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Short communication

Extraction of polycyclic aromatic hydrocarbons from contaminated soil using Soxhlet extraction, pressurised and atmospheric microwave-assisted extraction, supercritical fluid extraction and accelerated solvent extraction

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Abstract

Soxhlet extraction has been compared with pressurised and atmospheric microwave-assisted extraction, accelerated solvent extraction and supercritical fluid extraction for the extraction of polycyclic aromatic hydrocarbons (PAHs) from native, contaminated soil. The results indicate that the recovery of PAHs is dependent on the extraction technique. The highest recoveries of individual PAHs were consistently obtained by Soxhlet extraction. For the samples investigated here the preferred technique in terms of recoveries is Soxhlet extraction. © 1997 Elsevier Science B.V.

Keywords: Soil; Extraction methods; Polycyclic aromatic hydrocarbons

1. Introduction

The aim of any extraction technique in analytical chemistry is to effectively remove the analyte from its matrix, rapidly, with minimal solvent usage and quantitatively. The choice of extraction technique is frequently decided upon based on initial capital cost, operating costs, simplicity of operation, amount of organic solvent required and sample throughput. The range of approaches currently available makes the selection of the most appropriate extraction technique difficult. In this paper a range of extraction techniques are compared for their effectiveness to

extract polycyclic aromatic hydrocarbons (PAHs) from highly contaminated native soil. The extraction techniques investigated include Soxhlet extraction, pressurised and atmospheric microwave-assisted extraction (MAE), supercritical fluid extraction (SFE) and accelerated solvent extraction (ASE).

The ubiquitous nature of PAHs in soil is due to the incomplete combustion of coal, oil, petrol and wood [1]. The occurrence and relatively high levels of PAHs found in soil has meant that many workers have utilised the determinands as indicators for the effectiveness of various extraction methods. For example, this group has compared the effectiveness of SFE [2], MAE [3] and ASE [4] for the extraction of PAHs from soil. As yet however, no group has

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compared the effectiveness of Soxhlet extraction with SFE, MAE and ASE. As Soxhlet extraction is often considered to be the benchmark technique, its inclusion in this work was considered essential.

In addition, other workers have compared a range of techniques for the extraction of organic pollutants from environmental matrices. Van der Velde et al. [5] compared SFE with Soxhlet and liquid–solid extraction for the recovery of sixteen polychlorinated biphenyls (PCBs) and organochlorine pesticides spiked onto two types of soil (low and high organic carbon content). Soxhlet and SFE were found to give the highest recoveries from both types of soil. However, Soxhlet extraction required an extra clean-up step before analysis. As part of a European Union programme, under the auspices of the Measurement and Testing Programme, twenty-one selected and independent laboratories were involved in the certification of PCB congeners in industrial soil [6]. In the study SFE was compared with Soxhlet extraction. It was found that comparable results in terms of accuracy and precision were obtainable using SFE. However, SFE was able to offer savings in terms of extraction time (SFE: 36–50 min; Soxhlet: 2–24 h) and organic solvent (SFE: 10 ml; Soxhlet: between 60 and 500 ml). In a wider study Lopez-Avila et al. [7] compared MAE as an alternative to Soxhlet, sonication and SFE for the extraction of ninety-five organic pollutants listed in United States Environmental Protection Agency (US EPA) Method 8250. Freshly spiked soil samples and two reference materials were extracted with hexane–acetone (1:1) by MAE and Soxhlet extraction, with methylene chloride–acetone (1:1) by sonication extraction, and with 10% methanol modified supercritical carbon dioxide. The results showed that by MAE fifty-one compounds gave recoveries of >80%; thirty-five, 50–79% and two, <19%. Similar results were obtained by Soxhlet extraction: fifty recoveries were >80%; thirty-two, 50–79%; eight, 20–49% and four were <19%. Sonication recoveries were slightly higher: sixty-three values were >80%; twenty-five, 50–79%; four, 20–49% and two, <19%. SFE recoveries were the lowest: thirty-seven values were >80%; thirty-seven, 50–79%; twelve, 20–49% and eight, <19%. MAE gave the best precision: R.S.D.s were ≤10% for ninety of ninety-four compounds evaluated whereas Soxhlet extraction gave the worst

precision: only fifty-two out of ninety-four samples gave R.S.D.s of ≤10%.

