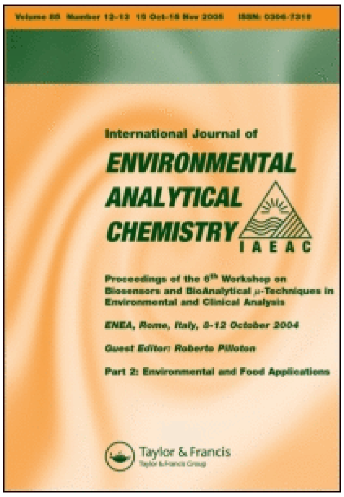

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COMPARISON OF SFE, SOXHLET AND SONICATION FOR THE EXTRACTION OF ORGANIC CONTAMINANTS FROM SANDSTONE

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Supercritical Fluid Extraction (SFE), Soxhlet and a fast sonication procedure were compared for the extraction of representative creosote contaminants with special attention for NSO compounds, from dried sandstone aquifer materials. Spiking levels were 0.2, 1 and 10 mg/kg for 2 PAHs, 3 phenols and 6 NSO compounds. The 0.2 mg/kg level cannot be determined with accuracy whatever the method. SFE showed recoveries higher than 100% in most cases and 0% for 2,3-benzofuran. This method could only be recommended for PAHs recovery at 10 mg/kg level. On the whole, sonication and Soxhlet gave similar results for phenols and PAHs while sonication showed higher recoveries for NSO compounds. The choice of extraction procedure must rely on procedural characteristics such as processing time, ease of use, number of sample, analyte concentration. Sonication, being much shorter than Soxhlet, was therefore recommended for the extraction of creosote contaminants from sandstone.

Keywords: Polycyclic aromatic hydrocarbons; creosote; soxhlet; sonication; supercritical fluid extraction; sandstone aquifer

INTRODUCTION

Contaminated-land policy within the European Union (EU) is primarily concerned with problems arising from old industrial sites contaminated by the disposal of waste. There is no generally accepted definition for "contaminated land" within the EU, although some individual countries such as Denmark, Germany, UK and The Netherlands have established definitions.[1] The Netherlands has produced generic criteria[2] based on target values representing: i)

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*Corresponding author. Fax: +33-238-643711. E-mail: l.amalric@brgm.fr background concentrations for naturally occurring substances, ii) analytical detection limits for man-made organic compounds and intervention values, and iii) the threshold above which remediation may be necessary. The Canadian Council of Ministers for the Environment (CCME) has published national assessment and remediation guidelines for contaminated land.[3]

Where coal-tar contamination is concerned, the criteria are based on determining the concentration of polycyclic aromatic hydrocarbons (PAHs) in the soil according to the Dutch[2] and Canadian[3] guidelines. Quantification of PAHs is generally done by gas chromatography (GC) or high-pressure liquid chromatography (HPLC), techniques that show the greatest sensitivity and selectivity when combined with mass spectrometry and fluorescence detection, respectively.[4] The major problem that remains is the uncertainty of the soil extraction efficiency.[5]

Current standard procedures for the extraction and quantification of PAHs in soil samples are based on Soxhlet,[6] sonication[7] and supercritical fluid extraction[8] (SFE). Additional extraction methods, more or less derived from USEPA procedures, are also reported in the literature for Soxhlet,[9–14] sonication,[10,15–18] shaking,[5,19] and SFE.[20–25] Soxhlet with methylene chloride showed recoveries from 31 to 121% with relative standard deviation values (RSD) below 20% for sediments spiked at various levels (0.05–2 mg/kg)[9,13,14,26,27] and from 46 to 115% for soils spiked to 1 to 1,000 mg/kg.[28] Other Soxhlet solvents used for sediments[10,29] yielded 34 to 118% recoveries. Sonication with methylene chloride showed recoveries from 69 to 80%, with RSD below 10% for spiked surface samples.[16] When sonication was applied with hexane/acetone, recoveries were 51 to 117% for spiked sediments.[10]

SFE with CO_2 showed recoveries from 97 to 103% with RSD below 14% in certified sediments;[22] when modifiers were added recoveries were 85 to 300% with RSD below 20%.[21,25] For 20 mg/kg spiked soils, recoveries were from 68 to 132% for PAHs with CO_2 and modifiers.[30]

