryness using an N_2 stream. The residue was recomposed in 1 ml of acetonitrile and the solution introduced into the chromatograph.

When pure subcritical water extraction was used,

the extract was passed through a C_{18} bonded column and eluted with 5 ml of methanol.

2.4.3. HPLC determination

The HPLC separation of the PAHs was performed using a gradient elution program in which an acetonitrile–methanol–water (85:1.8:13.2) mixture was used as initial mobile phase at a flow-rate of 0.8 ml/min. The gradient program was as follows: (1) the initial mobile phase was held for 5 min; then, two linear gradients were established in order to reach first a (90:1.8:8.2) composition in 15 min, and then a final (98.2:1.8:8.2) composition in 10 min more. Finally, 10 min was necessary for re-establishing the initial conditions. Photometric detection was performed at 240, 256 and 290 nm, meanwhile the fluorimetric detection was performed at 300 and 400 nm, for excitation and emission, respectively. The injection volume was 20 μl in all cases.

3. Results and discussion

3.1. Optimisation study

The overall method proposed here involved removal of the target analytes from the soil sample with continuous monitoring of the extraction kinetics, concentration of the extracts and chromatographic separation/dual detection. The order used in the optimisation of the steps was as follows: first the chromatographic separation of the target analytes using both photometric and fluorimetric detection was optimised for checking of the other previous steps when developed; then the preconcentration step was established, after a preliminary study of the extraction step in order to know approximately the extraction efficiency, for making it possible to optimise the preconcentration step.

The ranges over which the variables were studied, and the optimum values found are listed in Table 1. The univariate method was used in all instances.

3.1.1. Optimisation of the continuous subcritical water extraction step

The *variables concerning leaching* (namely temperature, type and concentration of surfactant) were studied using a 0.2-g amount of soil, a static extraction time of 10 min and a dynamic extraction time of 30 min. Since the extractor was not fitted with a pressure controller, a pressure of ~50 bar (created in the system by the working conditions) was used in all instances. This pressure was enough for keeping the extractant in the liquid state.

The temperature of the extraction chamber is the key variable when subcritical water is used as extractant. Its influence was studied between 50 and 200°C at a constant flow-rate of 1 ml/min. Extraction at 50°C failed to yield significant recoveries of any of the analytes. As the temperature was increased the recoveries of the PAHs increased substantially. Thus, the extraction efficiency improved from 6.6% for pyr and 50% for b(ghi)per to 20% and 63%, respectively, when the temperature was changed from 50 to 100°C, and from 20% to 50% for pyr and from 63% to 94% for b(ghi)per when this parameter rose from 100 to 150°C. Higher temperatures did not provide any improvement. A temperature of 150°C was selected as optimum for further experiments.

The *leacher composition* was also evaluated. Water was modified with a surfactant in order to obtain a micellar medium where the PAHs could be easily extracted. Different surfactants were studied at concentrations above their critical micellar concentration (CMC); namely, Triton X-100 in the range $3\cdot10^{-4}$–$1\cdot10^{-2}$ *M*, SDS, DBS (dodecylbenzene sulfonic sodium salt) in the range $2.5\cdot10^{-3}$–0.1 *M* were studied as non-ionic, anionic and cationic surfactants, respectively. The best results were obtained when the anionic surfactant was used. So another anionic surfactant, namely Aerosol OT (trademark of American Cyanamid), ranging from $2.5\cdot10^{-3}$–0.1 *M*, was also investigated and compared with SDS. The best results corresponded to SDS.

Two ways for introducing the surfactant in the system were assayed: in the water used as extractant or by direct addition of the surfactant solution into the extraction chamber. There were no differences in the recoveries when the SDS was used in continuous or 1 ml was added to the extraction chamber. The second approach was chosen for minimising reagent consumption.

