

Evaluation of SFE-CO₂ and Methanol-CO₂ Mixtures for the Extraction of Polynuclear Aromatic Hydrocarbons from House Dust

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Abstract

The extraction of native polynuclear aromatic hydrocarbons (PAHs) from house dust is studied using supercritical fluid extraction (SFE-CO₂); direct modified SFE; and mixtures of 10, 20, 30, and 40 mole percent methanol in CO₂. The temperatures studied are 50, 75, and 100°C. For the direct modified SFE experiments, the effect of adding 100 and 200 µL of methanol and 100 µL of water directly to the sample at 75 and 100°C is studied. The properties of the PAHs and of the dust matrix are used to explain the patterns observed in the recovery yields. The increase in the solvent strength of the methanol-CO₂ mixtures greatly increases the recoveries and decreases the total extraction time. Also, an increase in the extraction temperature positively affects the yields. The direct modified SFE and SFE-CO₂ experiments give similar extraction yields, and the extractions with the binary mixtures give optimum results.

Introduction

Supercritical fluid extraction (SFE) (1-3) has become the preferred choice for the extraction of environmental pollutants, superseding techniques like Soxhlet or sonication, which require longer extraction times and extreme extraction conditions (4). A common extraction fluid used in SFE is CO₂. CO₂ is a preferred extraction solvent because it is easily vented to atmosphere, it is nontoxic, and it solvates nonpolar to moderately polar compounds (1,5-7). The extraction of "real world" samples is controlled by numerous factors, among them the matrix-analyte attraction, the diffusion through an adsorbed water or organic layer, and analyte solubility (8). These processes often limit the yields in the extractions by SFE-CO₂. The matrix-analyte attraction can be minimized by using a high-solvent-strength extraction fluid. The diffusion through an adsorbed layer of water occurs in the extraction of most environmental matrices and will depend on the solubility of the water in the extraction fluid and the moisture and organic con-

tent of the matrix. To increase the solvent power of the fluid and increase the solubility of the water in the fluid, 5-10% (wt/wt) of organic modifiers is often added to the CO₂ (i.e., methanol) (1,2,7). This addition can be performed from a modifier pump or a premix CO₂-methanol cylinder or by adding the modifier to the sample matrix. However, the extraction of polar and high molecular weight compounds remains problematic (1,2,7).

Binary methanol-CO₂ mixtures with higher proportions of methanol have been used as an alternative to SFE and modified SFE (8-10). As much as 60% (wt/wt) liquid CO₂ could be added to methanol at room temperature before noticeable changes in solvent strength occurred (8). However, when more than 40% methanol is added to the CO₂, the viscosity of the mixture increases substantially, which makes CO₂-methanol mixtures with more than 40% methanol unattractive for extraction purposes.

House dust is a very difficult matrix for target analyses because of the heterogeneity of the compounds it contains (11). The major source of pesticides and polynuclear aromatic hydrocarbons (PAHs) in house dust is brought in on shoes from outdoors (11).

The work described here studies the optimization of the extraction of native PAHs from house dust. PAHs are found almost everywhere, and some are very strong carcinogens (12). Pollutants, such as PAHs, adsorbed onto house dust are more of a concern to the welfare of children than adults. Small children spend a considerable amount of time on household floors. It is also estimated that they ingest 2.5 times more soil and dust around the home than adults, whereas their body weight is only about 25% that of an adult (13). Therefore, reasonable exposure levels in house dust for children and adults may be significantly different.

Extraction and analysis of PAHs from environmental matrices using SFE-CO₂, direct modified SFE (1-10% [wt/wt] methanol addition on top of the sample), and modified SFE (1-10% [v/v] of methanol added to the CO₂) have been widely used for the extraction of PAHs from urban dust and soils with varying results (1,2,14,15).

In this study, SFE, direct modified SFE, and extractions with binary liquid mixtures were compared in the extractions of

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PAHs from house dust. Variables studied include temperature, composition of the extraction fluid, identity of the modifier (for direct modified SFE, methanol versus water), and volume of the static modifier added. Soxhlet extractions were performed and used for comparison purposes.

Experimental

Materials

A PAH standard (2000 µg/mL each) solution containing the 16 PAHs on the U.S. Environmental Protection Agency priority pollutant list (16) was obtained from Supelco (Bellefonte, PA). Table I summarizes the physical properties of these PAHs of interest. Carbazole (surrogate, 98%) and *p*-terphenyl (internal standard, 99.5%) were purchased from Aldrich Chemical (Milwaukee, WI). Reagent-grade sea sand was obtained from Jenneile Chemical (Cincinnati, OH).

Solvents used include methylene chloride (Optima, 99.9%) (Fisher Scientific, Fairlawn, NJ), acetone (99.9%) (Mallinckrodt, Paris, KY), and methanol (100%) (J.T. Baker, Phillipsburg, NJ). SFE-SFC-grade CO₂ (> 99.99%) was purchased from Air Products (Allentown, PA). Amber vials (2.0 mL) were purchased from National Scientific (Lawrenceville, GA) and amber collection vials (4.0 drams) were purchased from VWR Scientific (Bridgeport, NJ). Amber glassware was used throughout to protect the compounds from exposure to light.

House dust was collected from the entrance mats in chemistry buildings and from a dormitory at Ohio State University using a high-volume small surface sampler (HVS3, Cascade Stack Sampling Systems, Bend, OR) (17). This device is a modified residential vacuum cleaner with a filter that divides the particles into fractions of those with diameters greater than 5 µm and those with diameters less than 5 µm (17). The particles smaller

than 5 µm were collected in a regular vacuum cleaner bag that was discarded. The particles larger than 5 µm were collected in a removable polyethylene bottle and used for this project.