Although all these procedures have been established for PAHs, less attention has been paid to the simultaneous extraction of the overall coal-tar or creosote constituents from solids. Creosote is a complex mixture of over 200 major individual compounds. In general, it contains about 85% PAHs, 10% phenolic compounds, 5% heterocyclic NSO (nitrogen-, sulphur-, and oxygen-) compounds and a small fraction of BTEX (benzene, toluene, ethylbenzene and xylenes) compounds.[31,32] Some compounds, such as nitrogen heterocycles, are almost as well-known as PAHs, but generally very few of them have been considered as priority pollutants.[33] For this reason they have not been systematically identified in environmental studies, even though NSO compounds have been found in soils and groundwaters at sites contaminated with petroleum and wood-preserving waste,[34,35] and in relatively high concentrations in many other spill types.[36–38] Mueller[39] used a Soxhlet procedure with methylene chloride followed by a series of fractionations of the aqueous and organic phases, to extract and quantify 43 phenols, NSO compounds, and PAHs from a creosote-contaminated soil; the recoveries from 28 to 207% for 5–50 mg/kg-spiked surface soils are considered generally within acceptable limits for processing soils. For ortho-cresol, 2,6-dimethylphenol, phenanthrene, 2,3-benzofluorene, quinoline, dibenzofuran, dibenzothiophene and carbazole, values were 43, 36, 128, 99, 90, 73, 68, and 128%.[39] Pollard[40] extracted only dibenzothiophene and carbazole, in addition to PAHs, with Soxhlet and methylene chloride. Shaking with acetone[41] was used to extract PAHs and dibenzofuran (but not nitrogen- and sulphur-containing compounds). Nitrogen-containing aromatic compounds were extracted by shaking with methylene chloride from creosote oil and marine sediments.[19] For phenanthrene and dibenzofuran, SFE with CO_2 showed recoveries of 94 ± 3% and 122 ± 3% respectively for certified sediments.[24]

The purpose of the present study is to compare SFE, Soxhlet procedure and a fast sonication procedure applied to the extraction of representative creosote pollutants, with special attention being paid to NSO compounds, from sandstone aquifer materials. The number of NSO compounds in our experimental creosote mixture solution was emphasized, compared to the 85% PAHs and 5% phenols which usually constitute creosote.[31,32] The 11 molecules were 2 PAHs, phenanthrene and 2,3-benzofluorene, 3 phenols, phenol, ortho-cresol and 2,6-dimethylphenol and 6 NSO compounds, carbazole, quinoline, indole, dibenzothiophene, 2,3-benzofuran and dibenzofuran.

Extraction efficiencies have been shown to vary with analyte concentration[42] suggesting the need to investigate recovery efficiencies over a range of expected concentrations. PAH background concentrations in soils (in Europe and North America) range from 0.05–0.5 mg/kg,[43,44] to maxima in excess of 10 mg/kg due to contamination by vehicle[45,46] or industrial emission.[47–49] Industrial and municipal outfalls have shown PAH contamination in excess of 1,000 mg/kg dry weight.[17,50–52] Individual PAH concentrations in soils are very diversified, from 0.001 to 1,000 mg/kg[5,16,51,53–57] or even higher.[17,58] For creosote contamination, literature values are between 1.5 and 1,200 mg/kg.[41,54,59] Because of the large concentration range encountered, values from the Netherlands and the CCME (Table I) for PAHs and phenols were used to determine the spiking levels in the present study.

Analytes spiked on real uncontaminated samples may not be situated on the same binding sites as those of the analytes from contaminated solids because of the kinetic and diffusional limitations of the sorption process, and several possible interactions may exist simultaneously between a particular analyte and a

TABLE I Generic soil quality criteria (mg/kg) for some organic chemical adopted by The Netherlands[2] and Canada.[3]