The *surfactant concentration*, ranging from $5.4\cdot10^{-3}$ *M* (CMC) to 0.1 *M* was also studied. The efficiency of the extraction increased with concen-

Table 1
Optimisation of the method

Step	Variable	Ranged studied	Selected value
Extraction	Temperature (°C)	50–200	150
	Pressure (bar)	–	50
	Surfactant		
	Non-ionic	Triton X-100	
	Cationic	DBS	
		DTAB	
	Anionic	SDS	SDS
		Aerosol-OT	
	[SDS] (mol/l)	$5.4 \cdot 10^{-3}$–0.1	$5 \cdot 10^{-2}$
	Flow-rate (ml/min)	0.5–5.0	3.0
	Static extraction time (min)	0–30	15
	Dynamic extraction time (min)	0–30	10
Solid-phase preconcentration	Bonded column	C_{18}	
		C_{Si}	C_{Si}
	Eluent	Hexane	
		Trichloromethane	
		Dichloromethane	
		Acetonitrile	Hexane
		Cyclohexane	
		Methanol	
	Eluent volume (ml)	1–15	5
Chromatography	Initial mobile phase composition		8.5:1.8:13.2
	Column		C_{18}
	Flow-rate (ml/min)	0.6–1.5	0.8

tration but levelled off at concentrations higher than $5 \cdot 10^{-2}$ *M*. So, a $5 \cdot 10^{-2}$ *M* SDS concentration was fixed for subsequent experiments.

The *hydrodynamic variables*, namely flow-rate, and static and dynamic extraction times, were also evaluated.

The *flow-rate* of the subcritical water was studied for constant extractant volumes of 10 ml and values of the variable from 0.5 to 5.0 ml/min were investigated. The efficiency increased with flow-rates up to 3.0 ml/min, but at higher flow-rates gave rise to overpressure in the system, which hindered extraction, so, a 3.0 ml/min flow-rate was selected for all the experiments.

The *static extraction time* study ranged between 0 and 30 min with a constant dynamic extraction time of 5 min. This short time for dynamic extraction was selected in order to show clearly the influence of the static extraction. Shorter times for this study were not assayed in order to do not prolong excessively the overall extraction time as the static period is less effective that the dynamic one, but it favours the surfactant–soil contact and decreases dilution of the analytes. A 15-min static extraction time was selected as it provided the best signal, observing no improvement for longer times.

After optimising all the variables affecting the extraction step, the effect of temperature, as key variable, was checked again. Fig. 2 shows the extraction recovery of each analyte in the range of temperatures under study. Along this optimisation study no total or partial clogging due to deposit of the PAHs in the transfer line was detected for any sample size used despite to the narrow diameter of the transfer line. This undesirable phenomenon is usually detected by an overpressure in the dynamic system and its absence can be attributed to the micelle formation of the target analytes.

3.1.2. Optimisation of the solid-phase extraction step

Due to the necessity for preconcentrating the

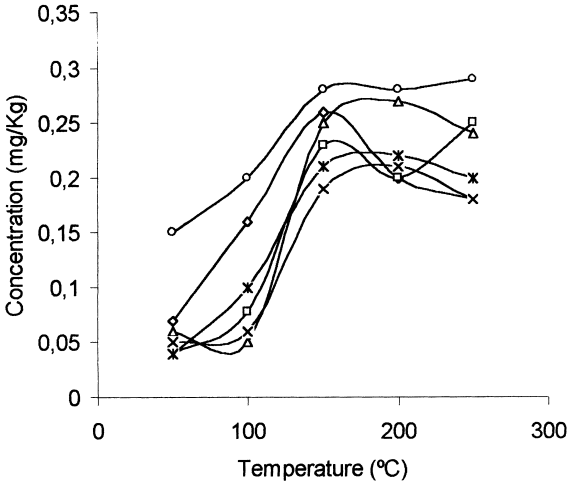

Fig. 2. Variation of the extraction efficiency with the temperature for each PAH. (○) b(ghi)per, (◇) pyrene, (□) b(e)ace, (△) b(a)ant, (∗) b(a)pyr, (×) b(k)flu.

target analytes, a solid-phase extraction step was required. The study concerning it consisted of selecting both the best bonded sorbent material in order to retain and separate the analytes from the extract, and the eluent required for proper elution of them.

Two *types of sorbents* were tested: C_{18} and C_{Si}. The former was used after extraction with pure water, due to the non-polar character of the PAHs. When the analytes were extracted as micelles, the use of a C_{Si} bonded column for clean-up/preconcentration of the analytes was mandatory because of the ionic nature of the surfactant.