The total organic content was 31 ± 1 wt% and 48 ± 3 wt% for the chemistry building dust and the dormitory dust, respectively, as determined by thermal gravimetric analysis (TGA) (9,18,19).

In addition, the water content was determined by volumetric Karl-Fisher titrations. The result for the chemistry building dust was 3.5 ± 0.2% (relative standard deviation [RSD] = 5%, 3 replicates), and the result for the dormitory dust was 3.0 ± 0.1% (RSD = 3%, 3 replicates). High levels of organic matter and significant levels of adsorbed water often cause strong retention of organic compounds (20). By comparison, both types of collected dust would be expected to be very retentive matrices. Also, the dust collected from the dormitory was expected to be more retentive than the dust collected from the chemistry building because of the higher levels of organic material.

Soxhlet extractions

Soxhlet extractions for both types of collected dust were performed using a micro-Soxhlet instrument (Ace Glass, Vineland, NJ). Dust (1.0 g) was weighed and placed in a pure cellulose thimble (10 × 50 mm, National Scientific). Fractions were collected after 2, 4, 8, and 24 h. Methylene chloride (15 mL) was selected as the extraction-collection solvent, and the carbazole surrogate (10 µg) was added to account for sample loss. After the fractions were collected, they were concentrated down to 0.1 mL with a low stream of N₂, 8 µg of internal standard (*p*-terphenyl) was added, and the solution was diluted to 1 mL with methylene chloride. These solutions were transferred via pipette to autosampler amber vials, and the samples were analyzed using gas chromatography-mass spectrometry (GC-MS). Four

Table I. Properties of the PAHs Used for Analysis (26,27)*

Compound	Boiling point (°C)	Molecular weight	Formula	Identifying fragmentation pattern	Soxhlet recovery 1 (µg/g)	Soxhlet recovery 2 (µg/g)
Naphthalene	218	128.17	C ₁₀ H ₈	128, 127, 129	0.3 (9)	0.3 (1)
Acenaphthylene	280	152.20	C ₁₂ H ₈	152, 151, 153	0.3 (28)	1.0 (1)
Acenaphthene	279	154.21	C ₁₂ H ₁₀	154, 153, 152	0.6 (17)	0.6 (1)
Fluorene	295	166.22	C ₁₃ H ₁₀	166, 165, 167	0.9 (17)	0.8 (1)
Phenanthrene	340	178.23	C ₁₄ H ₁₀	178, 152, 179	20.0 (13)	8.5 (2)
Anthracene	342	178.23	C ₁₄ H ₁₀	178, 179	4.0 (12)	1.5 (1)
Fluoranthene	384	202.24	C ₁₆ H ₁₀	202, 201, 203	40.8 (16)	14.7 (2)
Pyrene	404	202.24	C ₁₆ H ₁₀	202, 201, 203	32.2 (15)	11.0 (2)
Benzo(a)anthracene	437	228.28	C ₁₈ H ₁₂	228, 226, 114	12.5 (24)	4.7 (1)
Chrysene	448	228.28	C ₁₈ H ₁₂	228, 226, 229	17.9 (21)	7.8 (1)
Benzo(b)fluoranthene	N/A	252.30	C ₂₀ H ₁₂	252, 253, 126	24.8 (28)	2.7 (1)
Benzo(k)fluoranthene	480	252.30	C ₂₀ H ₁₂	252, 253, 126	24.8 (28)	2.7 (1)
Benzo(a)pyrene	495	252.30	C ₂₀ H ₁₂	252, 253, 126	8.0 (28)	2.5 (1)
Dibenz(a,h)anthracene	524	278.33	C ₂₂ H ₁₄	278, 139, 276	0.5 (30)	3.8 (2)
Indeno(1,2,3-cd)pyrene	536	276.31	C ₂₂ H ₁₂	276, 138, 277	4.0 (28)	0.9 (1)
Benzo(ghi)perylene	> 500	276.31	C ₂₂ H ₁₂	276, 138, 137	3.3 (29)	3.5 (1)

* The Soxhlet recovery is the value that corresponds to a 100% yield. The numbers in parentheses are the %RSDs. Soxhlet recovery 1 refers to the extractions of the chemistry building dust, and Soxhlet recovery 2 refers to the extractions of the dormitory dust.

replicates were done, and duplicate chromatographic runs were performed.

SFE-CO₂ and extractions with CO₂-methanol

The extractions were performed using an Isco SFX 220 (Lincoln, NE) supercritical fluid extractor equipped with a 260-D syringe pump. For the SFE-CO₂ experiments, only one pump that was filled directly from the CO₂ cylinder was used.

For the extractions with the binary fluid mixtures (BME), two pumps were needed. One pump contained CO₂ at constant pressure (233 atm), and the other pump was used to prepare the mixture. For the mixtures, the needed volume of the cosolvent was added to the empty pump, and room was then created for the CO₂ by using the refill mode. The mixtures were prepared on a mole ratio basis. The pump containing the mixture was pressurized to 238 atm and allowed to equilibrate for a minimum of 12 h to ensure a single-phase liquid (21,22). Pressures higher than 163 atm produce one-phase mixtures for temperatures less than or equal to 100°C for the entire range of possible methanol-CO₂ compositions (i.e., 0–1 mole fraction methanol) (21,22). The homogeneity of these mixtures was evaluated by measuring the amount of methanol collected through the vent valve after the dynamic step. This volume was measured in a graduated cylinder to verify that no solvent gradients were produced in the pump. Consistent volumes were measured for each extraction condition.

