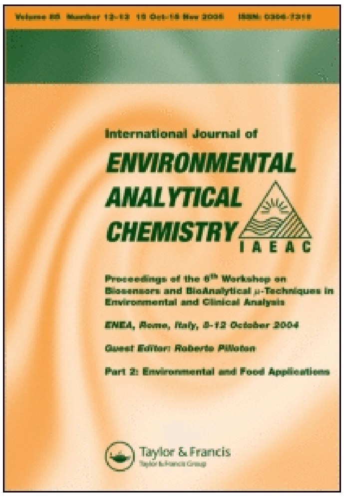

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Extraction of Polycyclic Aromatic Hydrocarbons from Soils: A Comparison Between Focused Microwave Assisted Extraction, Supercritical Fluid Extraction, Subcritical Solvent Extraction, Sonication and Soxhlet Techniques

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EXTRACTION OF POLYCYCLIC AROMATIC HYDROCARBONS FROM SOILS: A COMPARISON BETWEEN FOCUSED MICROWAVE ASSISTED EXTRACTION, SUPERCRITICAL FLUID EXTRACTION, SUBCRITICAL SOLVENT EXTRACTION, SONICATION AND SOXHLET TECHNIQUES

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Focused microwave, supercritical fluid and subcritical solvent extraction methods were compared with the classical Soxhlet and sonication procedures for routine determination of polycyclic aromatic hydrocarbons (PAHs) in contaminated soil. In each case the extraction efficiency was examined for 5 series (n=5) of 15 PAHs. Quantitative and pragmatic arguments were considered toward the selection of an appropriated method for routine analysis. The new extraction techniques yielded interesting alternatives to conventional ones, not least since their quantitative results proved more easily reproducible than those afforded either by Soxhlet and sonication. Besides, the automation of extraction systems is a crucial criterion for routine analysis.

Keywords: PAHs; microwave; SFE; subcritical solvent extraction; soxhlet; sonication

INTRODUCTION

Many analytical procedures have been established and subsequently applied in routine analysis for the surveillance of organic pollutants in the environment.

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Among the extraction methods included in these analytical procedures and of especial use for solid environmental samples such as soils and sediments, those more common are sonication and Soxhlet techniques[1–8]. However, for the ever-increasing number and frequency of controls undertaken in today's analytical laboratories these techniques seem to be unadequate. Alternatively, more recent extraction technologies, have been developed, namely Focused Microwave Assisted Extraction (FMAE), Supercritical Fluid Extraction (SFE) and Subcritical Solvent Extraction (SSE).

The application of microwave energy in the extraction of environmental solids has not yet been widely discussed[9–13]. During microwave irradiation, the nature of both sample and extraction solvent (characterised by its dielectric constant) fix the heating rate and the generated thermal energy, for an applied frequency and its related power. Thus, it is not recommended to use solvents with small dielectric constant such as hexane ($\varepsilon^{20°C} = 1.890$) or toluene ($\varepsilon^{25°C} = 2.379$). However, as it is required that the extraction solvent should render the analyte soluble, then a non-polar one is preferently selected. Therefore, a mixture of solvents with different polarities may be considered.

Numerous descriptions of the use of supercritical fluids to extract PAHs from soils or sediments have been reported[14–24]. Hawthorne *et al.*[25-28] have experimented with several supercritical fluids and under a variety of operating conditions. Carbon dioxide is the most frequently used for both easiness and safety[28–30]. Off-line collection and gas chromatographic-mass spectrometric (GC-MS) analysis have been widespread and frequently used in tandem[31–37]. The SFE technique has recently been the subject of a standard procedure (US EPA method 3561[38]) based in part upon the research of Gere *et al.*[39] concerning PAH compounds.

Few papers concerning subcritical solvent extraction appear in the literature[40–42]. This method is designed for solid matrix analysis and its principle is derived from that of SFE. By increasing the pressure and the temperature the improvement of the solvent's physico-chemical properties could be achieved. The pressure applied was up to the critical pressure of the organic solvent while the extraction temperature was lower than its corresponding critical level (subcritical state). The solvent remained in the liquid state. The effects of pressure contributed to i) the retention of the solvent beneath its boiling point despite an elevation in temperature, ii) a improved penetration of the solvent into matrix pores plugged by water or air bubbles. Temperature effects allowed i) an improvement in the solubility of both water and analyte in the organic solvent as well as enhancing the diffusion coefficients, ii) a reduction in solvent viscosity and superficial tensions. These two effects proved favourable to mass transfer. Hawthorne *et al.*[30] used water to extract PAHs from real contaminated soils with both SFE and SSE techniques. They observed an increase in extraction recoveries when the temperature raised from 50 °C to 400 °C at a constant pressure (35 MPa). This improvement is dependent upon a decrease in the fluid dielectric constant (from $\varepsilon^{50°C} = 71$ to $\varepsilon^{400°C} = 8$). However, authors had reported rapid deterioration of the stainless steel extraction cell after only a few uses at 300 °C and 400 °C. In another apparatus, the carbon dioxide under pressure pushed a methylene chloride/acetone mixture (1:1) into the extraction cell which was pressurised at 10.3 MPa and heated at 100 °C[43]. Two consecutive extractions (5 min. each) and employing 15 mL of solvent were necessary to extract 6 PAHs from 10 g soil with efficiencies ranging between 72% and 104% of the certified values. A high-pressure pump was used by Richter *et al.*[40] to extract 16 PAHs from a certified marine sediment. A 5 min. static mode followed by a 5 min. dynamic one (5 g, 100 °C, 13.9 MPa) permitted to obtain extraction recoveries ranging between 57% and 198%, according to the PAH compounds.

