

Extraction of Lignite Coal Fly Ash for Polynuclear Aromatic Hydrocarbons: Modified and Unmodified Supercritical Fluid Extraction, Enhanced-Fluidity Solvents, and Accelerated Solvent Extraction

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Abstract

A comparison among modified and unmodified supercritical fluid extraction (SFE), enhanced-fluidity liquid extraction, and accelerated solvent extraction (ASE) techniques was made for the extraction of polynuclear aromatic hydrocarbons (PAHs) from an aged, spiked lignite coal fly ash. All of the attempted extraction conditions allowed the extraction of the PAHs to some degree, but no single extraction technique proved to be superior for all of the PAHs used. Three groups of PAHs with similar extraction efficiencies were identified. The group with the lowest molecular weights was best recovered using a 90% CO₂-10% methanol mixture at 70°C and 238 atm. The group of medium-molecular-weight PAHs was recovered equally well using any of three extraction conditions: SFE (100% CO₂, 90°C, and 238 atm), enhanced-fluidity liquid mixture (60% CO₂-40% methanol, 70°C, and 238 atm), and a methanol ASE mixture. The group of high-molecular-weight PAHs seemed to be equally well recovered with all of the attempted extraction conditions, but the enhanced-fluidity conditions (60% CO₂-40% methanol, 70°C, and 238 atm) had extraction recoveries (> 85%) with the lowest standard deviations (\approx 5%).

Introduction

The rate-limiting step in analytical procedures is often the sample preparation step. The analysis of environmental samples for trace components involves extraction from the bulk matrix followed by concentration of the extract so that an analytical instrument can detect the species of interest. In the case of the extraction of organic species such as polynuclear aromatic hydrocarbons (PAHs) from environmental solids, the extraction methods of choice have traditionally been Soxhlet extraction and/or sonication using a variety of liquid solvents (1-3). These traditional extraction techniques usually take many hours to perform and use large volumes of solvent that must be evaporated in the concentration step.

In the past few years, several new extraction procedures have been investigated as replacements for the traditional Soxhlet and

sonication procedures. These methods include the use of supercritical fluids with a variety of solvents (CO₂, N₂O; ethane, pentane, and ammonia) (4-7), modified supercritical fluids (usually supercritical CO₂ with 1-10% organic solvent) (8-11), enhanced-fluidity liquid solvents (liquid organic solvent with liquid CO₂ as the "modifier") (12-15), and accelerated solvent extraction (ASE) (organic solvents such as methylene chloride under elevated pressure and temperature) (16-19).

Once optimized, all of these extraction procedures take less time than the traditional methods. In the case of supercritical fluids, the selectivity of an extraction can be "tuned" by changing the density of the extraction fluid as well as by the use of polar organic modifiers (20). Supercritical fluid extraction (SFE), modified SFE, and enhanced-fluidity liquid extraction (EFE) are not universal extraction procedures. Often the temperature and pressure conditions need to be optimized for each type of analyte and matrix under study.

A number of researchers have investigated the extraction of PAHs from coal fly ashes due to the extensive use of coal as a fuel for power production and the carcinogenicity of some PAHs. Soxhlet and ultrasonic extraction techniques were the extraction methods used in these studies (21-28). The PAHs that were studied ranged in size from naphthalene to benzo[*g,h,i*]perylene; in most of the studies, the efforts were concentrated on the recovery of benzo[*a*]pyrene (due to its known carcinogenicity). The solvents most often used in these studies were methylene chloride, benzene, and toluene. Extraction efficiencies for the PAHs from the fly ashes ranged from 25 to 90% depending on the individual PAH and fly ash matrix. In general, the PAHs with higher molecular weights showed lower recoveries than those with lower molecular weights.

These same Soxhlet and ultrasonic extraction techniques were also used to study the interactions of individual PAHs with fly ash matrices (29-35). In these studies, it was found that the carbon fraction of the fly ash (versus the mineral or magnetic fraction) was responsible for most of the adsorption of the PAHs. Fly ashes that have low carbon fractions may still adsorb vapor phase PAHs in the power plant stack, but these PAHs were found to be more susceptible to degradation because they were not bound as strongly to the matrix.