A 2.5-mL stainless steel extraction vessel was used to perform the extractions. To reduce the dead volume inside the extraction cartridge and retain the small dust particles inside the cell, clean sea sand was used. This sand was refluxed with methylene chloride for 30 h before use. Dust (1.0 g) was placed between 1.0 g of sand on the top and 1.5 g of sand on the bottom. A 0.5- μ m stainless steel frit was used to seal each end of the cartridge, and an Anodisc membrane (0.02 μ m, 13 mm) (Whatman, Fairfield, NJ) was used at the bottom end of the cartridge body, on top of the frit, to reduce plugging or particles escaping the frits and plugging the restrictor end. The Anodisc membrane is an inorganic filter membrane resistant to CO₂ and methanol. The flow rate was maintained at 0.4 mL/min using 30- μ m-i.d fused silica (24–28 cm) tubing (Polymicro Technologies, Phoenix, AZ). This flow rate was found to give the optimum trapping of solutes and less evaporation during the collection step, compared with 1.0 and 1.5 mL/min. This comparison was made by analyzing the recoveries for the carbazole surrogate. The average recovery for the surrogate was less than 65% for the 1.0- and 1.5-mL/min extractions and approximately 75% for the extractions at 0.4 mL/min.

Before each extraction, the extraction vessel and frits were sonicated in acetone for 20 min and dried with a heat gun. After loading the sample into the vessel, the vessel was allowed to equilibrate to the temperature of the extraction chamber for 15 min to ensure temperature uniformity throughout the cartridge. During this step, all valves were closed to avoid any loss of sample due to evaporation.

The collection vessel (15 mL) contained 5 mL methylene chloride and 10 μ g of the carbazole surrogate to account for sample loss. The extractions consisted of two steps: a 1-min static step followed by a 20-mL dynamic step for SFE-CO₂ (8),

or a 15-mL dynamic step for the extractions using binary mixtures. The pump pressure used for SFE-CO₂ was 233 atm, and 238 atm was used for the binary mixture extractions (8). The temperatures used for both SFE-CO₂ and BME were 50, 75, and 100°C. The binary mixtures were used at conditions above (supercritical fluid) and below (enhanced-fluidity liquid) the mixtures' critical parameters (23). The mixtures used at supercritical conditions were 10% methanol-CO₂ at 75 and 100°C, 20% methanol-CO₂ at 75 and 100°C, and 30% methanol-CO₂ at 100°C. The enhanced-fluidity liquid mixtures were 10% methanol-CO₂ at 50°C, 20% methanol-CO₂ at 50°C, 30% methanol-CO₂ at 50 and 75°C, and all the conditions at 40% methanol-CO₂.

Fraction-collection studies were performed to determine the optimum extraction volumes. Initial fraction collection for the SFE-CO₂ experiments included 5, 10, 15, 20, 25, and 30 mL (approximately 1.5 h). No trace of the compounds of interest was seen after 20 mL, so the final volume was reduced to 20 mL. For the methanol-CO₂ mixtures, fractions at 5, 10, 15, and 20 mL were used, but because no trace of the analytes was detected after 15 mL, the collection volume was once again reduced, this time to 15 mL. Restrictor plugging occurred occasionally when pure CO₂ was used because of ice formation at the tip of the restrictor. When this happened, the restrictor was quickly raised above the collection vessel and was warmed with a heat gun. This took only a few seconds and rarely happened; therefore, the effect of this heating process on the extraction yields was expected to be minimal. After extraction, the samples were concentrated down to 0.1 mL with dry N₂; the internal standard (8 μ g) was added, and the solution was diluted to 1 mL with methylene chloride. Four extractions were done per condition, and duplicate chromatographic runs were performed.

Direct modified SFE experiments

The modifier was added directly on top of the sample before the extraction cartridge was sealed. Because of the high concentration of modifier initially present, the solvent power of the fluid and the solubility of water in the fluid increased. Volumes of 100 and 200 μ L (this corresponds to 10% and 20% [vol modifier/wt] sample) were studied at 75 and 100°C, and methanol and water were used as the static modifiers. Water was used to determine the effect that the addition of moisture has on the extraction of environmental samples. The bulk extraction solvent used for these extractions was CO₂ at 233 atm. The extractions consisted first of a 10.0-min static step followed by a 10.0-mL dynamic step; the flow rate was 0.4 mL/min (the restrictor was a 30- μ m-i.d. fused silica tubing, 24–26 cm long).

Analyses of extracts

Analyses of the extracts were performed using a Hewlett-Packard (HP) (Wilmington, DE) 5890 series II Plus gas chromatograph equipped with an HP 5972 mass selective detector (MSD). An HP 7673 autosampler was used for the splitless injection of 1 μ L of solution. A 30-m \times 0.25-mm-i.d. (0.25- μ m film thickness) HP-5 MS (cross-linked, 5% phenylmethylpolysiloxane) fused silica capillary column was used. The initial temperature of the oven was 50°C (1.0 min) followed by a temperature increase of 8.5°C/min to a final temperature of

320°C. The solvent delay was 5.0 min to avoid the detection of the solvent peak and to protect the detector. The total running time was 32.8 min. The electronic pressure control device provided a pressure of 0.48 atm for the helium carrier gas (3.1 atm) throughout the entire run. This corresponded to a mobile phase flow rate of 1.0 mL/min and a linear velocity of 36.0 cm/sec. These pressure and temperature programs provided the optimum resolution for the compound peaks. The MSD transfer line and injector temperatures were 280 and 250°C, respectively. A tapered deactivated injector liner (HP part no. 5181-3316) was used for all the sample injections. Data acquisition and analyses were accomplished using a Gateway 2000 P5-90 equipped with HP Chem Station software. To identify the peaks of interest, ion chromatograms were analyzed with the "extract ion chromatogram" capability of the software. With this feature, the

retention time, mass, and fragmentation patterns for each compound were compared to the theoretical values for each compound (Table I).