After selection of the sorbent, different *eluents* were investigated in order to achieve elution of the PAHs from the solid-phase in a minimum volume. With this aim hexane, trichloromethane, dichloromethane, acetonitrile, cyclohexane, ethanol and methanol were assayed. Only two of the solvents yielded good results. Hexane and methanol were the best eluents for C_{Si} and C_{18}, respectively. The volume of solvent necessary for quantitative elution of the analytes was 5 ml in both cases.

3.1.3. Chromatographic variables

The experimental variables studied for obtaining appropriate separation of the analytes were the composition of the initial mobile phase, flow-rate and injection volume. Different initial methanol–acetonitrile–water ratios and different gradients were assayed for separation of the analytes from the Ultrabase C_{18} column. The influence of the flow-rate of the mobile phase was studied in the range 0.6–1.5 ml/min, and the best separation was obtained for a flow-rate of 0.8 ml/min. An injection volume of 20 μl was selected as a compromise in order to avoid both fluorimetric signal saturation (high volumes) and non-quantifiable photometric signal (low volumes).

Two in-series detectors were used after HPLC separation. The DAD system, included in the chromatograph, was used at the beginning of the research for peak identification and optimisation of the separation. However, it was not enough sensitive nor selective and, consequently, the chromatograms were obtained from liquid standards with concentration above 0.5 μg/ml (for each PAH) or soil spiked with very concentrated standard solutions, where the effect of other species extracted from the matrix on the analytes chromatogram was negligible. A chromatographic fluorescence detector located in series after the DAD system circumvented this drawback because of its higher sensitivity and selectivity, which made possible to work at the concentrations of PAHs usual in natural samples.

The chromatogram provided by the fluorimetric detector from a spiked soil under the optimum working conditions is shown in Fig. 3. As can be observed, 32 min was necessary in order to obtain complete separation of the six PAHs contained in the sample.

3.2. Features of the fluorimetric-determination step

Calibration graphs were run by the use of standard PAH solutions in HPLC-grade acetonitrile. The concentration of the standards fitted within the linear portion of the calibration graphs and ranged between 0.031 and 0.375 μg/ml for each PAH, except for pyrene whose concentration ranged between 0.025 and 1.750 μg/ml (this PAH is usually present in natural samples at higher concentrations than the others). Five points were used to run the curve in all instances. Hence, the total concentration of the PAHs in the standards ranged between 0.175 and 4.000 μg/ml. Higher concentrations produced quenching