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SFE using CO₂ or isobutane was investigated for the extraction of PAHs from coal fly ash (6). In this work, pyrene was deposited on the particles via vapor deposition (7.2 mg/g) and extracted from the carbonaceous fraction of a fly ash (67% C) using ultrasonic, Soxhlet, and SFE techniques. The SFE techniques using CO₂ or isobutane provided extraction recoveries virtually identical to those obtained using ultrasonic or Soxhlet extraction techniques, yielding extraction efficiencies from 62 to 68%. These semiquantitative recoveries (< 80%) may not properly represent the expected results from the studied techniques. The high carbon content of the fly ash provides very adsorptive surfaces, and the vapor deposition spiking procedure mimics the vapor deposition of "native" samples; however, the very high spiking concentration may prevent total matrix-analyte interactions (36). Thus a positive bias may have been introduced in the determined extraction efficiencies, no matter which extraction technique was used.

In another study, Hawthorne and Miller (37) investigated the SFE of PAHs from different environmental solids, including a fly ash sample. In their study, the fly ash was spiked with *d*₁₀-phenanthrene, *d*₁₀-pyrene, and *d*₁₂-perylene by suspending 2-g samples in 10 mL of methylene chloride and adding the appropriate amount of deuterated spike, then allowing the solvent to evaporate overnight. For two of the three deuterated PAHs, a mixture of supercritical N₂O–5% methanol provided better recoveries than those obtained from a 4-h sonication or an 8-h Soxhlet extraction using either benzene or methylene chloride. For example, *d*₁₀-phenanthrene had yields of 102% for SFE versus 60% for an 8-h Soxhlet extraction, and *d*₁₀-pyrene had yields of 74% for SFE versus 71% for an 8-h Soxhlet extraction. Liquid extractions using methylene chloride or benzene as solvents had higher recoveries for *d*₁₂-perylene (the PAH with the highest molecular weight studied) than any of the SFE techniques used (44% yield for SFE versus 69% yield for an 8-h Soxhlet extraction). The recoveries of the spiked PAHs decreased as the molecular weight of the PAH increased in all of the SFE extractions, showing a molecular weight dependency on the extraction efficiency.

In the study presented here, a lignite coal fly ash (low-carbon fly ash) was used to compare Soxhlet, SFE, EFE, and ASE techniques for the desorption of a number of PAHs. A 10-μg/g spiking level was chosen to ensure that the analytes were interacting with the fly ash matrix and that the extraction conditions were disrupting the analyte-matrix interactions and not the analyte-analyte interactions that occur with higher concentration spikes.

Experimental

Description of fly ash

The lignite coal fly ash was collected from the electrostatic precipitator of the Coal Creek Station Unit No. 1 in Underwood, North Dakota (38). The lignite fly ash had a surface area of 0.453 m²/g and a very low percentage of carbon (0.02% by weight). The fly ash had a very low moisture content (< 0.5% by mass). Surface area measurements were made using a Metronics Flow Sorb 2300 Surface Area Analyzer (VICI Metronics, Santa Clara, CA). Carbon analyses were performed by Combustion Engineering (Lombard,

IL) using a Leco CHN 600 (Leco Instruments, St. Joseph, MI). Moisture analyses were performed using an Metrohm/Brinkman Automated Karl-Fischer Water Analyzer (Brinkman Instruments, Westbury, NY).

The majority of the fly ash particles ranged from 6 to 16 μm in diameter. Particle size analyses were performed by Combustion Engineering. Particle sizes from 45 to 210 μm were obtained by passing a sample through a series of US Standard Testing Sieves. Particle sizes from 1 to 40 μm were obtained using ASTM Method F 662 with a Coulter Electronic Particle Counter (Coulter, Hialeah, FL).

Reagents

PAH standards were prepared from commercially available test mixtures (TCL Polynuclear Aromatic Hydrocarbon Mix Catalog No. 4-8905, 2000 μg/mL [Supelco, Bellefonte, PA] and SV Calibration Mix #5, Catalog No. 31011 [Restek, Bellefonte, PA]). The PAHs contained in these mixtures were naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene, benzo[*g,h,i*]perylene, and indeno[1,2,3-*c,d*]pyrene. Four compounds were added to the collection solvent prior to extraction to act as surrogates that could provide information on the collection efficiency. The four compounds were *p*-terphenyl (Aldrich Chemical, Milwaukee, WI), *d*₁₀-anthracene, *d*₁₀-pyrene, and *d*₁₂-benzo[*a*]pyrene (Cambridge Isotope, Woburn, MA). These compounds were chosen because they represent three-, four-, and five-ring systems that mimic the PAHs under study, thereby determining if any sample loss occurred in the collection and concentration steps. A 10-μL amount of a 10 mg/mL surrogate solution prepared in cyclohexane (Burdick and Jackson, Muskegon, MI) was added to each of the collection vessels.