Thus, FMAE, SFE and SSE techniques appear to present a great potential for the extraction of PAHs from soils and sediments. In this paper a comparison study of a wide range of methods (Soxhlet, sonication, FMAE, SFE and SSE) for the extraction of 15 PAHs from a real contaminated soil is reported. Quantitative and pragmatic criteria were taken into account in order to select the most appropriate technique for routine analysis in the laboratory.

EXPERIMENTAL

Standards and reagents

All reagents and solvents employed were of "pesticide" or analytical grade. Deionized water used was HPLC grade or was obtained from an ultra-filtration system (18 MΩ). Standard solutions were prepared by diluting commercial certified solutions (Ultra Scientific), containing 16 PAHs as a 2000 µg/mL concentration in benzene / methylene chloride (1:1)

Soil preparation

The contaminated soil originated from the storehouse of an abandonned station. The sample was air-dried for 24 hours, ground with a glass mortar and pestle, being 24 hours air-dried for a further 24 hours and then sieved to 2 mm to remove any sticks and other debris. The residual moisture was 9.9% by weight.

Finally, the sample was closed into an airtight, glass container and stored at 4 °C in darkness.

Extraction techniques

All the extraction apparatus employed were commercially available equipment. Experimental conditions were originally based upon usual Soxhlet parameters : a 5 g soil sample extracted with methylene chloride. For the SFE procedure, carbon dioxide was employed as the extractant, and methylene chloride was only used as the collection solvent. Relative standard deviations (RSD) were calculated from series of runs which included five replicates and an extraction blank (n=5).

Soxhlet extraction

The soil sample was weighed in a cellulose extraction thimble (80 mm × 30 mm i.d.) and inserted into the Soxhlet assembly. Once installed it was heated for 8 hours with 220 mL methylene chloride.

Ultrasonic extraction

A 100 mL centrifuge tube was filled with both the test portion, 30 mL of solvent and was covered with an aluminium foil. Each of the two consecutive extractions was carried out for 15 min. in an ultrasonic bath (48 kHz, 50 W).

Focused microwave assisted extraction

The focused microwave assisted extractions were performed using a single-module apparatus which delivered a frequency of 2450 MHz. The operating conditions for the PAHs extraction of soil were based upon those of a previous work[44]. The hydrated soil (20%, w/w) and 40 mL methylene chloride/acetone mixture (1:1) were introduced into a 250 mL quartz tube. This extraction tube was suspended by two clamps in a quartz glove finger surmounted by a PTFE ring on which the clamps were placed. The assembly was inserted into the microwave cavity and a Graham's cooling apparatus was connected to the quartz tube by a borosilicate glass extraction bend. The extraction procedure was performed at atmospheric pressure (open-vessel). The glove finger protected the inside of the apparatus from solvent splashing. During handling, the reflux ring was never permitted to rise above the first turn of the cooling apparatus. The heating power and the duration of microwave exposure were maintained at 30 W and 10 min., respectively. Under these operating conditions, no degradation of PAHs was generated by microwave irradiation[11].

Supercritical fluid extraction

All SFE experiments were accomplished using an off-line collection system. High temperature and pressure as well as polar modifier are effective parameters to improve the extraction recoveries of PAHs from solid environmental samples[20, 33–36]. In addition, anhydrous sodium sulphate placed at the outlet end of the extraction cell is recommended to avoid restrictor plugging due to the residual moisture in the matrix. Following several preliminary investigations, SFE was performed at 200 °C and 5800 psi (40 MPa), with a 15 min. static mode followed by a 60 min. dynamic one. The sample was introduced into a 5 mL stainless steel extraction vessel (20 mm i.d.), containing 1.5 g anhydrous sodium sulphate at the bottom of the cell. Methanol as polar modifier was added directly to the solid matrix into the extraction cell prior to extraction (5% (v/v) compared to cell volume). The fused-silica capillary restrictor (1 m × 50 μm) was heated at 160 °C. Extracted analytes were collected by bubbling the vented supercritical fluid through 15 mL methylene chloride in a 22 mL septum-capped vial open to the atmosphere. The collection vial temperature was controlled < 5 °C by placing the flask in an ice-water bath to improve trapping efficiency. Solvent volume was maintained at ca 15 mL during all of the extraction procedure using a 5 mL syringe. Blank extractions comprising only anhydrous sulphate were performed to control the carbon dioxide's quality grade and the contamination level of the extraction system.

Subcritical solvent extraction

The SSE apparatus has many things in common with the SFE system. A glass microfibre filter (porosity : 8 μm) was inserted into the outlet end of the extraction cell. The soil sample was weighed and dead volumes were minimised by the addition of diatomaceous earth, until the extraction vessel was filled to capacity and introduced into a temperature-controlled oven. The static valve was closed, so the cell filled with solvent was pressurised and heated (2000 psi (13.8 MPa), 100 °C). After a 5 min. static mode, the solvent was collected in a 60 mL septum-capped vial during system depressurisation (static valve opened). Fresh solvent was then pumped into the extraction chamber (dynamic mode), so that the solvent volume was 60% of the overall cell volume. Three extraction cycles were performed for 30 min.. Finally, the stainless steel tubing and the extraction vessel were purged with nitrogen (1 MPa) for 1 min.. The final volume of solvent collected into the septum-capped vial was ca 25 mL.