Compound	*Dutch soil quality criteria*			*Canadian soil quality criteria Remediation*		
	Target value	*Intervention value*	*Assessment*	*Agricultural*	*Residential /parkland*	*Commercial /industrial*
Phenol	0.050	40	0.1	0.1	1	10
Fluorathene	0.015					
Benzo(a)pyrene	0.025		0.1	0.1	1	10
Anthracene	0.050					
Dibenzo(a,h)anthracene			0.1	0.1	1	10
Benzo(a)anthracene	0.020		0.1	0.1	1	10
Benzo(g,h,i)perylene	0.020					
Benzo(k)fluoranthene	0.025		0.1	0.1	1	10
Benzo(b)fluoranthene			0.1	0.1	1	10
Indeno(1,2,3,c,d)pyrene	0.025		0.1	0.1	1	10
Naphthalene	0.015		0.1	0.1	5	50
Phenanthrene	0.045		0.1	0.1	5	50
Chrysene	0.020					
Pyrene			0.1	0.1	1	10
Total PAHs (10)	1	40				

complex matrix.[60–62] Since the retention of spiked analytes on or in the environmental matrices may often be less than for native analytes, the use of spike recovery may overestimate the efficiencies of extraction methods.[61] Nevertheless, spiked samples were preferentially used in this study to test the optimum efficiencies of the three extraction methods.

The partition coefficient between the solvent and the sample matrix, and the contact between the solvent and the soil particles, are two factors affecting recovery efficiency. Therefore, in order to test only the extraction procedure, the sonication and Soxhlet extractions were performed with the same solvent mixture, and the solid/liquid ratios, as well as all operations before and after the extraction, were identical for the three procedures (see *Experimental section*).

EXPERIMENTAL

Aquifer Material Sample

The rock sample (Sherwood Sandstone) was collected from an uncontaminated part of a sandstone aquifer near a former Rexco coking plant at Mansfield Colliery, Forest Town, Mansfield, Nottinghamshire, England. The core was air/dried, crushed in a mortar and sieved ($\leq$ 2 mm). The mineralogy was 60–70% quartz, 15–20% feldspath and 15–20% phyllosilicates.

Solvents and Standards

Methylene chloride, acetone and hexane (Merck Suprasolv quality) and methanol (Carlo Erba, RS quality) were used without further purification. All compounds, 2,3-benzofluorene (98%), 2,3-benzofuran (99.5%), carbazole (99%), dibenzofuran (99 + %), dibenzothiophene (99 + %), 2,6-dimethylphenol (99.8%), indole (99 + %), ortho-cresol (99%%), phenanthrene (99.5%), phenol (99 + %) and quinoline (98%) were purchased from Aldrich and used as received. Separate stock solutions of each compound were prepared in methanol (ca. 200 mg/L). Spiking solutions (2, 10 and 100 mg/L) were obtained by mixing adequate volumes of the 11 stock solutions.

Spiking Procedure

Because of the large concentration range encountered in literature, values from the Netherlands[2] and the CCME[3] (Table I) for PAHs and phenols were used to determine the spiking levels. Based on these criteria, the sandstone material was spiked to obtain 0.2, 1 and 10 mg/kg for each molecule. The 0.1 mg/kg level (Dutch assessment criteria,[2] Table I) was discarded because it was too close to the detection limit (0.05 mg/kg). The total spiking amount for the 11 molecules was therefore 2.2 to 111 mg/kg. The highest spiking level for each molecule, 10 mg/kg, may seem low compared to reported high contamination levels,[17,58] but since the extract of a very contaminated sample can easily be diluted before quantification, it seemed more appropriate to focus on low concentrations, that furthermore can correspond to target values, than on high concentrations.

Spiking of each subsample, 2 g for SFE or 15 g for Soxhlet and sonication, was preferred over spiking the total initial solid sample (1 kg), so as to avoid heterogeneity in later sampling of the spiked replicates. For sonication and Soxhlet, a 15.04 ± 0.05 g dried sample was spiked with 1.53 ± 0.02 mL (determined by weight) of the methanolic solution in three consecutive steps of 4.5 g and 0.5 mL, and a fourth step of 1.5 g solid. The procedure for SFE extraction was identical except for the solid mass, 2.03 ± 0.02 g, and the methanolic solution, 0.205 ± 0.007 mL. Blanks were 15.04 ± 0.05 g of solid for sonication and Soxhlet, and 2.03 ± 0.02 g for SFE. Five replicates were prepared for each spiking level and for the blanks of each extraction procedure. Dried samples were spiked directly into the Soxhlet extraction thimbles (Whatman 20 mm i.d. × 60 mm), SFE extraction containers (Hewlett Packard 12 mm i.d. × 95 mm) and sonication extraction glass tubes (30 mm i.d. × 110 mm). SFE containers and sonication tubes were closed; Soxhlet thimbles were put into closed plastic tubes whose inner walls were covered with aluminium foil. Samples were then stored at 14 ± 1°C for 67.5 ± 2.5 hours. This procedure does not claim to represent a real ageing, but it does minimize the risk of actually extracting directly the methanolic solution.