Data treatment

To calculate the concentration of the PAHs in the extracts, the response factor for each of the PAHs was first calculated from the calibration curves (PAH standards at 2.5, 5.0, 10.0, 25.0, and 50.0 ng/ μ L). Using these data, the concentration of each PAH in the extract was determined. The extraction yields for SFE and the extractions using the binary mixtures were determined by assuming that the amount extracted by Soxhlet corresponded to 100% yield.

To determine if the extraction yields under various conditions were statistically different at the 95% confidence level, an analysis of variance (ANOVA) was done using SYSTAT (Evanston, IL) software. Using ANOVA, the effects on extraction yields of temperature and fluid composition (for the SFE-CO₂ and binary mixture extractions); temperature, modifier volume, and modifier identity (for the direct modified SFE); and fluid composition and matrix identity were determined.

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Results and Discussion

Surrogate quantitation

The carbazole surrogate was used to account for sample loss during the collection and concentration steps for the extractions. For the Soxhlet extractions, the concentration step (lowering the liquid volume by blowing dry N₂ over the sample) was the only possible source of sample loss because the collection step is similar to a reflux, in which no sample can be lost due to evaporation because the trapping is very efficient. The average recovery for the concentration step of the Soxhlet extractions was 105% (RSD = 5%). The concentration step therefore did not measurably reduce the extraction yields.

For the SFE-CO₂, BME, and direct modified SFE, the extraction recoveries may be lower because of the collection step. During this collection step, the extraction solvent flows into methylene chloride at a rate of 0.4 mL/min. The recovery of the surrogate was monitored when the extraction solvent was at 50, 75, and 100°C for the SFE-CO₂ and the BME conditions, while, for the direct modifier SFE conditions, surrogate recovery was monitored at 75 and 100°C. Under all the conditions studied, the temperature of the extraction solvent had no effect on the recovery of the surrogate. The average surrogate

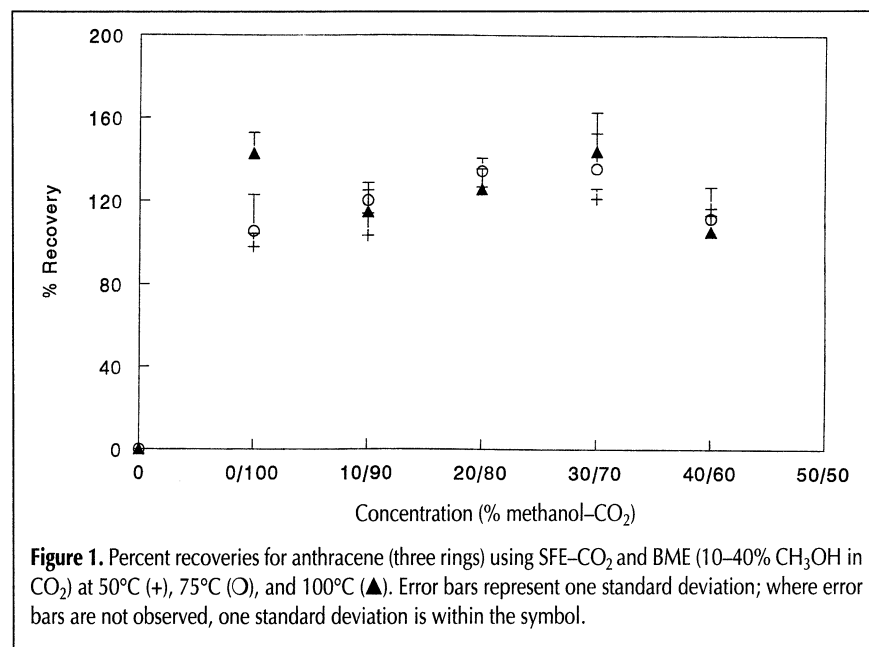


Figure 1. Percent recoveries for anthracene (three rings) using SFE-CO₂ and BME (10–40% CH₃OH in CO₂) at 50°C (+), 75°C (O), and 100°C (▲). Error bars represent one standard deviation; where error bars are not observed, one standard deviation is within the symbol.