Finally, ASE has been compared with Soxhlet and liquid–solid extraction for the recovery of organophosphorus pesticides and herbicides from spiked soils [8]. The results obtained by ASE were found to be equivalent to those obtained by conventional solvent extraction techniques.

2. Experimental

2.1. Soil preparation

Coal-derived contaminated land soil (organic carbon content, 10.2%) was sampled from known sites and transported to the laboratory where it was air-dried for 24 h and then sieved through a 2 mm sieve. The fine powdered soils were then stored in air-tight containers until required.

2.2. Standards and solvents

Standard PAH mixture was supplied by Chem Service, West Chester, PA, USA (PAH mixture 610/525/550). Two internal standards (3,6-dimethyl phenanthrene and 6-ethyl chrysene) were purchased from Lancaster Chemicals (Lancashire, UK). All solvents (acetone, dichloromethane, methanol) used were of analytical grade (Merck, Poole, Dorset, UK).

2.3. Soxhlet extraction procedure

Soxhlet extractions were performed using 10 g portions of soils to which was added 10 g of anhydrous sodium sulfate. The mixture was transferred into a cellulose extraction thimble and inserted into a Soxhlet assembly fitted with a 250 ml flask. A 150 ml portion of dichloromethane was added and the whole assembly was heated for 24 h using an isomantle. The extracts were concentrated to 10 ml using a rotary evaporator and then diluted two-fold before the addition of the internal standards.

2.4. Pressurised microwave-assisted extraction procedure

Microwave extractions were performed using a

MES-1000 microwave sample preparation unit (CEM Microwave Technology, Buckingham, UK). A portion of soil (2 g) was accurately weighed into a PTFE liner. To each vessel was added 40 ml of acetone. New rupture membranes were fitted into each cap which screwed onto the vessels. The vessels were then placed symmetrically on the microwave turntable together with the control containing the temperature and pressure sensory equipment. The magnetron power was set at 30%, with a constant temperature of 120°C for an extraction time of 20 min. After the extraction was completed, the vessels were allowed to cool. The contents of each vessel were then quantitatively transferred through GF/A glass microbore filter (Whatman, Maidstone, UK). The extracts were concentrated to 5 ml using a rotary evaporator before the addition of internal standards.

2.5. Supercritical fluid extraction procedure

All extractions were carried out using a Jasco SFE system (Mettler-Toledo, Halstead, Essex, UK) consisting of dual pumps for carbon dioxide and modifier addition and fitted with a back pressure regulator. Into each sample cell was placed 1 g of soil. After equilibration, the sample was extracted by use of the following conditions: pressure, 250 kg cm⁻²; temperature, 70°C; 30 min dynamic extraction time preceded by a 5 min static period; flow-rate 2 ml min⁻¹; and a 20% concentration of methanol. Two portions of the 1 g extracts were combined and then concentrated to 5 ml using a rotary evaporator before the addition of internal standards.

2.6. Accelerated solvent extraction procedure

Extractions were done using an ASE 200 accelerated solvent extractor [Dionex (UK), Camberley, Surrey]. Samples (7 g) were accurately weighed into 11 ml cells. The sample cells were then closed, to finger tightness, and placed into the carousel of the ASE 200 system. Extractions were done using a dichloromethane (DCM)–acetone (1:1, v/v) mixture. The operating conditions were as follows: oven temperature of 100°C with 5 min heat-up time at a pressure of 2000 p.s.i. (1 p.s.i.=6894.76 Pa) and a static period of 5 min. The extracted analytes were

purged from the sample cell using pressurized nitrogen (125–150 p.s.i.). The extracts were concentrated to 5 ml using a rotary evaporator and then diluted two-fold before the addition of internal standards.

2.7. Atmospheric microwave-assisted extraction procedure

Extractions were performed using a Soxwave-100 (Merck), with a maximum power output of 300 W. A portion of soil (2 g) was accurately weighed into the extraction flask and 70 ml DCM was added. The flask was placed into the microwave module and a condenser was then attached to the flask. Extraction was done using 99% power for 20 min. The extract was then quantitatively transferred through GF/A glass microbore filter (Whatman). The extracts were then concentrated to 5 ml using a rotary evaporator before the addition of internal standards.