Soxhlet Extraction

Samples were extracted according to USEPA method 3540.[6] Soxhlet extraction was performed into 40 mL of 1:1 (v:v) methylene chloride:acetone with 45 min boiling and 90 min rinsing using a Tecator Soxtec system HT 1043 extraction unit. The resulting extracts were weighed and evaporated, using a gentle stream of nitrogen, to approximately 1 mL and then stored in glass vials with PTFE-lined screw caps ready for analysis by gas chromatography/mass spectrometry (GC-MS).

Sonication Extraction

To maintain a constant solid/liquid ratio between the methods, 40 mL of 1:1 (v:v) methylene chloride:acetone solvent was added to each tube and the sample was sonicated (35 kHz) in an ultrasonic bath (Branson 1200) for 30 min at room temperature, followed by centrifugation (2000 g, 30 min). The accurately weighted supernatant (36.1 ± 0.3 mL) was transferred with a pipette from the extraction tube to a glass bottle for evaporation, using a gentle stream of nitrogen, to approximately 1 mL.

Supercritical Fluid Extraction

A Hewlett Packard model 7680T was used with an ODS (octadecylsilane) trap. The SFE method was initially developed with a factorial design by varying fluid temperature (2 values), fluid density (4 values), type (dynamic and static) and time of extraction (2 values). During the extraction, the containers were kept at 89 bars and at 40°C, while the restrictor and trap were kept at 60 and 10°C respectively. Fluid flow (100% CO_2) was 2 mL/min. On completion of the extraction (5 min static and 7 min dynamic), the system was slowly brought back to atmospheric pressure and room temperature. The restrictor temperature was decreased to 30°C and the ODS trap was washed at 1 mL/min with 1 mL hexane, which was then stored in glass vials with PTFE-lined screw caps ready for GC-MS analysis. This method yielded no recovery for quinoline. A second consecutive extraction with 95% CO_2 and 5% methanol (v:v) was therefore conducted for each sample, aiming specifically at the recovery of quinoline. This second extraction was identical except for the fluid pressure, 104 bars, that varied because of the modifier. Table II presents a comparative summary of the three extraction methods.

Analysis

For complex environmental matrices such as sediments and soils, a clean-up step is necessary for the accurate identification and quantification of the analytes. Biogenic or other interfering compounds present in the extract can co-elute with the analytes of interest and prevent accurate quantitation.[63] For coal-tar contaminated samples a clean-up may be required to carefully separate the aliphatic material from the analytes and improve the detection of the aromatic. In the present study, the clean-up step was not necessary because the blank unspiked sandstones, extracted by any of the three procedures, showed no trace of organic

TABLE II Comparative summary of extraction methods.

Step	*Sonication*	*Soxhlet*	*Supercritical Fluid Extraction (SFE)*
Sample weight	15 g	15 g	2 g
Solvent	methylene chloride/ acetone	methylene chloride/ acetone	methanol, hexane
Total Volume	40 mL	40 mL	2 mL
Extraction	30 min	135 min	15 min
Temperature	ambient	110°C	40°C
Separation	Centrifuge 30 min	None, but 30 min cooling	None
Concentration	Nitrogen blow down 30 min	Nitrogen blow down 30 min	None
Vessel transfer	Yes, before concentration	Yes, before concentration	None
Total time	120 min	195 min	15 min
Number of samples per cycle	8	6	1

pollutant nor any gas chromatographic response that might interfer with the molecules to be analysed.