Six compounds from a commercially available mixture were used as internal standards for the gas chromatographic-mass spectrometric (GC-MS) analyses: *d*₄-1,4-dichlorobenzene, *d*₈-naphthalene, *d*₁₀-acenaphthene, *d*₁₀-phenanthrene, *d*₁₂-chrysene, and *d*₁₂-perylene (Semivolatiles Internal Standard Mix, Catalog No. 4-8902, 2000 μg/mL [Supelco]).

SFC-SFE-grade CO₂ (> 99.99%) (Air Products, Allentown, PA) was used for the SFE and EFE. Methanol for the modified SFE, EFE, and ASE was Baker Analyzed grade (100%) (Baker Chemical, Phillipsburg, NJ). Methylene chloride was used as the collection solvent in the collection vials and as the extractant in the ASE experiments (High Purity grade, 99.99% [Burdick and Jackson]). Toluene used in the ASE experiments was GR grade (99.99%) (EM Science, Gibbstown, NJ).

Spiking procedure

In order to have a known amount of analyte on the fly ash and to make comparisons among all of the extraction procedures (including Soxhlet), the fly ash was spiked with a known amount of PAHs by the following procedure. A known amount of fly ash was placed in an amber bottle that had been rinsed with methylene chloride and allowed to air-dry. The ash samples were soaked with methylene chloride so that the solvent level in the bottle was a few centimeters above the level of the fly ash. Using the com-

mercially available standard PAH mix, the appropriate amount of standard was spiked on top of the solvent to produce a 10- $\mu\text{g/g}$ sample. The ash-solvent mixture was stirred, and the bottle was closed and then allowed to equilibrate overnight. After overnight equilibration, the solvent was evaporated under a gentle stream of nitrogen. The ash was allowed to equilibrate further under dry conditions inside the bottle for a period of no less than two weeks; the bottles were shaken once every day during the equilibration period. This minimum two-week period allowed the analytes to be fully incorporated into the pores of the matrix, thus producing a matrix that emulated the analytes in a native sample (39).

Soxhlet extractions

All Soxhlet extractions were performed with 0.5 g of sample for 16 h using 400 mL of methylene chloride with a cycle time of approximately 10–15 min. After the extractions were completed, the surrogate solution was added to the extracts. The extracts were then filtered through quartz fiber filters (Fisher Scientific, Pittsburgh, PA) and concentrated using a Kaderna-Danish apparatus to a final extract volume of 1 mL where the internal standard was added. The samples were then stored at -4°C until the time of analysis.

Extraction apparatus

All non-Soxhlet extractions were performed using the same extraction apparatus, Isco model 260D Syringe Pumps (Isco, Lincoln, NE) attached to an Isco model 210 extractor. The solvent flow rate was controlled by a restrictor made of fused-silica capillary with an inner diameter of either 30 or 50 μm , cut to the appropriate length to provide a desired flow rate (0.4–1.0 mL/min). A 1-g amount of fly ash was weighed and placed between two plugs of silanized glass wool in the 2.5-mL Isco extraction vessel. Dynamic extractions were used unless otherwise specified. Extracts were collected in 8-mL amber vials (Baxter Scientific, McGaw Park, IL) that contained approximately 2 mL of methylene chloride and 10 μL of the surrogate mix. Fractions were collected during the extraction procedure and stored in the amber vials. The extracts were concentrated in the amber vials by dry nitrogen slowly blowing over the solvent. The samples were concentrated in the amber vials to minimize analyte loss during transfers.

SFE conditions

Extractions with CO_2 were performed by filling the syringe pump directly from the CO_2 cylinder. The pump was then pressurized to 238 atm and allowed to equilibrate for approximately 1 h before extractions were performed. Extractions were carried out over a range of temperatures (40, 50, 60, 70, 80, 90, and 150°C).