2.8. Analysis of extracts by GC

Gas chromatographic separation and identification of the PAHs was performed on a Carlo Erba HRGC 5300 Mega Series (Fisons, Crawley, Surrey, UK) with on-column injection and flame ionization detection. A 30 m×0.32 mm I.D., 0.1 µm film thickness DB-5 HT capillary column (J&W Scientific, Phase Separations, Clwyd, UK) was used to achieve separation with the following temperature programme: initial column temperature, 50°C; hold for 2 min; increase at 15°C min⁻¹ to 90°C; hold for 2 min; increase at 6°C min⁻¹ to 300°C; hold for 8 min. The detector temperature was set at 290°C. PAH quantitation was carried out using a four-point calibration plot containing 50, 40, 30 and 20 mg ml⁻¹ PAH standard mixture and 25 mg ml⁻¹ internal standards (3,6-dimethyl phenanthrene and 6-ethyl chrysene). Correlation coefficients between 0.9997 and 0.9888 were obtained. No sample clean-up was done on the extracts prior to analysis.

2.9. Analytical procedure

All the extraction techniques were operated under (a) standard conditions, (b) optimized conditions, as previously determined in this laboratory for PAHs, or (c) on the basis of manufacturers' recommendations.

In the case of the standard conditions, Soxhlet extraction was done in accordance with US EPA method 3540 [9]. Both SFE [2] and pressurised MAE [3] were operated using optimized conditions as previously determined in this laboratory, using an experimental design approach, for the extraction of PAHs from native contaminated soil. Soxhlet and ASE were operated in accordance with recommendations provided by the manufacturer's concerned. In the case of ASE the chosen operating conditions are the basis of a proposed EPA Method 3545 [10].

3. Results and discussion

The results for each extraction technique, using

the procedures discussed above, are shown in Table 1. Each sub-sample of the contaminated soil was extracted six times and analysed using GC–FID. In each case, sixteen individual PAHs were identified and the recovery obtained reported. Using GC–FID it was not possible to differentiate between benzo[*b*]fluoranthene and benzo[*k*]fluoranthene; a combined concentration was therefore reported. In addition, dibenz[*ah*]anthracene was not detected in any of the samples because of its low level of occurrence in the soil (<15 mg kg⁻¹). Statistical treatment of the data was done on the fourteen PAHs reported. As the method of Soxhlet extraction is regarded as the benchmark technique against which all other extraction techniques for solid matrices are compared it is prudent to investigate for statistical significance

Table 1
Extraction of individual PAHs from native, contaminated soil: comparison of extraction techniques

Compound	Soxhlet extraction ^a Mean (%R.S.D.)	Pressurised microwave-assisted extraction ^b Mean (%R.S.D.)	Atmospheric microwave-assisted extraction ^c Mean (%R.S.D.)	Supercritical fluid extraction ^d Mean (%R.S.D.)	Accelerated solvent extraction ^e Mean (%R.S.D.)
Naphthalene	214 (14)	229 (19)	169 (22)	193 (10)	195 (16)
Acenaphthylene	30 (16)	28 (10)	25 (11)	25 (9)	25 (10)
Acenaphthene	56 (10)	51 (10)	52 (10)	48 (12)	57 (4)
Fluorene	102 (6)	100 (9)	97 (6)	107 (5)	99 (6)
Phenanthrene	291 (7)	288 (9)	292 (9)	311 (4)	293 (6)
Anthracene	82 (5)	87 (7)	66 (7)	73 (6)	78 (12)
Fluoranthene	219 (5)	217 (7)	225 (19)	223 (5)	204 (6)
Pyrene	181 (10)	172 (6)	171 (8)	156 (7)	182 (5)
Benz(<i>a</i>)anthracene	87 (14)	92 (17)	79 (8)	92 (9)	108 (9)
Chrysene	49 (22)	48 (15)	53 (5)	59 (9)	46 (11)
Benzo[<i>b</i>]fluoranthene +benzo[<i>k</i>]fluoranthene	139 (11)	98 (9)	89 (12)	89 (10)	107 (7)
Benzo[<i>a</i>]pyrene	39 (23)	32 (17)	49 (10)	45 (10)	33 (18)
Indeno[123- <i>cd</i>]pyrene	76 (10)	78 (10)	71 (16)	75 (12)	64 (5)
Dibenz[<i>ah</i>]anthracene	nd	nd	nd	nd	nd
Benzo[<i>ghi</i>]perylene	58 (9)	58 (18)	54 (11)	48 (4)	46 (5)
Total	1623	1578	1492	1544	1537

(*n*=6) (all concentrations in mg kg⁻¹).