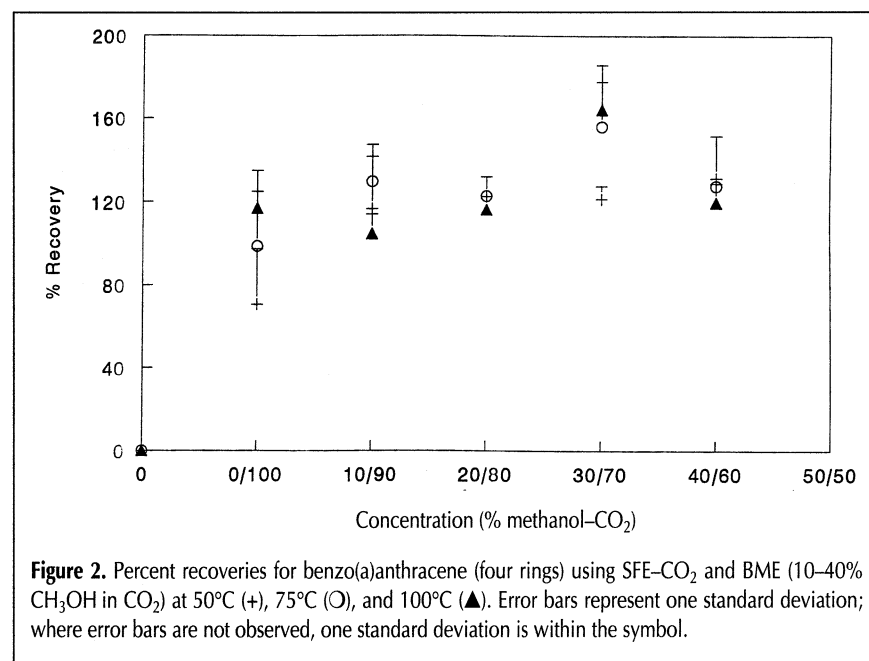


Figure 2. Percent recoveries for benzo(a)anthracene (four rings) using SFE-CO₂ and BME (10–40% CH₃OH in CO₂) at 50°C (+), 75°C (O), and 100°C (▲). Error bars represent one standard deviation; where error bars are not observed, one standard deviation is within the symbol.

recovery for SFE-CO₂ was 73% (RSD = 4%); for direct modified SFE, it was 72% (RSD = 2%); and for BME, it was 74% (RSD = 3%). As expected, the yields of the surrogate were lower than those for the Soxhlet extractions. However, as illustrated later, the extraction yields using methanol-CO₂ mixtures at optimum conditions were markedly greater than those obtained by Soxhlet, except for naphthalene and acenaphthylene (the most volatile PAHs studied).

Soxhlet extractions

Soxhlet extractions were performed for comparison between the results of the SFE-CO₂, direct modified SFE, and BME experiments. The results from Soxhlet extractions were taken as a 100% yield for each compound. For the chemistry building dust, the Soxhlet extractions reached a maximum after 4 h of

extraction. The average PAH recovery from 0–4 h was 96% (RSD = 1%). The 24-h overall recovery was taken as a 100% yield. For the fractions from 4 to 24 h, only 4% PAH recovery was obtained with an RSD of 22%. However, for the dust from the dormitory to reach the maximum extraction recovery, a 24-h extraction was needed. For a 0–8-h extraction time, a recovery of 84% (RSD = 0.2%) was found, and for 8–24 h, the recovery was 16% (RSD = 2%). As mentioned earlier, the dormitory dust was expected to be more retentive than the dust from the chemistry building because of the higher organic and water content found in the dormitory dust. Table I shows the quantity of each PAH extracted by Soxhlet and the precision obtained for each extraction. Even for the Soxhlet extraction, the RSDs were high.

Extractions of dust from the chemistry building

Analysis of data

To simplify the analyses of trends in the recoveries for and the behavior of the 16 PAHs, these compounds were divided according to the number of rings in the molecule. The PAHs for the house dust extractions were divided into the following four groups: (a) two to three rings (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene), (b) four rings (fluoranthene, pyrene, benzo[a]anthracene, and chrysene), (c) five rings (benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, and dibenz[a,h]anthracene), and (d) six rings (indeno[1,2,3-cd]pyrene and benzo[ghi]perylene). Data for a different representative compound of each group are shown in Figures 1–4 and Table II.

Compounds with two to three rings

For the extractions using SFE-CO₂ and BME (Figure 1 and Table II), all six compounds had the same optimum extraction conditions: 30% methanol-CO₂ and 100°C. For the two-ring compound (naphthalene) and acenaphthylene (three rings), the optimum recoveries were 97% and 61%, respectively. However, for the other four three-ring compounds, the optimum extraction conditions provided yields greater than 100% when compared with Soxhlet results. For example, under these conditions, the extraction yield for anthracene is 146 ± 1. Naphthalene and acenaphthylene are the most volatile of all the PAHs studied; vaporization during the collection and concentration steps may have caused the lower yields for these two compounds (15,24). Another possible cause of diminished yields is degradation. Acenaphthylene degrades when adsorbed to many surfaces. In some cases,

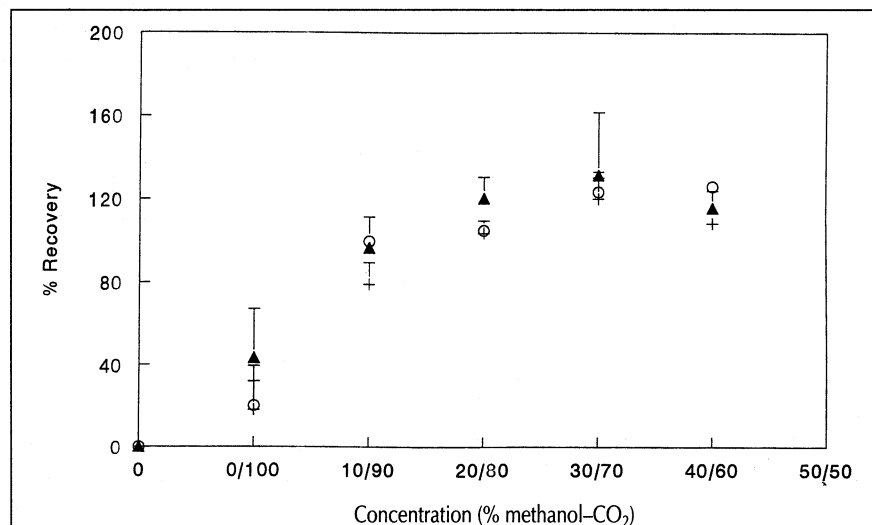


Figure 3. Percent recoveries for benzo(a)pyrene (five rings) using SFE-CO₂ and BME (10–40% CH₃OH in CO₂) at 50°C (+), 75°C (O), and 100°C (▲). Error bars represent one standard deviation; where error bars are not observed, one standard deviation is within the symbol.