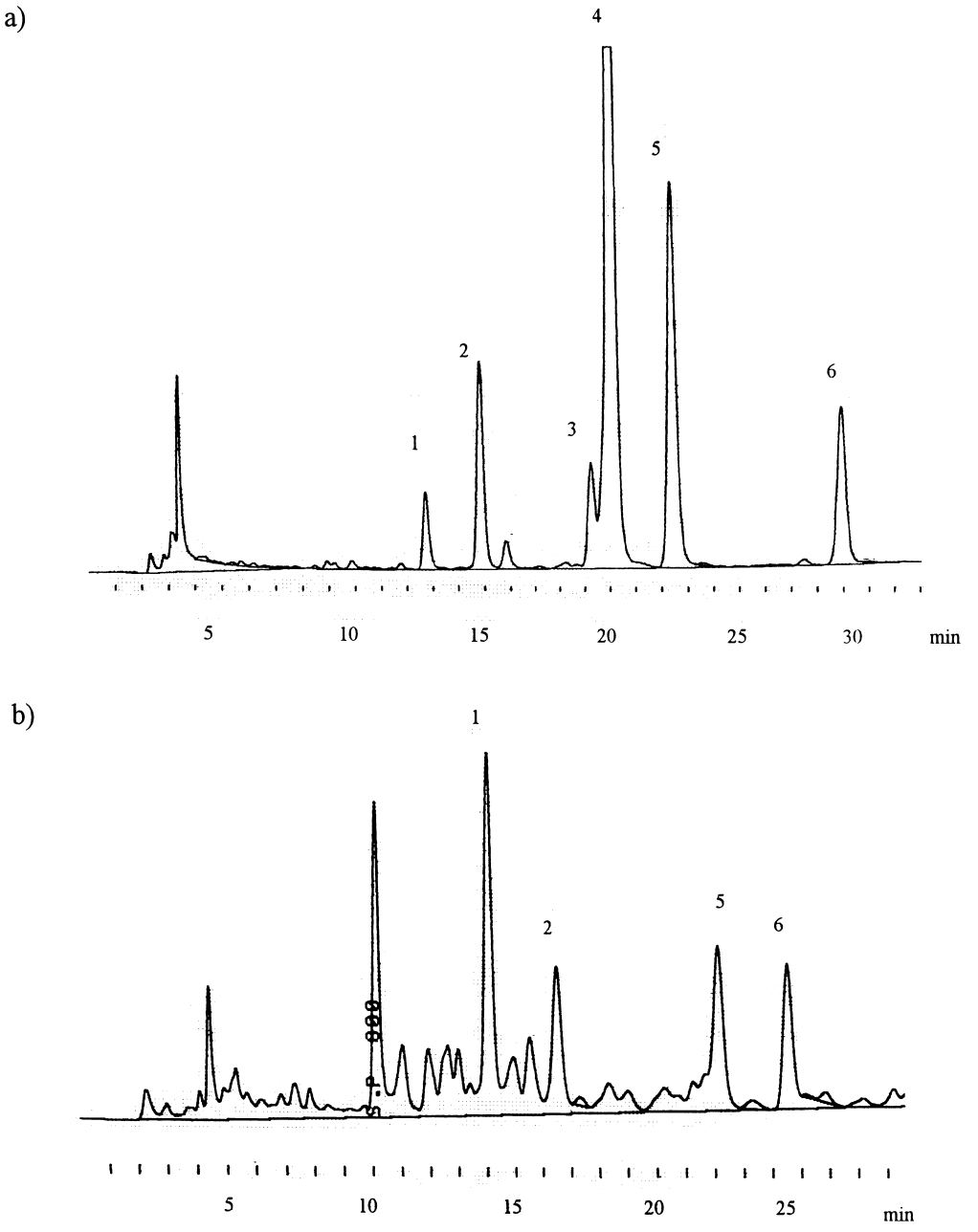

Fig. 3. Chromatograms of the target analytes obtained under optimum conditions for (a) spiked soil and (b) reference material. (1) Pyr; (2) b(a)ant; (3) b(e)ace; (4) b(k)flu; (5) b(a)pyr; (6) b(ghi)per.

of fluorescence and thus, curvature of the fluorescence–concentration relationship. Each concentration point was calculated by triplicate experiment. The results obtained are listed in Table 2, where statistically different to zero intercepts can be observed. This fact can be explained by high slopes, which magnify small deviations of the calibration lines. The repeatability of the HPLC detection, expressed as

Table 2
Features of the determination method

Analyte	Equation	Linear range (μg/ml)	Precision[a] (RSD, %)	Regression coefficient (r^2, %)	Detection limit (μg/ml)	Quantification limit (μg/ml)
Pyr	$y=(3068\pm835)+(223\,246\pm892)x$	0.025–1.750	4.03	99.96	0.028	0.094
b(a)ant	$y=(-4658\pm977)+(730\,151\pm6053)x$	0.031–0375	3.86	99.91	0.008	0.027
b(e)ace	$y=(-1747\pm598)+(245\,326\pm3045)x$	0.031–0375	3.75	99.80	0.015	0.050
b(k)flu	$y=(6618\pm2999)+(2\,400\,583\pm15\,595)x$	0.031–0375	3.84	99.95	0.008	0.026
b(a)pyr	$y=(-25\,547\pm3294)+(2\,178\,852\pm15\,317)x$	0.031–0375	2.59	99.94	0.009	0.031
b(ghi)per	$y=(-4926\pm2017)+(667\,029\pm10\,260)x$	0.031–0375	4.77	99.69	0.019	0.062

[a] Concentration of PAHs in the repeatability study: 0.15 μg/ml.

RSD, for each analyte, was obtained using seven solutions of 0.175 μg/ml of the mixture and is also reported in Table 2.

3.3. Comparison of extraction in the presence and absence of surfactant

A comparison between the kinetic extraction curves for dynamic subcritical water extraction with SDS (SDS–SWE) and without the help of the ionic surfactant (SWE) is shown in Fig. 4 (after 15 min of static extraction in all instances). The kinetics of the extraction depends on the amount of the extractant passed through the extraction chamber but, as can be proved, when the surfactant is added to the chamber an improvement in the static step of the extraction makes possible the quantitative extraction of the target analytes in a time shorter than without micelle formation.