Concentration step

A preconcentration step for the Soxhlet extracts was performed on a rotary evaporator to reduce the large volumes of solvent. For Soxhlet, sonication and FMAE procedures, samples were filtered through a hexane-rinsed glass wool. The same procedure was applied to all studied methods. The concentration step was performed until ca 1 mL under nitrogen stream (< 30 °C). A specific acetylation step was performed upon extracts designed for phenolic compound determination. The results related to these analytes are not discussed in this paper, so no more details are exposed below. The extract was acetylated with 8 mL K_2CO_3 0.1 mol./L and 100 µL acetic anhydride 10.6 mol./L. Analytes were retrieved in hexane, acetylated 2,4-dibromophenol (2,4-DBP) was used as internal standard (IS) and the volume was adjusted to 1 mL with hexane.

Extract analysis

Analyses were performed by GC-MS using a 30 m × 0.32 mm i.d. × 0.25 µm fused-silica capillary column (5% diphenyl-, 95% dimethylsiloxane).

The sample extract was injected (2 µL) in splitless mode. The injector and detector temperatures were maintained at 250 °C and 280 °C, respectively. The oven temperature was held at 60 °C for 1 min. followed by temperature programming to 290 °C with a ramp of 10 °C/min. and a final hold at 290 °C for 5 min.. Helium was used as the carrier gas (1.5 mL/min., constant flow).

The electronic impact spectra were recorded in the m/z 60 to 300 range. Quantitation was performed on the parent ions of each PAH component.

Statistic exploitation

The following statistic techniques were used for results exploitation:

- parametric statistics (Normal distribution): statistics in connection with means (ANOVA, Kolmogorov's test, Shapiro's test, Fisher's PLSD test, Student's T test) and statistics in connection with variances (Cochran's test, Fisher's F test).
- non parametric statistics : Friedman's test, Khi square test.

Accuracy is expressed by:

- the mean (for average concentration) $m_{meth} = \frac{\sum_{i=1}^{n} x_i}{n}$
  where:

  x_i are the different replicates

  n is the number of replicates

  "meth" indicate the extraction technique : "stx" = Soxhlet
  "us" = Sonication
  "fmae" = FMAE
  "sfe" = SFE
  "sse" = SSE

- the repeatability $r_{meth} = t_{(n-1;0,975)} \times \sqrt{2} \times \sqrt{\frac{1}{n-1} \times \sum_{i=1}^{n} (x_i - m_{meth})^2}$

  where $t_{(n-1;\ 0,975)}$ is the Student t value with (n-1) degrees of freedom and $\alpha = 5\ \%$.

- the relative standard deviation

$$RSD = \frac{\sqrt{\frac{1}{n-1} \times \sum_{i=1}^{n} (x_i - m_{meth})^2}}{m_{meth}} \times 100$$

RESULTS AND DISCUSSION

Comparison between sonication and Soxhlet extraction

The sonication procedure provided better extraction recoveries for high-molecular-weight PAHs than the Soxhlet technique (Table I), while offering lower relative standard deviations (RSD). This latter procedure presented a significant spread of results (dispersion), notably for phenanthrene and benzo(b)fluoranthene. The preconcentration step included only in the Soxhlet procedure may have made a partial contribution to these observations. In addition these results were found for analyte concentrations close to quantitation limits, particularly for benzo(a)pyrene, indeno(1,2,3-c,d)pyrene and benzo(g,h,i)perylene. The quantities of analyte in the soil sample seem to be related to spread of results. Thus, variations generated by the sample treatment step (extraction/concentration) and the extract analysis (detection/integration) appear to be more significant when these quantities are low. All these phenomena may explain high RSD encountered for the Soxhlet method.

TABLE I Effect of the substitution of conventional extraction method (Soxhlet) by sonication technique (n=5 – real world contaminated soil)

PAHs	*Soxhlet^{a} (reference)*				*Sonication^{b}*			
	m_{stx} (mg/kg)	*r_{stx} (mg/kg)*	*RSD (%)*	*RE^{e} (%)*	*Bias^{c} (mg/kg)*	*r_{us}-r_{stx}^{cd} (mg/kg)*	*RSD (%)*	*RE^{e} (%)*
Naphthalene	0.164	0.052	8.1	100.0	**-0.0794**^{c2}	-0.028^{c1}	7.4	51.4
Acenaphthylene	0.074	0.053	18.4	100.0	-0.0092^{c1}	+0.020^{c1}	29.0	87.6
Acenaphthene	0.073	0.060	20.8	100.0	-0.0164^{c1}	-0.005^{c1}	24.4	77.5
Fluorene	0.101	0.087	22.1	100.0	-0.0201^{c1}	+0.007^{c1}	29.7	79.5
Phenanthrene	1.235	1.266	26.1	100.0	+0.0067^{c1}	-0.291^{c1}	20.0	100.5
Anthracene	0.258	0.134	13.2	100.0	+0.0130^{c1}	+0.081^{c1}	20.2	105.0
Fluoranthene	2.308	1.853	20.5	100.0	+0.4058^{c1}	+0.073^{c1}	18.1	117.6
Pyrene	1.685	1.368	20.7	100.0	+0.2876^{c1}	-0.207^{c1}	15.0	117.1
Benz(a)Anthracene	1.325	1.145	22.0	100.0	+0.2091^{c1}	+0.015^{c1}	19.3	115.8
Chrysene	1.901	1.689	22.6	100.0	+0.1039^{c1}	-0.506^{c1}	15.0	105.5
Benzo(b)Fluoranthene	2.256	2.382	26.9	100.0	+0.1438^{c1}	-1.238^{c1}	12.1	106.4
Benzo(k)Fluoranthene	1.397	1.306	23.8	100.0	+0.1333^{c1}	-0.413^{c1}	14.9	109.5
Benzo(a)Pyrene	1.431	1.538	27.4	100.0	+0.2324^{c1}	-0.761^{c1}	11.9	116.2
Indeno(1,2,3-c,d)Pyrene	1.528	1.882	31.4	100.0	+0.3065^{c1}	-0.963^{c1}	12.8	120.1
Benzo(g,h,i)Perylene	1.243	1.755	36.0	100.0	+0.2331^{c1}	-0.882^{c1}	15.1	118.7