The analysis was carried out using a Varian Saturn 3 GC-MS. Sample extracts (1 μL) were injected with a Varian 8100 model autosampler. Chromatographic separation was carried out using a XTI5 capillary column, 30 m long, 0.25 mm i.d., 0.25 mm film thickness (RESTEK) with helium carrier gas at 12.5 psi head pressure. The splitless injector was set at 120°C with the GC temperature programmed at 50°C for 5 min, rising to 220°C at 5°C/min, and then to 30°C at 10°C/min to be held at 300°C for 3 min. The transfer line and detector were set at 260 and 280°C respectively. The MS was operated in the EI mode (70 eV). The detection limit was 0.05 mg/kg for each molecule. Many GC-MS analysis methods rely on the internal standard quantification technique to enhance accuracy. Eventhough the use of internal calibration is recommended,[64] it can also lead to a systematic bias in the calibration of GC-MS intruments.[65] Furthermore, the choice of an internal standard would have been difficult in this study where analysis was performed for contrasted molecule types, phenols, PAHs and NSO compounds. External calibration was therefore used here. Standard solutions (0.5–20 mg/L) were obtained by mixing adequate volumes of the 11 stock solutions in methylene chloride. Calibration curves were linear for the 11 molecules.

RESULTS AND DISCUSSION

The results of the three procedures are presented in terms of average recovery (AVG) and relative standard deviation (RSD $[\mathit{100}.\ \sigma/\bar{x}]$) of the 5 replicates for

TABLE III Average recovery (AVG,%) and relative standard deviation (RSD,%) for spiked sandstone extraction (5 replicates except for the first SFE at 10 mg/kg spiking level) with sonication, Soxhlet and SFE procedures. The first SFE was 100% CO_2 and the second was 95% CO_2 with 5% methanol.

	SONIFICATION		*SOXHLET*		*1st SFE*		*1st and 2nd SFE*	
	AVG %	*RSD* %	*AVG* %	*RSD* %	*AVG* %	*RSD* %	*AVG* %	*RSD* %
10 mg/kg								
Phenol	90.6	3.1	82.6	11.5	68.4	8.0	68.4	8.0
2,3-Benzofuran	89.9	4.0	68.6	13.9	0.0		0.0	
Ortho-cresol	79.2	3.0	71.0	12.3	67.5	7.2	67.5	7.2
2,6-Dimethylphenol	67.9	5.3	56.2	14.0	46.3	21.1	46.3	21.1
Quinoline	83.2	3.3	79.0	11.9	0.0		46.0	8.8
Indole	79.6	4.9	71.6	12.5	70.8	6.7	70.8	6.7
Dibenzofuran	88.7	3.8	80.0	12.6	94.8	6.4	94.8	6.4
Dibenzothiophene	88.0	2.0	76.9	12.2	95.6	2.4	95.8	2.4
Phenanthrene	83.7	13.3	77.5	12.5	98.0	5.3	98.5	5.0
Carbazole	80.6	6.1	70.1	12.3	68.8	12.7	84.1	6.9
2,3-Benzofluorene	75.7	4.4	71.2	10.8	77.5	6.5	84.1	3.2
1 mg/kg								
Phenol	102.6	9.3	88.1	15.8	93.7	48.1	93.7	48.1
2,3-Benzofuran	76.3	8.6	65.2	15.7	5.1	223.6	5.1	223.6
Ortho-cresol	86.8	7.7	74.3	18.0	117.6	48.8	117.6	48.8
2,6-Dimethylphenol	73.7	7.7	60.7	15.8	71.8	48.2	71.8	48.2
Quinoline	69.9	14.8	74.4	14.4	0.0		123.9	37.5
Indole	86.2	8.3	75.8	18.2	134.2	34.7	134.2	34.7
Dibenzofuran	94.9	7.3	82.8	15.4	124.1	42.1	124.1	42.1
Dibenzothiophene	99.8	8.5	81.7	14.0	127.6	38.6	127.6	38.6
Phenanthrene	96.9	8.2	80.2	15.0	120.4	35.7	123.8	31.6
Carbazole	104.1	10.7	80.3	17.7	99.6	37.8	119.9	46.9
2,3-Benzofluorene	109.0	8.7	94.0	16.9	111.1	31.6	114.6	32.7
0.2 mg/kg								
Phenol	69.9	13.3	80.8	34.6	81.8	25.5	81.8	25.5
2,3-Benzofuran	35.6	59.0	49.2	28.6	0.0		0.0	
Ortho-cresol	54.5	34.5	68.3	31.0	113.3	9.2	113.3	9.2
2,6-Dimethylphenol	46.0	57.2	58.2	29.0	95.9	9.6	95.9	9.6
Quinoline	45.9	12.9	64.9	36.0	0.0		145.2	23.2
Indole	57.0	12.7	67.4	33.4	137.3	15.6	137.3	15.6
Dibenzofuran	51.8	20.5	85.7	39.4	130.2	9.9	130.2	9.9
Dibenzothiophene	55.4	11.3	71.9	36.0	126.2	8.6	126.2	8.6
Phenanthrene	54.3	10.9	72.3	38.1	141.5	22.8	141.5	22.8
Carbazole	55.1	8.9	73.4	44.2	89.3	11.7	140.2	25.8
2,3-Benzofluorene	51.3	10.4	79.4	43.6	107.6	10.5	107.6	10.5