Modified SFE and EFE conditions

The preparation of binary mixtures required the use of two syringe pumps. On a mole fraction basis, the appropriate volume of methanol was added to an empty syringe pump. The second pump contained CO_2 held at a constant pressure and temperature and was used to add the appropriate volume of CO_2 at a known density to the pump containing the methanol. The binary mixtures were then pressurized to either 238 or 408 atm (depending on the experiment). The binary mixture was allowed to equi-

brate for at least 12 h prior to use. (Methanol and CO_2 are readily miscible; however, this equilibration time has become standard practice in this research group for all pressurized mixture preparations.) Extractions were carried out at temperatures of 40, 50, 60, 70, 80, 90, and 150°C . The methanol percentages utilized were 10, 20, 40, 60, and 80 mol%.

ASE conditions

The solvents used for the ASE experiments were methylene chloride, toluene, and methanol. The solvents were prepared by filling the pump with the appropriate solvent, pressurizing the fluids to 136 atm, and allowing the solvent to equilibrate for approximately 1 h. The extraction solvent flow rate for these experiments was the same as that used for the SFE and EFE (0.4–1.0 mL/min). Methanol ASE experiments were performed at 40, 50, 60, 70, 80, 90, and 150°C . Extractions using methylene chloride were performed at 150°C . All extractions (Soxhlet and non-Soxhlet) were performed in triplicate.

Sample extract concentration

All SFE, modified SFE, EFE, and methylene chloride and methanol ASE extracts were concentrated using the same procedure. The extracts stored in the 8-mL amber vials were opened, and the solvents were evaporated to dryness using a gentle stream of nitrogen with an immediate addition of 200 μL of methylene chloride. The vials were vortexed, and an appropriate amount of internal standard mix was added. Then the vials were vortexed again, and the concentrated extracts were transferred by a Pasteur pipet to amber GC vials that contained a 200- μL glass insert (Baxter Scientific, McGaw Park, IL).

Analysis conditions

All of the extracts were analyzed using a Hewlett Packard 5970 MSD (Palo Alto, CA) with a direct transfer line from a Hewlett Packard 5890 GC. The MS was set to scan between 35 and 500 amu in 1 s. All of the extracts that were dissolved in methylene chloride (SFE, EFE, and methylene chloride and methanol ASE) were analyzed using the same conditions. The GC injection port (splitless) temperature was 280°C . The column was a Restek RTx5 (DB-5, 30 m \times 0.25-mm i.d., 0.25- μm film thickness) with a temperature program consisting of a 40°C initial column temperature that was held for 4 min, then increased at $10^{\circ}\text{C}/\text{min}$ to 300°C and held for 10 min.

Results and Discussion

Collection efficiency

As mentioned earlier, three deuterated PAHs (d_{10} -anthracene, d_{10} -pyrene, and d_{12} -benzo[a]pyrene) and *p*-terphenyl were added to the collection solvent just prior to the extraction and were used to measure collection efficiency and losses during the extract concentration steps. The collection efficiency of d_{10} -anthracene averaged $73\% \pm 13$, the recoveries for d_{10} -pyrene averaged $88\% \pm 28$, the recoveries for d_{12} -benzo[a]pyrene averaged $101\% \pm 25$, and the collection efficiency for *p*-terphenyl averaged $70\% \pm 16$ for all of the extraction conditions attempted.

Table I. Results of the Extraction Efficiencies* from the Different Extraction Procedures Used on the Lignite Coal Fly Ash