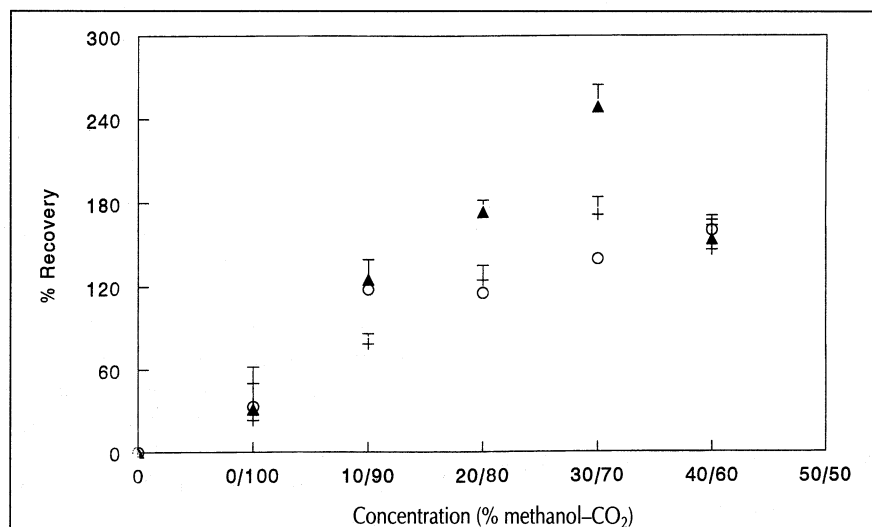


Figure 4. Percent recoveries for indeno(1,2,3-cd)pyrene (six rings) using SFE-CO₂ and BME (10–40% CH₃OH in CO₂) at 50°C (+), 75°C (O), and 100°C (▲). Error bars represent one standard deviation; where error bars are not observed, one standard deviation is within the symbol.

the degradation is so severe that its presence is no longer detectable (25, D.V. Kenny and S.V. Olesik. Extraction of coal fly ashes: Evaluation of extraction methodologies SFE, modified SFE, enhanced fluidity solvents, and ASE, unpublished).

By ANOVA, fluid composition and temperature were found to be statistically significant factors which affect the extraction recoveries. Increasing proportions of methanol increased the extraction yield up to a limiting proportion of 30% methanol-CO₂. Increased temperatures also increased the extraction yield over the entire temperature range studied.

The extraction yields of the two- and three-ring compounds were not improved by the direct addition of (100 or 200 µL) methanol or water to the dust. The extraction yields that were found for the direct addition of modifiers were approximately the same as those for SFE-CO₂, and these were markedly lower than those found with the methanol-CO₂ mixtures. According to the ANOVA results, the variation in extraction temperature

or the amount of modifier added to the matrix had no significant effect on the extraction recovery for these PAHs.

Pairwise comparison (*t*-test, 95% confidence level) of the extraction yields for the optimum extraction conditions (30% methanol-CO₂ at 100°C) and those for the next best conditions (30% methanol-CO₂ at 75°C and 100% CO₂ at 100°C) indicated no statistical difference between the yields. Therefore, for the extraction of two- and three-ring PAHs from house dust, either adding methanol to CO₂ or increasing the temperature to at least 100°C was effective in achieving high extraction yields.

Compounds with four rings

For the SFE-CO₂ and BME extractions, the extraction yields for all four compounds (fluoranthene, pyrene, benzo[a]anthracene, and chrysene) were greater than 100% (124–164%) when compared with Soxhlet extractions. The ANOVA results

Table II. Summary of the Recoveries for the Chemistry Building Dust at All the Extraction Conditions Used