[a] 5g soil sample; CH_2Cl_2; 8 hours.

[b] 5g soil sample; CH_2Cl_2; 2×15 min.

[c] For bias (= $m_{meth} - m_{stx}$) and deviation of repeatability (= $r_{meth} - r_{stx}$):

[c1] The value is not significantly different from zero (risk α>5%).

[c2] The value is significantly different from zero with a risk α<1%.

[d] Deviation of repeatability.

[e] Relative efficiency compared to Soxhlet extraction.

Comparison between FMAE and classical extraction methods

The FMAE reveals better bias (m_{meth}- m_{sxt}) for light compounds than the sonication technique although remains less efficient than Soxhlet extraction (Tables I and II). When naphthalene (a relatively volatile compound) is extracted by sonication, it presents extraction efficiencies and RSD lower than all low-molecular-weight PAHs, and equally so with the two other methods. In the same way, the difference between Soxhlet recoveries and those obtained after sonication or FMAE is significant for low-molecular-weight PAHs. Indeed, the combination of the siphon and the cooling apparatus in the Soxhlet assembly permitted the recovery of low-molecular-weight PAHs (it was the same for FMAE but not for sonication) and their reintroduction into a non-equilibrated system with the siphon (it was not the case for the two other methods). Thus, during sonication extraction, volatilisation losses, with the exception of naphthalene, are implicated in the significant spread of results. The cooling apparatus for the FMAE technique limited this loss through volatility. This fact may explain differences of RSD observed between these two techniques and encountered with relatively volatile PAHs (globally until anthracene).

The sonication technique shows operating specifications close to FMAE technique for lower investment (especially for simultaneous extraction steps). However the FMAE procedure revealed a reduction in noise level when compared to sonication while providing narrower spreads of results than the conventional techniques with an average relative efficiency of 96.4%.

Comparison between SFE and classical extraction methods

Recoveries by SFE extraction are similar to those obtained via Soxhlet (Tables I and II). However, the variability in Soxhlet results is greater or at least equal to that of SFE. Yet this large spread of results may not encourage the conclusion that high-molecular-weight PAHs are more easily extracted by this method. The spread of SFE results is relatively significant for lower-molecular-weight analytes (ca 20%), which may be related to an off-line collection effect. This collection technique seems not to be suitable to extraction of volatile compounds. However, it remains the most commonly used. For lower-molecular-weight PAHs, sonication recoveries are lower than those obtained from SFE, although above that for higher-molecular-weight PAHs. The SFE procedure revealed a good, global average for relative efficiency, 98.5% against 101.9% for sonication. In addition for almost all PAHs, the SFE technique presented a lower RSD than either of the two conventional extraction methods.

TABLE II Effect of the substitution of conventional extraction method (Soxhlet) by the new extraction methods : FMAE, SFE and SSE (n=5 – real world contaminated soil)