The kinetic study was made under optimum conditions (150°C, 3.0 ml/min and 15 min of static extraction time). As can be observed, some PAHs such as pyrene, benzo[*a*]anthracene, benzo[*k*]-fluoranthene and benzo[*a*]pyrene were extracted with SDS–SWE within 10 min of dynamic extraction. Times over 40 min were necessary for quantitative recovery of the spiked analytes when only SWE was used. Benzo[*a*]acenaphtene was completely extracted in 6 min in the presence of surfactant but a recovery of 30% was obtained with SWE even after extraction for 1 h. Benzo[*ghi*]perylene extraction was complete in a short time in both cases: 2 and 5 min were necessary for quantitative leaching in the presence and absence of surfactant, respectively.

These results demonstrate the usefulness of using a micellar medium in order to achieve complete extraction in a very short time.

3.4. Validation of the method

First, the method was applied to a spiked soil and the results obtained from the treated extract are shown in Table 3.

The use of a certified reference material (CRM) in this research had a double aim. First of all, it was used in order to demonstrate the efficiency of using micelle formation for fast, quantitative extraction of endogenous PAHs in soil; in addition, the use of CRM showed the independence of the system on the sample matrix effect.

The certified material used was CRM 524 (Community Bureau of Reference, BCR, Brussels, Belgium), an industrial soil in which a mixture of eight PAHs (five of them; namely [pyr], [b(a)ant], [b(e)pyr], [b(k)flu] and [b(a)pyr] coinciding with those used for spiking) and some traces of pentachlorophenol (PCP) are the certified analytes. Although the CRM contains eights PAHs, the method was validated for four of them, those that were used in the optimisation study and available in our laboratory. Thus, the optimised conditions were applied to 0.2 g of CRM.

As can be seen in Table 4, the amount of each PAH extracted by the proposed method is in a good agreement with the certified value.