Condition	Naphthalene (two rings)	Phenanthrene (three rings)	Chrysene (four rings)	Dibenz(a,h)anthracene (five rings)	Benzo(ghi)perylene (six rings)
SFE-CO ₂					
50°C	51 ± 9 (17)	98 ± 6 (6)	54 ± 16 (29)	54 ± 10 (19)	21 ± 5 (22)
75°C	57 ± 14 (25)	106 ± 18 (17)	73 ± 22 (30)	64 ± 13 (21)	29 ± 8 (27)
100°C	70 ± 6 (9)	143 ± 14 (10)	104 ± 26 (25)	61 ± 2 (4)	27 ± 1 (2)
10% CH ₃ OH					
50°C	67 ± 11 (17)	103 ± 11 (11)	91 ± 7 (8)	102 ± 7 (7)	71 ± 4 (6)
75°C	72 ± 19 (27)	120 ± 10 (8)	119 ± 36 (30)	145 ± 35 (24)	116 ± 35 (30)
100°C	85 ± 5 (6)	115 ± 12 (10)	96 ± 12 (12)	131 ± 20 (15)	121 ± 15 (12)
20% CH ₃ OH					
50°C	40 ± 12 (29)	127 ± 5 (4)	111 ± 7 (6)	135 ± 23 (17)	125 ± 15 (12)
75°C	59 ± 2 (3)	135 ± 8 (6)	116 ± 3 (3)	163 ± 29 (18)	108 ± 24 (22)
100°C	68 ± 7 (11)	126 ± 13 (10)	109 ± 5 (5)	136 ± 11 (8)	178 ± 9 (5)
30% CH ₃ OH					
50°C	55 ± 7 (13)	121 ± 6 (5)	118 ± 19 (16)	153 ± 14 (9)	179 ± 23 (13)
75°C	54 ± 4 (7)	136 ± 37 (27)	127 ± 32 (25)	159 ± 25 (16)	125 ± 15 (12)
100°C	97 ± 18 (19)	144 ± 13 (9)	123 ± 6 (5)	241 ± 43 (18)	205 ± 21 (10)
40% CH ₃ OH					
50°C	45 ± 3 (7)	117 ± 12 (10)	113 ± 20 (18)	156 ± 42 (27)	155 ± 42 (27)
75°C	53 ± 1 (2)	112 ± 1 (1)	110 ± 1 (1)	173 ± 7 (4)	155 ± 22 (16)
100°C	67 ± 4 (6)	106 ± 8 (8)	104 ± 7 (7)	139 ± 14 (10)	153 ± 15 (10)
100 µL CH ₃ OH					
75°C	66 ± 1 (1)	102 ± 9 (9)	86 ± 20 (23)	40 ± 12 (29)	22 ± 4 (20)
100°C	48 ± 12 (26)	99 ± 12 (12)	98 ± 16 (16)	33 ± 4 (12)	15 ± 4 (27)
200 µL CH ₃ OH					
75°C	58 ± 7 (12)	91 ± 12 (13)	68 ± 14 (21)	34 ± 4 (13)	26 ± 7 (26)
100°C	49 ± 13 (27)	114 ± 8 (7)	82 ± 24 (29)	34 ± 5 (16)	15 ± 3 (19)
100 µL H ₂ O					
75°C	39 ± 7 (18)	86 ± 11 (13)	109 ± 12 (11)	65 ± 1 (1)	26 ± 1 (3)
100°C	41 ± 7 (16)	83 ± 2 (2)	86 ± 24 (28)	29 ± 8 (29)	13 ± 2 (19)

* The numbers in parentheses are the %RSDs, and the number of rings refers to rings in the molecule.

indicated that increasing temperature and adding methanol both improved the extraction yields. The optimum extraction condition for all four compounds could be reached either by adding methanol or by increasing the temperature to 100°C with 100% CO₂.

The direct modified SFE experiments (Table II) showed no improvement over SFE-CO₂; the extraction yields using the direct addition of modifiers were also lower than those observed using premixed methanol-CO₂. The ANOVA results showed that neither the variation in extraction temperature or the amount of modifier added to the matrix had any significant effect on the extraction recovery for these PAHs.

Like the two- and three-ring compounds, a pairwise comparison (*t*-test, 95% confidence interval) of the three optimum recoveries (30% methanol-CO₂ at 100°C and 75°C and 100% CO₂ at 100°C) for the four-ring compounds showed the same results as for the three-ring compounds. No significant differences were found between the three conditions that gave the highest extraction yields, which were most often 30% methanol-CO₂ at 100°C, 30% methanol-CO₂ at 75°C, and 100% CO₂ at 100°C.

Compounds with five rings

These compounds are benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, and dibenz(a,h)anthracene. For all the compounds, a common optimum extraction condition was found (30% methanol, 70% CO₂ at 100 °C), and for this mixture composition, all the extraction recoveries were higher than the results from Soxhlet extractions (132–241%). When CO₂ was used as the extraction solvent, the recoveries never reached 100% relative to Soxhlet. The optimum SFE-CO₂ yields for benzo(b)fluoranthene and benzo(k)fluoranthene, benzo(a)pyrene, and dibenz(a,h)anthracene were 68%, 43%, and 64%, respectively; when 30% methanol and 70% CO₂ were used at 100°C, the yields were 159%, 132%, and 241%, respectively.

The ANOVA results indicated that the addition of methanol

significantly improved the extraction yields for all four compounds. Temperature variation was not found to be statistically significant over the extraction conditions studied for these four compounds. The optimum extraction condition for all four compounds involved using either a 30 or 40% methanol-CO₂ mixture at 75–100°C. Pairwise comparison (*t*-test, 95% confidence interval) showed that the extraction recoveries over this range of extraction conditions (30–40% methanol-CO₂) were statistically the same for each of the five-ring compounds.

In the studies of the direct addition of modifier to the matrix, the addition of 100 µL water at 100°C was the optimum extraction condition for benzo(b)fluoranthene and benzo(k)fluoranthene, and 100 µL water at 75°C for benzo(a)pyrene and dibenz(a,h)anthracene. The optimum recoveries under these conditions were between 59 and 90%, relative to the Soxhlet extractions, which were markedly lower than those observed with methanol-CO₂ mixtures. ANOVA results indicated that the variation in extraction temperature or the amount of modifier added directly to the dust had no significant effect on the extraction recovery for these PAHs.

Compounds with six rings

For the SFE-CO₂ and BME, the optimum extraction condition for these two compounds (benzo[ghi]perylene and indeno[1,2,3-cd]pyrene) was 30% methanol-CO₂ at 100°C. Pairwise comparison (*t*-test, 95% confidence interval) between the extraction yields for this condition and the next best extraction yields indicated that 30% methanol-CO₂ was the true optimum condition. The extraction recoveries for each were more than 200%, relative to Soxhlet extraction (205% for benzo[ghi]perylene and 249% for indeno[1,2,3-cd]pyrene). For both compounds, the ANOVA results indicated that both increased temperature and increased methanol content significantly improved the extraction recoveries.