PAHs	*FMAE*^{a}				*SFE*^{b}				*SSE*^{c}			
	Bias^d *(mg/kg)*	r_{fmae}-r_{stx}^{de} *(mg/kg)*	*RSD (%)*	*RE*^{f} *(%)*	*Biasd (mg/kg)*	r_{sfe}-r_{stx}^{de} *(mg/kg)*	*RSD (%)*	*RE*^{f} *(%)*	*Bias*^{d} *(mg/kg)*	r_{sse}-r_{stx}^{de} *(mg/kg)*	*RSD (%)*	*RE*^{f} *(%)*
Naphthalene	-0.0477^{d2}	+0.015^{d1}	14.7	70.8	+0.0719^{d2}	+0.146^{d2}	21.4	144.0	-0.0126^{d1}	+0.082^{d1}	22.7	92.3
Acenaphthylene	-0.0016^{d1}	-0.009^{d1}	15.7	97.8	+0.0045^{d1}	+0.012^{d1}	21.2	106.1	+0.0051^{d1}	-0.031^{d1}	7.3	106.8
Acenaphthene	-0.0164^{d1}	-0.029^{d1}	13.6	77.6	+0.0012^{d1}	-0.012^{d1}	16.4	101.7	+0.0090^{d1}	-0.025^{d1}	10.9	112.3
Fluorene	-0.0140^{d1}	-0.039^{d1}	14.1	85.5	-0.0050^{d1}	-0.037^{d1}	13.3	94.2	-0.0124^{d1}	-0.046^{d1}	11.7	87.2
Phenanthrene	+0.1386^{d1}	-0.369^{d1}	16.6	111.2	+0.0215^{d1}	-0.582^{d1}	13.9	101.7	+0.0688^{d1}	-0.479^{d1}	15.4	105.6
Anthracene	+0.0381^{d1}	-0.002^{d1}	11.4	114.8	+0.0156^{d1}	-0.036^{d1}	9.2	106.1	+0.0413^{d1}	-0.039^{d1}	8.1	116.0
Fluoranthene	+0.6491^{d1}	+0.140^{d1}	17.2	128.1	-0.0282^{d1}	-0.849^{d1}	11.2	98.8	+0.2689^{d1}	-0.732^{d1}	11.1	111.7
Pyrene	+0.4419^{d1}	-0.157^{d1}	14.5	126.2	+0.0522^{d1}	-0.420^{d1}	13.9	103.1	+0.3356^{d1}	-0.560^{d1}	10.2	119.9
Benz(a)Anthracene	+0.0595^{d1}	-0.624^{d1}	9.6	104.5	-0.0882^{d1}	-0.570^{d1}	11.8	93.3	+0.0278^{d1}	-0.818^{d1}	6.2	102.1
Chrysene	+0.0941^{d1}	-0.688^{d1}	12.8	105.0	-0.0418^{d1}	-0.810^{d1}	12.0	97.8	+0.0631^{d1}	-1.160^{d1}	6.9	103.3
Benzo(b)Fluoranthene	-0.2027^{d1}	-1.563^{d1}	10.2	91.0	+0.1216^{d1}	-1.271^{d1}	11.9	105.4	+0.4125^{d1}	-1.722^{d2}	6.3	118.3
Benzo(k)Fluoranthene	-0.2241^{d1}	-0.790^{d1}	11.2	84.0	-0.2553^{d1}	-0.857^{d1}	10.0	81.7	-0.5995^{d2}	**-1.084**^{d3}	7.1	57.1
Benzo(a)Pyrene	-0.2172^{d1}	-1.070^{d2}	9.8	84.8	-0.1721^{d1}	-0.906^{d1}	12.8	88.0	-0.0629^{d1}	-1.154^{d2}	7.1	95.6
Indeno(1,2,3-c,d)Pyrene	-0.2234^{d1}	-1.153^{d1}	14.2	85.4	-0.3980^{d1}	-1.361^{d2}	11.8	73.9	-0.3515^{d1}	-1.394^{d2}	10.6	77.0
Benzo(g,h,i)Perylene	-0.2556^{d1}	-1.321^{d2}	11.2	79.4	-0.2192^{d1}	-1.107^{d1}	16.1	82.4	-0.3234	**-1.468**^{d3}	8.0	74.0

[a] 5g soil sample hydrated with 20% water; CH_2Cl_2/acetone; 30W; 10 min.

[b] 5 g soil sample; CO_2, 5% Methanol; CH_2Cl_2; 200°C/40MPa; 75 min.

[c] 5g soil sample; CH_2Cl_2; 100°C/13.8MPa; 3 cycles of extraction ; 30 min.

[d] For bias (= $m_{meth} - m_{stx}$) and deviation of repeatability (= $r_{meth} - r_{stx}$):

[d1] The value is not significantly different from zero (risk $\alpha > 5\%$).

[d2] The value is significantly different from zero with a risk $1\% < \alpha < 5\%$.

[d3] The value is significantly different from zero with a risk $\alpha < 1\%$.

[e] Deviation of repeatability.

[f] Relative efficiency compared to Soxhlet extraction.

Comparison between SSE and classical extraction methods

The average SSE recovery (98.6%) is comparable to that achieved by the Soxhlet extraction (Tables I and II). Recoveries range from 74% to 118%. In general the RSD values for SSE are about half of those obtained with either sonication or Soxhlet procedures (10% against 17.7% and 22.7%, respectively). The partial co-elution of benzo(b)fluoranthene with benzo(k)fluoranthene produces an efficiency overestimation of the first compound which occurs at the expenses of the second. The SSE procedure is less efficient than sonication for high-molecular-weight PAHs, proving to be more suitable for lower-molecular-weight PAHs. Consequently, SSE provides slightly lower efficiency than either the sonication or Soxhlet procedures, alternatively the dispersion of its results is less significant.

Statistical comparison

Tables III and IV present the comparison of measurement accuracies (repeatability and bias) according to the extraction method.

Repeatabilities (r_{meth}) and bias are classified in ascending order : the rank 1 for the lowest value (the best repeatability or the worst bias) to the rank 5 for the highest value (the worst repeatability or the best bias).

The number of rank observed for each extraction technique summarise the classification upon all the molecules (Tables III and IV). For each extraction technique, a roundup of the ranks displays molecule groups with close behaviours. The Friedman's test is used when the number of molecules in the group is superior or equal to 5. The Khi square test is applied in the other case (< 5).

The probability (value p) associated to the hypothesis of the lack of effect following the substitution of method, indicates that the bias generated (Table III) is not significant except for 4 molecules (group B : benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene). In addition, it must be noted that the behaviour of two molecules (naphthalene and to a lesser extent acenaphthylene) contrasts radically with those of the other molecules.

The substitution of traditional extraction techniques (Soxhlet, sonication) by a new technique (FMAE, SFE, SSE) has a significant impact on the accuracy of the analysis (Table IV). It leads to a significant improvement of the repeatability. It appears three distinct groups of methods : classical methods (worse results), FMAE and SFE techniques, and finally the SSE method. For 11 molecules in 14 among the group A (Table IV), the lowest repeatability is observed when the extraction is performed with the SSE technique.