^a Soxhlet conditions: sample, 10 g mixed with 10 g anhydrous sodium sulfate; solvent, 150 ml of dichloromethane; heating, 24 h.

^b Pressurised microwave-assisted extraction conditions: sample, 2 g of soil; solvent, 40 ml of acetone; heat, 30% power at 120°C; time, 20 min.

^c Atmospheric pressure microwave-assisted extraction conditions: sample, 2 g of soil; solvent, 70 ml of dichloromethane; heat, 99% power; time, 20 min.

^d Supercritical fluid extraction conditions: sample, 1×2 g; solvent, supercritical CO₂ and 20% methanol; temperature, 70°C; pressure, 250 kg cm⁻²; time, 30 min.

^e Accelerated solvent extraction conditions: sample, 7 g; solvent, dichloromethane–acetone (1:1, v/v); temperature, 100°C; pressure, 2000 p.s.i.; time, 10 min.

nd=not detected i.e., <15 mg kg⁻¹.

using a paired *t*-test approach [11]. As the soil sample was extracted six times, using each extraction technique, it was possible to evaluate for statistical significance for each individual PAH and the combined benzo[*b*]fluoranthene and benzo[*k*]fluoranthene peak. Statistical significance was determined at the 95% confidence interval as a *p*-value >2.57. It is seen from the results (Table 2) that the majority of PAH determinations were not significant for both pressurised and atmospheric pressure MAE. However, statistical significance was noted for both SFE and ASE. In all cases, with the exception of benz[*a*]anthracene by ASE, the statistically significant results shown in Table 2 gave extraction recoveries less than Soxhlet extraction.

In addition to extraction recoveries it is interesting to compare the relative merits of each extraction technique. The parameters chosen to compare are relative capital cost, organic extraction solvent volume, extraction time and sample weight. The relative capital cost of the extraction techniques are: Soxhlet < atmospheric MAE < pressurised MAE < ASE. For organic extraction solvent volume the relative order is: Soxhlet (150 ml, DCM) > atmospheric MAE (70 ml, DCM) > pressurised MAE (40 ml, acetone) > ASE (25 ml, DCM/acetone) > SFE (12 ml, methanol), while for extraction time (excluding cooling time) the order is Soxhlet (24 h) > SFE (1 h) > atmospheric MAE (20 min) > ASE

(12 min) > pressurised MAE (20 min per four samples or 5 min per sample). Finally, the relative order for sample weight is: SFE (1 g) < pressurised MAE (2 g) ~ atmospheric MAE (2 g) < ASE (7 g) < Soxhlet (10 g). As can be seen the desirable features of low cost, minimal organic solvent volume, fast extraction time and a large sample size does not immediately emphasise one particular extraction technique.

In addition to the parameters discussed above, the selection of one extraction technique in preference to another is usually made on the basis of the availability of a standard method e.g., US EPA. In this situation, and for the extraction techniques discussed, several US EPA methods are available for the extraction of PAHs from contaminated soil, namely, Method 3540 for Soxhlet extraction, Method 3561 for SFE and Method 3545 (proposed) for ASE. Based on the data presented in this paper the method of choice still appears to be Soxhlet extraction. However, it is anticipated that the other extraction techniques described will challenge Soxhlet in the near future.

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Table 2
Statistically significant extraction data for individual PAHs compared to Soxhlet extraction^a (*p*-values reported)

Compound	Pressurised MAE	Atmospheric MAE	SFE	ASE
Naphthalene				
Acenaphthylene			2.8	
Acenaphthene			3.7	
Fluorene				
Phenanthrene				
Anthracene		6.5	3.4	
Fluoranthene				2.6
Pyrene			2.9	
Benz[<i>a</i>]anthracene				3.0
Chrysene				
Benzo[<i>b</i>]fluoranthene + Benzo[<i>k</i>]fluoranthene	6.1	4.9	5.6	4.4
Benzo[<i>a</i>]pyrene				
Indeno[123- <i>cd</i>]pyrene				3.1
Dibenz[<i>ah</i>]anthracene				
Benzo[<i>ghi</i>]perylene			3.5	5.6

^a Statistical significance was determined using a paired *t*-test at which significance was determined to be a *p*-value >2.57.

Note: Dibenz[*ah*]anthracene was not detected.

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