For the direct modified SFE (Table II), optimum recoveries were found with the direct addition of 100 µL water at 75°C;

Table III. Extraction Yields for the Dormitory Dust*

Compound	100% CO ₂ 100°C	10:90% methanol-CO ₂ 50°C	10:90% methanol-CO ₂ 100°C
Naphthalene	71 ± 4 (23)	112 ± 7 (11)	106 ± 1 (1)
Acenaphthylene	3 ± 1 (15)	14 ± 9 (26)	14 ± 1 (11)
Acenaphthene	80 ± 12 (11)	120 ± 3 (4)	102 ± 1 (2)
Fluorene	80 ± 7 (9)	120 ± 5 (8)	109 ± 1 (1)
Phenanthrene	89 ± 7 (12)	123 ± 4 (7)	115 ± 1 (1)
Anthracene	144 ± 8 (15)	89 ± 15 (26)	90 ± 3 (6)
Fluoranthene	84 ± 11 (18)	98 ± 2 (3)	99 ± 4 (7)
Pyrene	77 ± 19 (27)	89 ± 4 (5)	93 ± 3 (4)
Benzo(a)anthracene	85 ± 5 (5)	86 ± 2 (3)	110 ± 12 (18)
Chrysene	100 ± 7 (12)	107 ± 19 (27)	118 ± 4 (5)
Benzo(b) and (k)fluoranthene	283 ± 1 (1)	142 ± 2 (3)	271 ± 2 (3)
Benzo(a)pyrene	122 ± 6 (10)	103 ± 2 (3)	213 ± 1 (1)
Dibenz(a,h)anthracene	38 ± 10 (25)	39 ± 5 (8)	93 ± 9 (14)
Indeno(1,2,3-cd)pyrene	39 ± 3 (6)	50 ± 7 (11)	106 ± 3 (4)
Benzo(ghi)perylene	27 ± 2 (3)	39 ± 7 (11)	64 ± 15 (30)

* Numbers in parentheses are %RSDs.

however, the extraction yields were low (37% for indeno[1,2,3-cd]pyrene and 26% for benzo[ghi]perylene, relative to Soxhlet). ANOVA results indicated that, for these two compounds and direct modifier addition only, temperature variation was statistically significant.

Extractions of house dust collected from a different environment

As mentioned before, the properties of the dormitory dust were different from those of the dust collected from the chemistry building area. The organic content was much higher (48%) in the dormitory dust; therefore, longer Soxhlet extractions were needed to completely extract the compounds. Also, with this matrix, only 100% CO₂ and 10% methanol-CO₂ were used for the extractions because, when the 20, 30, and 40% methanol binary mixtures were used, the flow restrictor plugged constantly, regardless of the amount of dust sample (0.5 or 1.0 g) and sand used. Particles that looked similar to the dust matrix itself were observed in the collection solution.

The extracts were analyzed by GC-MS as before, using the same parameters and conditions. Table III shows the recoveries for these extractions. Again, the addition of methanol to the CO₂ improved the recoveries, particularly for the high molecular weight PAHs. For example, the extraction yield for dibenz(a,h)anthracene increased from 38% for SFE with 100% CO₂ at 100°C to 93% for 10% methanol-CO₂ at 100°C. For six of the 16 compounds, 10% methanol-CO₂ at 100°C was the optimum extraction condition; for four compounds, the optimum extraction condition was 10% methanol-CO₂ at 50°C, for two compounds the optimum extraction condition was CO₂ at 100°C, and three compounds (fluoranthene, pyrene, and chrysene, three of the four-ring compounds studied) were extracted to the same extent under all extraction conditions studied as determined by pairwise comparison (*t*-test, 95% confidence interval) of the extraction yields. Acenaphthylene did not extract well under any of the conditions studied. ANOVA at the 95% confidence level was used to characterize the importance of the fluid composition on observed extraction yields. The composition of the fluid (amount of methanol added) also significantly affected the observed extraction yield, especially for the higher molecular weight PAHs.

Conclusion

For most compounds, extractions with methanol-CO₂ mixtures (both for supercritical and enhanced-fluidity liquids) were found to be the best choice for extraction conditions, over SFE-CO₂ and direct modified SFE (Table II). For the high molecular weight PAHs, the extraction recoveries from the binary mixture extraction were at least a factor of 10 larger than when SFE-CO₂ was used. The state of the extraction fluid did not matter because enhanced-fluidity liquids extracted as fast as supercritical fluids, and the solvent strength improved with the increase in the methanol composition.

Increasing temperature improved the extraction yields for all PAHs studied with the exception of the five-ring PAHs. Previously, Langenfeld et al. (14) reported that, in order to have

yields of 100% for low molecular weight PAHs, high temperatures (200°C) were needed, but even at 200°C, the SFE-CO₂ recoveries for the high molecular weight PAHs (molecular weights of 276 and 278) were still below 30%.

From the results described above, the limiting step for the extraction of PAHs from house dust seems to be the desorption step. Sometimes low recoveries are obtained using SFE-CO₂ because the low solvent strength of CO₂ does not provide enough interaction energy to desorb the analyte. Increasing the extraction temperature and solvent strength decreases the activation energy, which enhances the desorption process.

Unlike numerous previous studies, the direct addition of modified SFE (Table II) was not the best choice to obtain good extraction yields. For the house dust extractions, direct modified SFE showed no improvement over SFE-CO₂. This corresponds with that found in two previous studies (1,15). When the results for SFE-CO₂, direct modified SFE, and BME were compared, the recoveries for the first two techniques were always lower than those from BME, particularly for the high molecular weight compounds.

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