each spiking level (Table III). Erratic recovery for one replicate of 10 mg/kg extracted with SFE required that those values be eliminated and the average be calculated using only four replicates for that SFE level.

Table III shows that for the 10 mg/kg level, recoveries ranged from 56.2 to 98.5% for the three methods, except for SFE where dimethylphenol and quinoline showed recoveries of 46.3 and 46.0% and where 2,3-benzofuran was not recovered. The RSD ranged from 2.0 to 21.1%, the highest values being for Soxhlet. SFE and sonication showed similar RSD (2.0 to 8.8%), except for 2,6-dimethylphenol and phenanthrene. Comparison of the two SFE extraction methods, with and without methanol, shows that CO_2 could not extract quinoline from sandstone whatever the spiking level, and that the addition of methanol was necessary. However, quinoline recoveries were not consistent for any of the 3 spiking levels (46.0, 123.9 and 145.2%) and it was therefore impossible to determine whether the added amount of methanol, 5%, was adequate. Neither of the two SFE procedures extracted 2,3-benzofuran from the sandstone whatever the spiking level; only one sample showed a 2,3-benzofuran recovery of 25.5% (1 mg/kg). The 5 replicates of each spiking level were spiked with the same solution and almost simultaneously for each of the 3 extraction methods. The hypothesis of 2,3-benzofuran having been omitted for the SFE samples must therefore be discarded since 2,3-benzofuran was recovered by sonication and Soxhlet. A second ODS trap washing using a polar solvant could have been used to tentitavely increase the recovery for polar compounds but as the recovery yields were already high using hexane (Table III) a second washing was not applied. The increase in recovery observed for quinoline using methanol as modifier clearly showed that the lack of recovery for benzofurane and quinoline was mostly due to the lack of desorption from the sandstone, not to a lack of elution from the ODS trap. No justification can reasonably be proposed for the lack of 2,3-benzofuran recovery by SFE.

For the 1 mg/kg level, sonication and Soxhlet gave similar recoveries ranging from 60.7 to 109.0% according to the molecule. The RSD were below 18.2% for both methods, and particularly low for sonication, 3.1 to 14.8%. Except for 2,3-benzofuran, which was not recovered, the SFE AVG recoveries were higher than 100% in most cases, reaching 134.2%. The RSD were particularly high at more than 31.6%. These high recoveries, which occurred also at the 0.2 mg/kg level, might suggest that SFE was particularly suitable for extracting the original pollutants contained in the sandstone. The sandstone cores were, however, free of creosote contamination, with the blanks (unspiked samples) showing no trace of organic pollutant when extracted by any of the three procedures. The 20–45% excess recovery showed by SFE corresponds to 0.04–0.08 mg/kg. Such concentrations, if present in the blank, would have been detected by GC-MS for which the limit of detection was 0.05 mg/kg. Moreover, MS detection is based on the compound mass and not only on the retention time, and the MS quantification was based on the specific mass of each compound. The overestimation observed with SFE could not therefore correspond to interfering compounds. As all the procedural steps, i.e. spiking solution, date of spiking, ageing time, date of extraction, analysis method, date of injection, date of data treatment and operator—were identical for the 3 procedures and the 3 spiking levels, the erratic SFE recoveries for both the 0.2 and 1 mg/kg spiking levels could only be attributable to the SFE extraction itself. For SFE using CO_2, or CO_2 and modifier, recoveries greater than 100% have been reported, but either not discussed[30] or attributed to a co-elution of the analyte with another compound in the extract having a mass spectrum showing very little difference with that of the spiked molecule.[25]

For the 0.2 mg/kg spiking level, the sonication and Soxhlet procedures gave AVG ranging from 35.6 to 69.9% and from 49.2 to 85.7% respectively, whereas the respective mean RSD were 22.9 and 35.8%. SFE again showed high recoveries (81.8 to 145.2%, except for 2,3-benzofuran that was not recovered), and RSD (9.2 to 25.8%).