TABLE III Ranking extraction techniques for bias study ($m_{meth} - m_{sxt}$): rank 1 correspond to the lowest value and rank 5 correspond to the highest value

PAHs	*Effect*[a]	*Soxhlet*	*Sonication*	*FMAE*	*SFE*	*SSE*	*Groups of PAHs*
		Rank	*Rank*	*Rank*	*Rank*	*Rank*	
Naphthalene		4	1	2	5	3	unclassifiable
Acenaphthylene	x	3	1	2	4	5	A
Acenaphthene		3	1	2	4	5	unclassifiable
Fluorene	x	5	1	2	4	3	A
Phenanthrene	x	1	2	5	3	4	A
Anthracene	x	1	2	4	3	5	A
Fluoranthene	x	2	4	5	1	3	A
Pyrene	x	1	3	5	2	4	A
Benzo(a)Anthracene	x	2	5	4	1	3	A
Chrysene	x	2	5	4	1	3	A
Benzo(b)Fluoranthene	x	2	4	1	3	5	A
Benzo(k)Fluoranthene		4	5	3	2	1	B
Benzo(a)Pyrene		4	5	1	2	3	B
Indeno(1,2,3-c,d)Pyrene		4	5	3	1	2	B
Benzo(g,h,i)Perylene		4	5	2	3	1	B
Rank		*Number of rank observed for each extraction technique*					
Rank 5	x	1	2	3	0	3	A (Friedman's test, p value = 0.0949)
Rank 4	x	2	2	3	2	2	
Rank 3	x	1	1	0	3	4	
Rank 2	x	4	2	2	1	0	
Rank 1	x	3	2	1	3	0	
Rank 5		0	4	0	0	0	B (Khi square test, p value < 0.0001)
Rank 4		4	0	0	0	0	
Rank 3		0	0	2	1	1	
Rank 2		0	0	1	2	1	
Rank 1		0	0	1	1	2	

[a] Non significant extraction technique effect with parametric statistics.

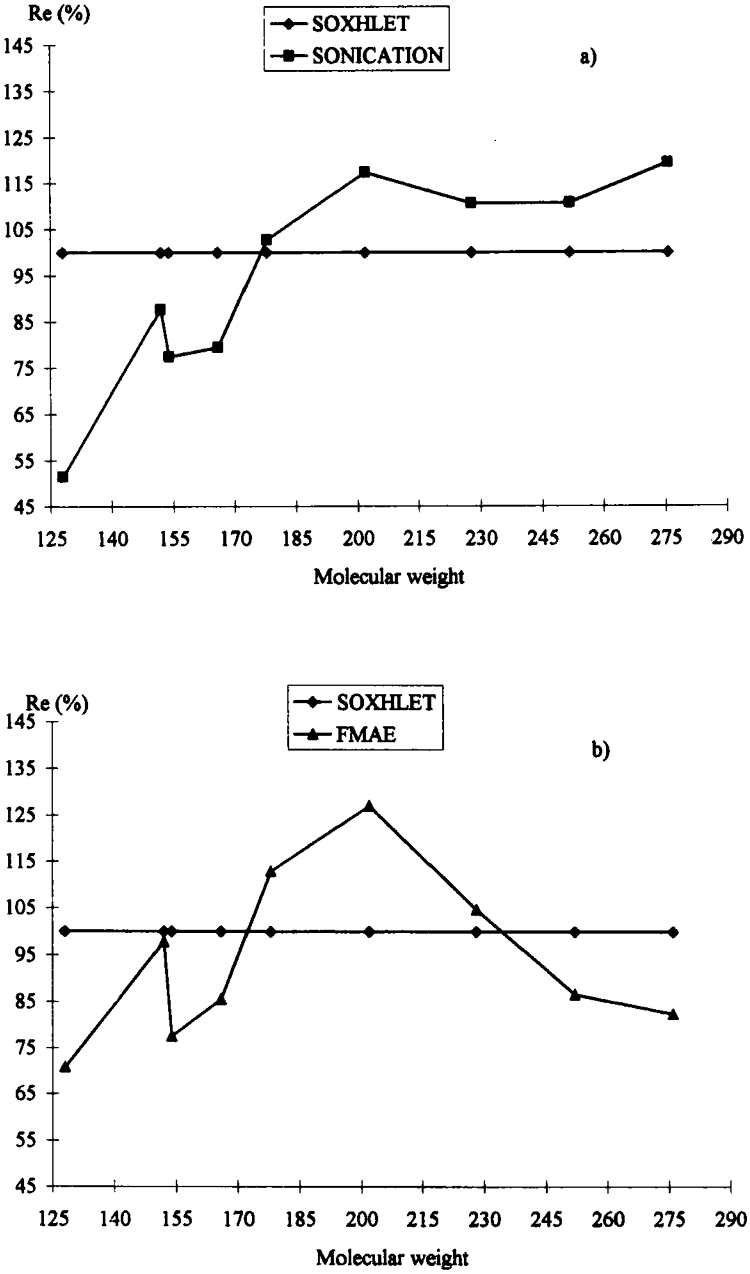
TABLE IV Ranking extraction techniques for repeatability study (r_{meth}): rank 1 correspond to the lowest repeatability (better repeatability) and rank 5 correspond to the highest repeatability (worse repeatability)