Compound	Soxhlet	CO ₂	90% CO ₂	60% CO ₂	Methanol	Methylene
		90°C, 238 atm	10% methanol 70°C, 238 atm	40% methanol 70°C, 238 atm	ASE†	chloride ASE†
Naphthalene	7 (1) [‡]	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
Acenaphthylene	50 (5)	21 (8)	47 (17)	30 (14)	28 (1)	21 (9)
Acenaphthene	59 (4)	29 (9)	56 (20)	23 (10)	31 (3)	26 (10)
Fluorene	69 (5)	60 (10)	74 (13)	50 (8)	45 (2)	42 (14)
Phenanthrene	82 (4)	105 (5)	93 (6)	96 (3)	83 (7)	73 (27)
<i>d</i> ₁₀ -Anthracene [§]		48 (3)	58 (1)	65 (5)	107 (2)	110 (3)
Anthracene	72 (5)	108 (5)	84 (6)	105 (6)	97 (10)	75 (30)
Fluoranthene	89 (3)	133 (1)	74 (5)	104 (5)	102 (9)	71 (23)
<i>d</i> ₁₀ -Pyrene [§]		48 (5)	68 (1)	67 (5)	106 (3)	118 (3)
Pyrene	87 (4)	104 (5)	70 (8)	98 (5)	102 (8)	93 (27)
Terphenyl [§]	75 (1)	50 (3)	51 (2)	66 (6)	114 (3)	114 (3)
Benzo[<i>a</i>]anthracene	83 (5)	129 (6)	93 (6)	104 (7)	96 (4)	69 (22)
Chrysene	76 (5)	62 (1)	86 (5)	112 (6)	125 (9)	81 (30)
Benzo[<i>fluoranthene</i> s]	85 (3)	102 (8)	79 (7)	120 (12)	92 (3)	71 (21)
<i>d</i> ₁₂ -Benzo[<i>a</i>]pyrene [§]		55 (2)	81 (2)	86 (4)	113 (1)	115 (3)
Benzo[<i>a</i>]pyrene	82 (3)	85 (1)	58 (6)	86 (5)	83 (2)	67 (21)
Indeno[1,2,3- <i>c,d</i>]pyrene	93 (2)	81 (4)	57 (5)	89 (2)	84 (10)	89 (31)
Dibenzo[<i>a,h</i>]anthracene	90 (4)	110 (6)	95 (12)	97 (2)	103 (10)	98 (24)
Benzo[<i>g,h,i</i>]perylene	87 (2)	100 (6)	94 (14)	98 (3)	94 (7)	93 (27)

* Recovery values corrected for surrogate recoveries.

† ASE conditions: 136 atm at 150°C.

‡ Numbers in parentheses represent one standard deviation.

§ Surrogates.

Because there was a wide range of collection efficiencies for the surrogate compounds during the triplicate runs of the same extraction procedure as well as between extraction conditions, these compounds were not only used as a measure of collection efficiency but as a means to "normalize" the recovery data to avoid equating extraction efficiency with collection efficiency. All of the data shown in the table were corrected for surrogate recovery, and the surrogate recoveries of the deuterated PAHs and *p*-terphenyl are shown as uncorrected. *d*₁₀-Anthracene was used to normalize the recoveries of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene. *d*₁₀-Pyrene was used to normalize the recoveries of fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, and the benzo[*fluoranthene*s]. *d*₁₂-Benzo[*a*]pyrene was used to normalize the recoveries of benzo[*a*]pyrene, indeno[1,2,3-*c,d*]pyrene, dibenzo[*a,h*]anthracene, and benzo[*g,h,i*]perylene.

The collection vials for the extractions at 150°C were cooled by placing them in an ice bath prior to use. For the high-temperature extractions, *d*₁₀-anthracene recoveries averaged 109%, the recoveries for *d*₁₀-pyrene averaged 112%, those for *d*₁₂-benzo[*a*]pyrene averaged 114%, and those for *p*-terphenyl averaged 114%. Each replicate set of extractions had standard deviations less than 3%. It is therefore recommended to cool the collection solvent prior to extraction to obtain higher and more reproducible collection efficiencies.

Lignite coal fly ash

During all of the extraction conditions attempted (SFE, modified SFE, EFE, and ASE), all of the PAHs (except naphthalene) were recovered to some extent from the lignite fly ash. Table I shows the results of the extraction efficiencies from a Soxhlet

extraction, two SFEs (100% CO₂ and 90% CO₂-10% methanol), an EFE (60% CO₂-40% methanol), and two ASEs (methanol and methylene chloride). The selected extraction conditions shown in Table I are representative of each technique. Naphthalene, the most volatile compound in this study, always had low recoveries. This was most likely due to volatilization during the storage-equilibration period. The low carbon content of the matrix would have low adsorption for the analyte.

Within the 16 PAHs, three subgroups showing similar extraction recoveries emerged: a group of the low-molecular-weight PAHs consisting of naphthalene, acenaphthylene, acenaphthene, and fluorene; a group of medium-molecular-weight PAHs consisting of phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, and the benzo[*b* and *k*]fluoranthenes; and a group of high-molecular-weight PAHs consisting of benzo[*a*]pyrene, indeno[1,2,3-*c,d*]pyrene, dibenzo[*a,h*]anthracene, and benzo[*g,h,i*]perylene.