The AVG recoveries observed for the three methods and the three spiking levels are, except the non-extraction of 2,3-benzofuran with SFE, in good agreement with recoveries reported in the literature.[9,10,13,14,16,22,25,27–29,39,66] The RSD of the present study were generally in the same range as reported values,[10,13,16,22,25,28,66] although sometimes higher (SFE and 0.2 mg/kg for the three methods).

Statistical Significance of Differences Between Procedures

Recoveries for the three procedures were compared for each spiking level. A first comparison was based on the results of the 11 pooled molecules treated as a single data set. Mean recoveries for each of the 3 molecule types treated as 3 subsets (phenols, PAHs and NSO compounds) were also compared. Differences were tested by Student's test with 0.01 level of significance.[67]

On the basis of all 11 molecules (Table IV), the three procedures differed significantly from each other for the 0.2 mg/kg spiking level. The mean recoveries increased in the order sonication, Soxhlet and SFE. Since SFE showed (i) recoveries much higher than 100% that could not be explained, and (ii) very high RSD (Table III), Soxhlet could be considered as the most suitable method for 0.2 mg/kg, despite its lower mean. For 1 mg/kg, sonication and SFE yielded similar recoveries, both significantly higher than Soxhlet. For the same reason as with the 0.2 mg/kg level, sonication was considered better than SFE. For the 10 mg/kg level, sonication showed significantly higher recoveries than Soxhlet and SFE, which yielded similar recoveries. Sonication appears to be the most appropriate method to recover the overall 11 representative creosote molecules from sandstone.

TABLE IV Mean recoveries for the extraction methods for each spiking level, on the basis of all 11 molecules and of the 3 molecule types. Values in the same row followed by the same letter are not different at the 0.01 level.

	SONICATION	*SOXHLET*	*SFE*
11 molecules			
0.2 mg/kg	52^{a}	70^{b}	111^{c}
1 mg/kg	91^{a}	78^{b}	105^{a}
10 mg/kg	82^{a}	73^{b}	70^{b}
Molecule types			
Phenols (3 molecules)			
0.2 mg/kg	57^{a}	69^{a}	97^{b}
1 mg/kg	88^{a}	74^{a}	94^{a}
10 mg/kg	79^{a}	70^{ab}	61^{b}
PAHs (2 molecules)			
0.2 mg/kg	53^{a}	76^{a}	124^{b}
1 mg/kg	103^{a}	87^{b}	119^{ab}
10 mg/kg	80^{a}	74^{a}	91^{b}
NSO (6 molecules)			
0.2 mg/kg	50^{a}	69^{b}	113^{c}
1 mg/kg	88^{a}	77^{b}	106^{ab}
10 mg/kg	85^{a}	74^{b}	65^{ab}

On the basis of molecule types, there was no significant difference between the sonication and Soxhlet procedures for the phenols (phenol, ortho-cresol and 2,6-dimethylphenol) at the three spiking levels (Table IV). SFE yielded a significantly higher mean recovery (Table IV) and much lower RSD (Table III) than the two other methods for the 0.2 mg/kg levels of the three phenols. SFE could therefore be recommended for cases at this level. For the 1 mg/kg level SFE cannot be recommended even though the three extraction procedures gave similar results, because of the high RSD around 48% (Table III). For the 10 mg/kg level SFE and Soxhlet gave no significant difference in recoveries but SFE recovery was lower than sonication. On the whole, both sonication and Soxhlet are suitable for recovering phenols from sandstone.