PAHs	*Effect*[a]	*Soxhlet*	*Sonication*	*FMAE*	*SFE*	*SSE*	*Groups of PAHs*
		Rank	*Rank*	*Rank*	*Rank*	*Rank*	
Naphthalene		2	1	3	5	4	unclassifiable
Acenaphthylene	x	3	5	2	4	1	A
Acenaphthene	x	5	4	1	3	2	A
Fluorene	x	4	5	2	3	1	A
Phenanthrene	x	5	4	3	1	2	A
Anthracene	x	4	5	3	2	1	A
Fluoranthene	x	3	4	5	1	2	A
Pyrene	x	5	3	4	2	1	A
Benzo(a)Anthracene	x	4	5	2	3	1	A
Chrysene	x	5	4	3	2	1	A
Benzo(b)Fluoranthene		5	4	2	3	1	A
Benzo(k)Fluoranthene		5	4	3	2	1	A
Benzo(a)Pyrene		5	4	2	3	1	A
Indeno(1,2,3-c,d)Pyrene		5	4	3	2	1	A
Benzo(g,h,i)Perylene		5	4	2	3	1	A
Rank		*Number of rank observed for each extraction technique*					
Rank 5		9	4	1	0	0	
Rank 4		3	9	1	1	0	A (Friedman's test, p value < 0.0001)
Rank 3		2	1	5	6	0	
Rank 2		0	0	6	5	3	
Rank 1		0	0	1	2	11	

[a] Non significant extraction technique effect with parametric statistics.

Choice of the extraction technique

The choice of the extraction method was based upon a variety of factors.


Re (%)
SOXHLET
SONICATION
a)
145
135
125
115
105
95
85
75
65
55
45
125 140 155 170 185 200 215 230 245 260 275 290
Molecular weight
Re (%)
SOXHLET
FMAE
b)
145
135
125
115
105
95
85
75
65
55
45
125 140 155 170 185 200 215 230 245 260 275 290
Molecular weight

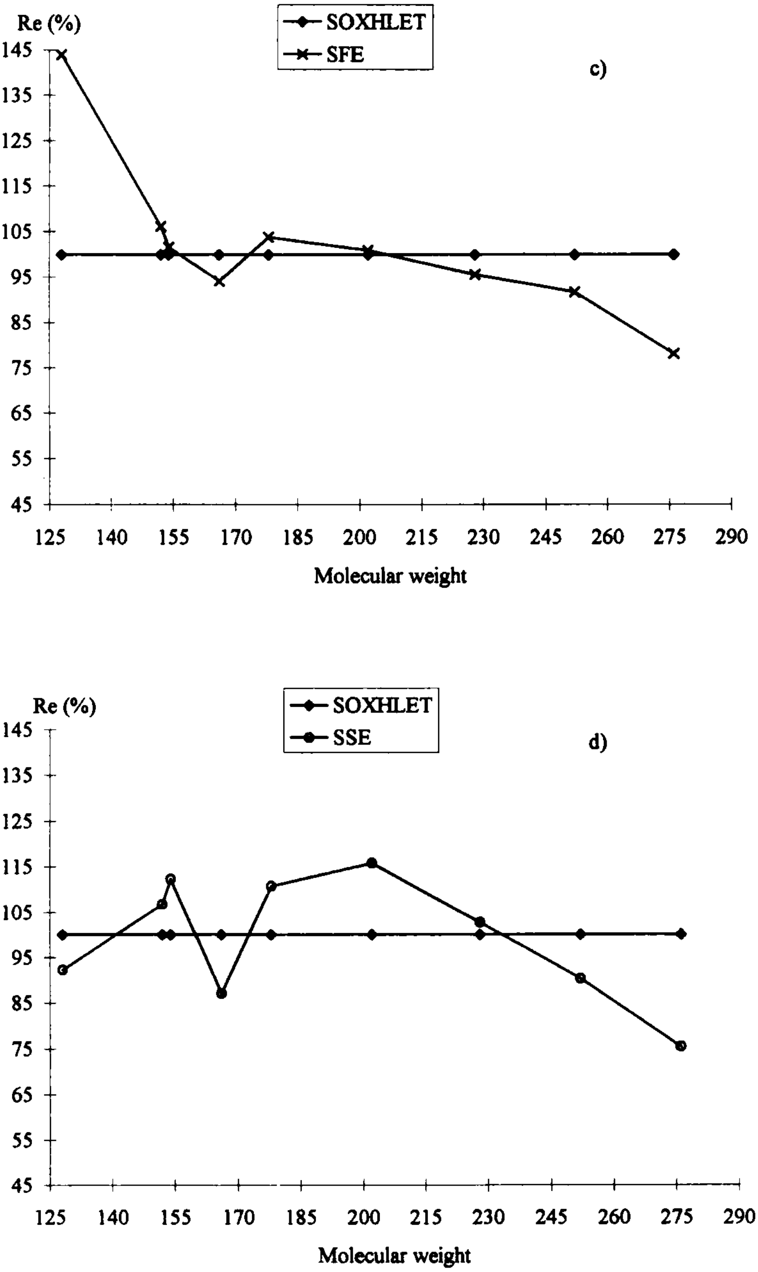


FIGURE 1 Variation of relative extraction efficiencies (Re) as a function of PAHs molecular weight

The first consideration was simply a quantitative criterion. Following the individual assessment of the new extraction techniques, it appears that of the five methods tested all provide good recoveries : mean efficiencies ranged from 96.4% to 101.9% when compared to the Soxhlet extraction. Nevertheless, it is necessary to observe i) the extraction discrimination of lower and higher-molecular-weight compounds, and ii) the spread of results for all PAHs compounds.