The low-molecular-weight species were slightly better recovered with the Soxhlet extraction and modified SFE techniques (90% CO₂-10% methanol at 70°C and 238 atm); recoveries ranging from 47 to 74% (excluding naphthalene) were attained. The Soxhlet technique had lower standard deviations than the modified SFE technique (standard deviation of 5% for Soxhlet versus 17% for the modified SFE technique).

The medium-molecular-weight species had extraction recoveries that varied from 62 to 133%. The techniques that used 100% CO₂, 90°C, and 238 atm and 60% CO₂-40% methanol, 70°C, and 238 atm had an average recovery of 106%. The methanol ASE condition had an average recovery of 100% for the medium-molecular-weight PAHs. The Student's *t*-test also showed that

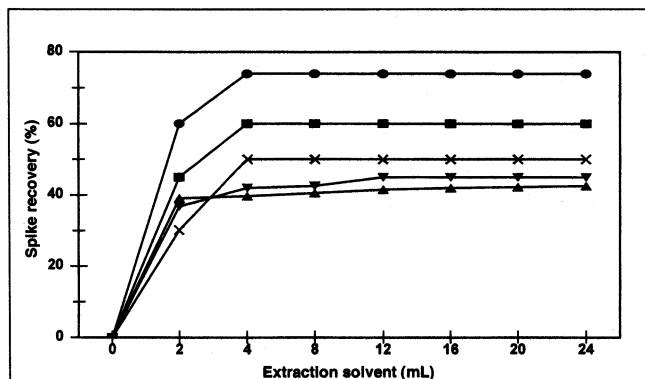


Figure 1. Extraction profiles for fluorene using (■) 100 mol% CO₂-0 mol% methanol, 90°C, and 238 atm; (●) 90 mol% CO₂-10 mol% methanol, 70°C, and 238 atm; (x) 60 mol% CO₂-40 mol% methanol, 70°C, and 238 atm; (▼) methanol ASE; and (▲) methylene chloride ASE on lignite coal fly ash.

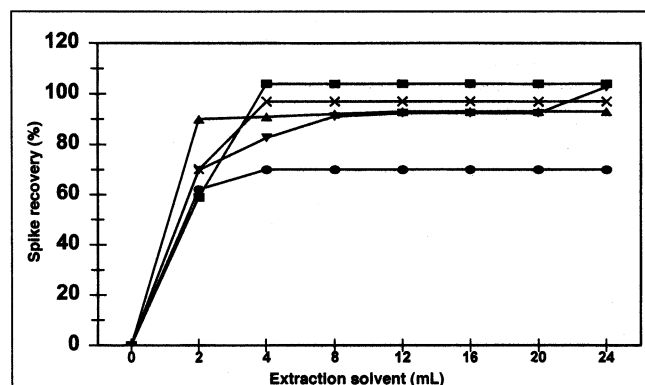


Figure 2. Extraction profiles for pyrene using (■) 100 mol% CO₂-0 mol% methanol, 90°C, and 238 atm; (●) 90 mol% CO₂-10 mol% methanol, 70°C, and 238 atm; (x) 60 mol% CO₂-40 mol% methanol, 70°C, and 238 atm; (▼) methanol ASE; and (▲) methylene chloride ASE on lignite coal fly ash.

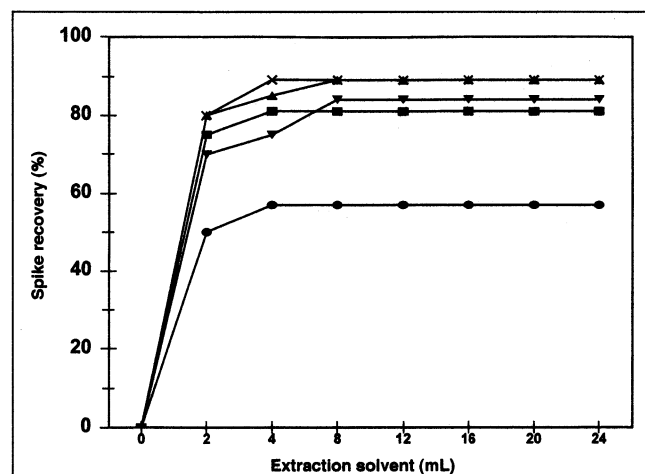


Figure 3. Extraction profiles for indeno[1,2,3-c,d]pyrene using (■) 100 mol% CO₂-0 mol% methanol, 90°C, and 238 atm; (●) 90 mol% CO₂-10 mol% methanol, 70°C, and 238 atm; (x) 60 mol% CO₂-40 mol% methanol, 70°C, and 238 atm; (▼) methanol ASE; and (▲) methylene chloride ASE on lignite coal fly ash.

there was no difference at the 95% confidence level between the results of these two extraction conditions.