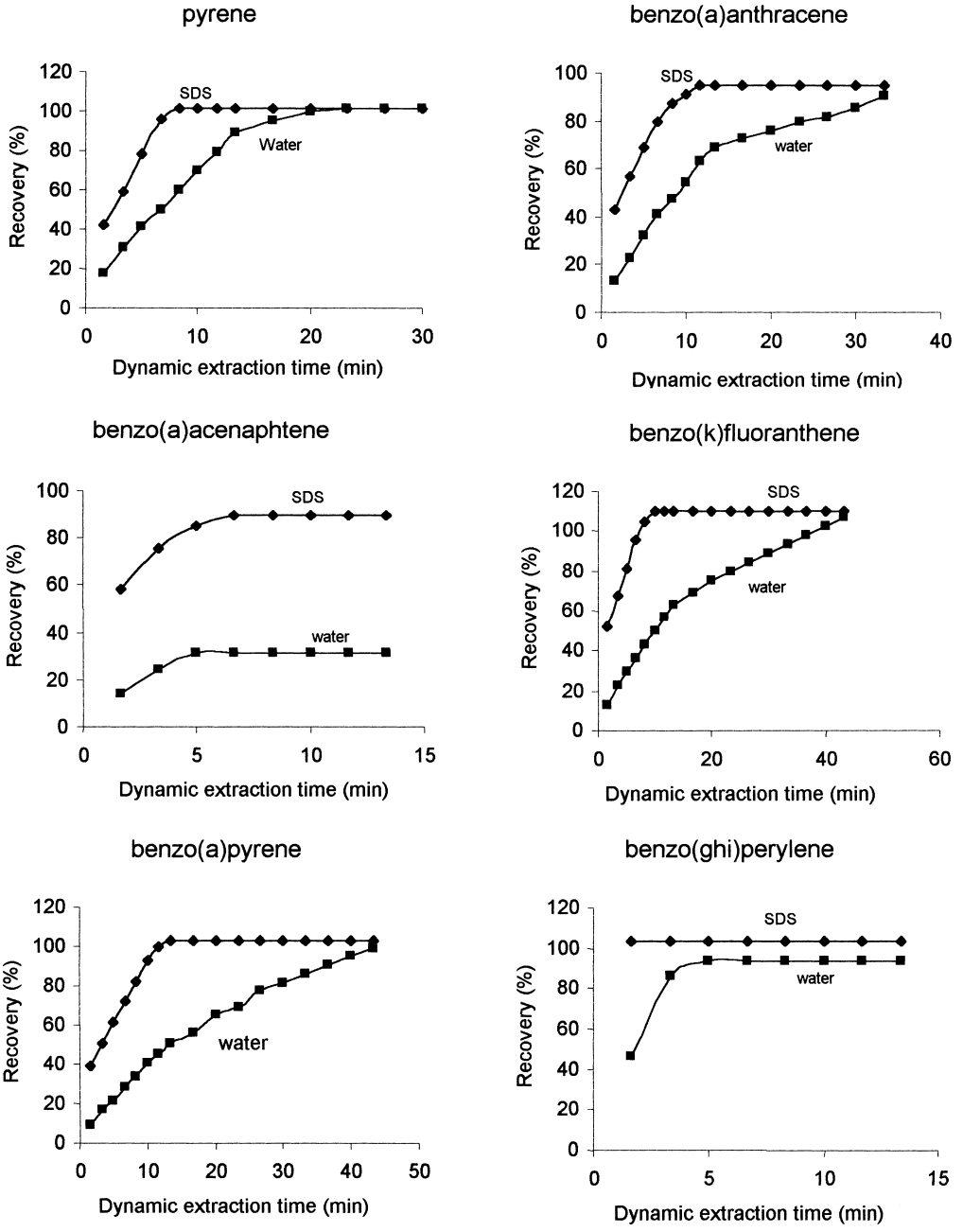

Fig. 4. Kinetic curves of the six PAHs leached under the optimum working conditions by SDS–SWE and SWE.

4. Conclusions

A comparison of the use of subcritical water as extractant with and without micelle formation of the target PAHs using an anionic surfactant indicated that whilst the recoveries for long extraction times are comparable in both cases, the use of SDS significantly shortens the extraction time. A kinetic

Table 3
Application of the method to a spiked soil

Analyte	Spiked concentration (μg/g)	Found concentration (μg/g)	RSD[a] (%)	Recovery (%)
Pyr	0.30	0.305	10.4	101.8
b(a)ant	0.30	0.220	11.5	73.6
b(e)ace	0.28	0.269	10.2	96.8
b(k)flu	0.28	0.309	7.4	110.4
b(a)pyr	0.29	0.309	9.3	106.5
b(ghi)per	0.30	0.312	1.2	104.0

[a] $n=8$.

study shows the suitability of using a surfactant, such as SDS, for quantitative extraction of PAHs from a solid sample. About 10 min of dynamic extraction are enough for leaching the target analytes when SDS is used, but times over 40 or 50 min for complete extraction in the absence of surfactant are necessary. Only one PAH, benzo[*ghi*]perylene has almost similar extractabilities in both cases. The results of this study demonstrate that SDS is an enhancer for the extraction of non-polar organics from soils (see Fig. 3).

The most significant aspect of lowering the temperature required for quantitative water extraction is the fact that deterioration of the extractor due to the corrosiveness is decreased as far as the temperature is lowered. In addition, energy costs are also reduced. This fact can compensate the surfactant cost. Another additional advantage of micelle formation in these systems is the avoidance of clogging in the transfer line as no precipitation occurs when the effluent is cooled, as demonstrated by the constant pressure in the dynamic system.

As compared with other leaching techniques such as microwave-assisted extraction (MAE), the time required by the method based on this (between 10 and 40 min) is either similar or longer than that of the method proposed here, but the former require 30–40 ml/sample of organic solvents as extractants (namely, dichloromethane [28], acetone [29], hexane–acetone [30–32] or hexane–dichloromethane [33] mixtures).

Table 4
Application of the method to CRM (524)

Analyte	Certified value (μg/g)	Found value (μg/g)
Pyr	173±11	169±13.52
b(a)ant	22.5±1.8	19.7±2.82
b(k)flu	6.2±0.6	6.05±1.51
b(a)pyr	8.6±0.5	7.5±1.39

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