i. Various profiles of behaviour appear when relative extraction efficiencies are considered according to PAHs molecular weights (Figure 1). Thus, the sonication technique (a) demonstrates a weight-dependent behaviour when compared to Soxhlet extraction. The recoveries increase proportionally with respect to molecular weight. The FMAE (b) revealed difficulties for the extraction of PAHs of molecular weights of extreme character (whether higher and lower). SFE (c) and SSE (d) profiles are relatively similar, the sole exception being naphthalene. However, the SFE profile displayed little variation to the Soxhlet profile, its behaviour proving similar to that of the Soxhlet.
ii. Alternatively, all of the new extraction techniques demonstrated a spread of results less marked than their classical counterparts (cf. statistical comparison).

We concluded that it is better to obtain recoveries slightly lower than the Soxhlet if a high level of reproducibility (low RSD) can be maintained, in preference to higher recoveries with a greater spread of results. The use of FMAE, SFE or SSE techniques then becomes more suitable for the extraction of PAHs from contaminated soil than the use of conventional extraction methods. Among these new methods, the SSE procedure provides high PAHs recoveries with lowest dispersion of results.

Further criteria related to technical parameters are equally taken into account to decide the final choice (Table V).

Sequential extractions are recommended when methods include a static system. Indeed, a thermodynamic equilibrium appears within these systems. Nevertheless, the extraction time must be as short as possible. The SSE technique permits three extraction cycles within 30 min. (each cycle corresponding to an extraction step) or one cycle within 18 min.. The FMAE procedure, which also presents a static system, provides the lowest extraction time per extraction (10 min.). This is the same as to performing three sequential extractions for 30 min.. Thus, this two techniques present similar advantages with respect to time.

The use of only small quantities of hazardous solvents is an instant recommendation to laboratories in terms of safety, waste treatment and cost effectiveness. Considering these benefits, the SSE method proves to be the most convenient technology. Of note is the fact that the SFE technique requires the same volume of organic solvent but also a significant quantity of carbon dioxide extractant.

TABLE V Complimentary criteria for the assessment of the extraction techniques

Parameters	*Soxhlet*	*Sonication*	*FMAE*	*SFE*	*SSE*
Extraction time (with rising of temperature and pressure)	8 h	30 min.	10 min.	1 h 50 min. (35 min.)	30 min.
Sequential extraction number	1 (reflux)	2	1	1	3
Volume of organic solvents	220 mL	60 mL	40 mL	25 mL (+ CO_2)	25 mL
Sample number per apparatus	6 (ramp)	6	1	4	24
Automation degree:					
experimented	none	none	semiautomatic	none	automatic
existing	semiautomatic	none	semiautomatic	automatic	automatic
Volume of washing solvents	high	medium	high	low	low
Space overcrowding per sample	high	low	high	medium	low
Operator time	high	low	medium	medium	low
Operator skill	low	low	medium	high	low
Cost of experimented equipment (US $)	~ 2 650	~ 400	~ 7 250	~ 18 250	~54 000
Operating cost per sample (US $)[a]	~ 11.3	~ 5.2	~ 7.8	~ 27.1	~ 7.3

[a] based on 20 samples treated per day and considering : cost of equipment amortisation (calculated on 5 years), operator cost, solvent price, glassware price, consumable price.

The automation of the SSE device (designed to accept 24 extraction cells onto a trial) combined with fast extractions permits the treatment a high number of samples in a very short time. This is a crucial factor for laboratories undertaking routine analysis. Not all extraction equipment has the facility to accomplish this, for example, it is not afforded to either automated SFE or the Soxhlet procedure.

Similarly, automated SFE and SSE effectively reduce operator time : system assembling/dismantling, sample loading/unloading, filtration/concentration of extracts, etc.. In addition, space restriction due to the presence of numerous apparatus undertaking simultaneous extractions is minimised.

Finally, the operating cost is also an essential parameter for laboratories. The sonication procedure appears to be the cheaper method and remains interesting when compared to extraction by Soxhlet by reducing extraction periods (30 min. against 8 hours), volumes of organic solvents and particularly initial investment. However, despite these advantages, by comparison of its quantitative results it was never to be considered as a reference extraction method.

Consequently, after considering of observations and discussions recorded above, the SSE method presents many advantages and would seem to match up to the expectations of laboratories. This fact is due initially to its satisfactory quantitative results, its automation and its facility.

CONCLUSION

Conventional procedures (Soxhlet and sonication), presented quantitative results which are less satisfactory than the three new methods (FMAE, SFE and SSE) since they demonstrate a greater dispersion.

The new extraction techniques appear to differ from each other more from a practical point of view than a quantitative one. Among these three new technologies, SSE seems to comprise the principal requirements necessary for adoption by laboratories undertaking routine analysis. This technique permits both the treatment of a large number of samples and an improvement in result reproducibility when compared to the classical methods, while equally reducing extraction times and the use of large volumes of hazardous solvents. Moreover, this method demands a short operating time and its use is easier than SFE or microwave methods.

Arising to this study, it appears that the decisive argument for the choice of an extraction method for PAHs, after the quantitative criterion, remains the degree of automation of the system. Thus, the automation of the alternative extraction methods should lead laboratories to adopt them for their higher productivity and greater convenience.

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