The Soxhlet (90% CO₂-10% methanol, 70°C, 238 atm) and the methylene chloride ASE conditions gave overall average recoveries ranging from 76 to 82% for the medium-molecular-weight species. Using the *t*-test at a 95% confidence level, a difference was found between the results of these two sets of conditions (100% versus 80% recovery groups). No correlation could be made as to the specific extraction condition parameter (i.e., temperature, organic solvent content, etc.) that was responsible for the observed differences.

The PAHs with higher molecular weights were equally recovered with all extraction conditions. Recoveries of individual PAHs ranged from 57 to 110%, and overall recoveries for this group ranged from 76 to 94%. The *t*-test at the 95% confidence level showed that there was no statistical difference between the extraction techniques when considering the overall group recovery except for the technique using 90% CO₂-10% methanol, 70°C, and 238 atm, which had slightly lower recoveries for these high-molecular-weight species.

A two-factor analysis of variance (ANOVA) at the 95% confidence level (40) was used to compare the extraction efficiencies from the techniques shown in Table I; the first factor was used to determine if there was a difference in the recoveries of the individual PAHs, and the second factor was used to determine the difference in extraction efficiency between each set of extraction methods or conditions. The results of the first factor showed that there was indeed a difference in the recoveries of the individual PAHs, as was discussed earlier. There were three groups of PAHs with similar extraction efficiencies. The results of the second factor showed that there was a significant difference at the 95% confidence level between extraction conditions.

From the data discussed above, it was the recovery of the low- and medium-molecular-weight species that permitted differentiation between the extraction techniques, though no one technique was best for all of the PAHs used in this study.

Figures 1-3 show the percent recovery as a function of the extraction solvent volume for the extraction of fluorene, pyrene, and indeno[1,2,3-c,d]pyrene, respectively. These compounds represent low-, medium-, and high-molecular-weight PAHs, respectively, for each type of extraction condition (SFE, modified SFE, an enhanced fluid solvent, and two ASE conditions). The shapes of the curves show that the rate of extraction was similar for each method and compound; nearly all of the recoveries took place within the first 8 mL of solvent collected. These results show that the desorption from the matrix was fast, and because there was little water adsorbed onto the matrix, there was no diffusion barrier through the water layer that would have inhibited the extraction. Further, it is apparent that the PAHs were soluble in the fluids used because recoveries were good for the medium- and high-molecular-weight analytes.

Interactions between the lignite fly ash matrix and the PAHs were considered to be minimal because weaker solvents were able to desorb the analytes efficiently from the fly ash. Each of the extraction techniques used had the desorption energy required to remove the analytes from the matrix surface because the extraction efficiencies were considered to be quantitative.

Conclusion

A comparison among SFE, modified SFE, EFE, and ASE techniques was made for the extraction of PAHs from an aged, spiked lignite coal fly ash. All of the attempted extraction conditions allowed the extraction of the PAHs to some degree. In order to efficiently extract low-, medium-, and high-molecular-weight PAHs from the lignite fly ash samples used here, a multistep extraction procedure that combines SFE and EFE conditions in series may be the best choice. The low-molecular-weight species were best recovered using 90% CO₂-10% methanol, 70°C, and 238 atm as SFE extraction conditions. The medium-molecular-weight PAHs were recovered using SFE (100% CO₂, 90°C, and 238 atm), an enhanced-fluidity solvent (60% CO₂-40% methanol, 70°C, and 238 atm), and a methanol ASE. High-molecular-weight species seemed to be equally recovered using all of the extraction conditions, and the enhanced-fluidity conditions (60% CO₂-40% methanol, 70°C, and 238 atm) yielded good recoveries with the lowest standard deviations.

Overall, no correlations between general analyte recovery and solvent composition could be made. Increasing the methanol proportion did increase the recovery of particular analytes, but a universal trend did not exist. Increasing the temperature of the extraction conditions appeared to aid in the recovery of the PAHs with higher molecular weights, but there were exceptions; some low-temperature extractions recovered the high-molecular-weight PAHs as well.

Acknowledgments

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