With the PAHs (phenanthrene and 2,3-benzofluorene), SFE showed the highest mean for the three spiking levels. For the 0.2 and 1 mg/kg levels (Table III), SFE recoveries were however much higher than 100% and the RSD were very high; SFE therefore seems better only for the 10 mg/kg level. No significant difference existed between sonication and Soxhlet at the 0.2 mg/kg level. Despite the higher mean recovery by Soxhlet at the 0.2 mg/kg level, sonication, because its lower RSD (Table III), will enable the amount extracted from a field sample to be more consistently corrected for the percentage recovery. For the 1 mg/kg level, sonication showed significantly higher recoveries than Soxhlet. To conclude, sonication can be used to extract PAHs from sandstone.

For NSO compounds (quinoline, indole, carbazole, dibenzothiophene, 2,3-benzofuran and dibenzofuran), the three procedures yielded significantly different recoveries for the 0.2 mg/kg level. Soxhlet can be considered the most appropriate, despite its lower mean and its higher RSD compared to SFE (Table III), because SFE showed recoveries higher than 100% in most cases and 0% recovery for 2,3-benzofuran. For the same reasons, sonication being significantly different from Soxhlet, should be preferred to SFE for the 1 and 10 mg/kg levels. Improvement of the SFE recoveries for NSO compounds might be achieved by modifying the contact time between the fluid and the sample, or the amount and type of modifier, but this was not a goal of the present study. On the whole, sonication is appropriate to recover NSO compounds from sandstone.

Literature data indicate that Soxhlet extraction with hexane/acetone gives significantly higher recoveries than a mixer/shearer extraction with acetone for PAH-contaminated soil.[42] Somewhat higher recoveries, 12%, using Soxhlet compared to sonication[7] were also observed for PAH-contaminated soil (1–2,500 mg/kg).[68] The difference was not sufficient, however, to lead to the recommendation of one method of another.[68] In another study using 4 different PAH-contaminated soils and surrogate spikes,[69] no consistent differences in recovery were observed between Soxhlet, sonication and batch (shaking). However, the solvents were different between the three methods. The literature data are therefore difficult to compare with the results of the present study. However, like the results of the present study, they do show that the choice between different extraction methods is not straightforward when only recoveries are considered.

CONCLUSION

The efficiency of extraction procedures is dependent on the analyte concentration. Conclusions for the 0.2 mg/kg level were systematically lower than the other two levels. The conclusions regarding the method to use were however identical for the highest spiking levels, i.e. 1 and 10 mg/kg, whether one considers the 11 molecules together, or the phenols and the NSO compounds separately. These results are in agreement with those of Fowlie[42] who observed higher recovery at 50 mg/kg than at 5 mg/kg when a soil spiked with PAHs was extracted with Soxhlet or Polytron (a high velocity mixer/shearer). Harrison[70] also found the recovery of radio-labelled benzoanthracene from fly ash extracted by a rotary shaker to increase from 5 to 94% when the spike increased from 0.001 to 10 mg/kg. A systematic check of recovery efficiencies must therefore be conducted over the range of concentration expected for the extraction method used. The particularly high RSD for the 0.2 mg/kg level indicate that this level cannot actually be determined with accuracy. Losses during procedural steps (vessel transfer, concentration with N_2) are probably most pronounced at this level and might be responsible for the low AVG and the high RSD (on average 2 times higher than the Soxhlet and sonication RSD). In most environmental samples, contaminants present at very low levels do, in fact, require more complex methods to be separated and recovered with sufficient purity for subsequent analysis, since many other extractable materials are present simultaneously. An isolation technique is usually recommended.[29]

The choice of an extraction procedure must rely partly on procedural characteristics such as processing time, ease of use, number of samples and analyte concentration. SFE, as used in the present study, is not recommended because of its exceedingly high recoveries and RSD (see results on Table II). Sonication is faster than Soxhlet and is also less dangerous because the solvents are not heated. Sonication is more onerous as tubes have to be transferred from the ultrasonic bath to the centrifuge, and the liquid needs pipetting before the concentration step. Nevertheless, because the number of samples that can be processed per day is greater with sonication, this procedure is recommended for the simultaneous extraction from sandstone of the 11 phenols, PAHs and NSO compounds representative of the creosote studied here, at a level in the order of 1–10 mg/kg. At lower concentrations, none of the three procedures studied enables determination with a good precision, the RSD being in the 8.6–59.0% range.

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