

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

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Abstract

A comparison among supercritical fluid extraction (SFE), modified SFE, enhanced-fluidity extraction, and accelerated solvent extraction (ASE) techniques was made for the extraction of polynuclear aromatic hydrocarbons (PAHs) from an aged, spiked bituminous coal fly ash. Non-ASE extraction techniques used in this study could not recover PAHs with molecular weights greater than that of pyrene. ASE techniques using methylene chloride (with and without a static step) and toluene were able to recover most of the PAHs studied. None of the ASE techniques could quantitatively extract the low-molecular-weight PAHs from the bituminous fly ash. The medium-molecular-weight PAHs were best recovered with toluene ASE. The high-molecular-weight PAHs were best recovered with the toluene ASE technique (> 80%), but the overall precision of these measurements was low. Methylene chloride ASE with a static step recovered the high-molecular-weight PAHs with the next highest efficiency (approximately 55%) and had standard deviations less than 10% (longer extraction times [> 30 min] with the methylene chloride would increase the recoveries of these analytes.) A comparison of the results from this study with those of a previous study using lignite coal fly ash illustrates the difficulty in developing and adapting analyte-specific extraction methods for analytes that are adsorbed on different matrices.

Introduction

Extraction procedures fall into two classes, universal or specific. Universal extraction procedures such as Soxhlet extraction are very rigorous and can be used to efficiently extract a wide array of compound classes, depending on the extraction solvent used. The advantage of these systems is that very efficient extractions can be performed. The disadvantages of the universal procedures are that they require a great deal of time

and that they extract many nontarget analytes along with the target analytes. Soxhlet extractions usually require 8–24 h to efficiently extract target analytes, depending on the analytes and matrix. When a large quantity of non-target analytes is co-extracted, cleanup steps are required to concentrate and separate the target analytes from the non-target analytes. All of the above steps require additional time and require the disposal of waste solvents.

In an effort to reduce extraction times and cleanup procedures, more specific extraction techniques such as supercritical fluid extraction (SFE) and enhanced-fluidity liquid extraction (EFE) techniques have been explored. By reducing the extraction times from tens of hours to tens of minutes and by “tuning” the extraction solvents to extract the specific analytes of interest, the analyst can become more productive and efficient in providing the final results.

In developing extraction procedures that are analyte-specific, the matrix from which the analytes are to be extracted can significantly affect the extraction efficiencies. A set of extraction conditions that works well for one matrix may not work well for another matrix for the same target analytes. The analyst is then once again faced with the same disadvantages that occur in the universal extraction methods. The analyst must increase extraction times or use a more rigorous (universal) method that may require many cleanup steps before analysis of the extract.

This study on the extraction of a bituminous fly ash for polynuclear aromatic hydrocarbons (PAHs) complements previous research on the extraction of PAHs from lignite fly ash (1). In both extraction studies, the same target analytes were used, and similar extraction procedures were utilized. The primary difference between these two studies was the specific fly ashes matrices utilized. In general, fly ashes consist of spherical glass particles, irregular crystalline grains, unburned coal, and soot. Bituminous coals have a higher carbon content than the lignite; thus, the residual fly ashes usually have a higher residual carbon content. (This will depend on the specific com-

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bustor configurations and combustion conditions [2]). Differences in the extraction efficiencies between these two "similar" matrices will be shown and discussed. Implications of these results illustrate the difficulty in developing methods for a set of target analytes and applying them to dissimilar matrices.

Experimental

The bituminous coal fly ash was collected from the electrostatic precipitator of the Niles Station Boiler No. 2 in Niles, Ohio.

Reagents

All PAH standards were prepared from commercially available mixtures (TCL Polynuclear Aromatic Hydrocarbon Mix Catalog No. 4-8905, Supelco, Bellefonte, PA and SV Calibration Mix #5, Catalog No. 31011, Restek, Bellefonte, PA). The PAHs contained in these mixes 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 and as a measure of 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 to determine if any sample loss occurred due to the collection and concentration steps. A 10- μ L amount of a 10-mg/mL surrogate solution prepared in cyclohexane (Burdick and Jackson, Muskegon, MI) was used.

Six compounds from a commercially available mix 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 (Semi-volatile Internal Standard Mix, Catalog No. 4-8902, Supelco).

Extraction solvents were the same as previously described (1). Toluene used in the ASE experiments was GR-grade (99.99%, EM Science, Gibbstown, NJ). The same spiking procedure was used as reported in the lignite study (1,4). All non-Soxhlet extractions were performed using 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 either 30 or 50 μ m in inner diameter and cut to the appropriate length to provide a desired flow rate (0.4–1.0 mL/min).

ASE conditions

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 solvent flow rates for the ASE were the same as those used for the other non-Soxhlet extraction. Methanol ASE experiments were performed at 40, 50, 60, 70, 80, 90, and 150°C. Extractions using methylene chloride and toluene were performed at 150°C. All extractions (Soxhlet and non-Soxhlet) were performed in triplicate.

Sample extract concentration

All sample extracts in methylene chloride were concentrated under a gentle stream of nitrogen. Because the boiling point of toluene (111°C) prevents the rapid evaporation of the solvent at room temperature, the toluene ASE extraction samples had to be concentrated using a different procedure. The sample extracts were transferred from the amber collection vial to a 25-mL round-bottom flask. The individual collection vials were rinsed two times with methylene chloride, and the rinsates were added to the round-bottom flask. The extract was then rotovaped (Buchii Rotovap, Flawil, Switzerland) to less than 300 μ L using a water bath temperature of 45°C, a vacuum of 26.5 in. of mercury, and a rotation of 100 rpm. The extract was then transferred from the 25-mL round-bottom flask to a Chromflex (Kontes, Vineland, NJ) vial that had marked volume graduations. The round-bottom flask was rinsed two times with methylene chloride, and the rinsates were added to the Chromflex tube. The solvent was evaporated under a gentle stream of nitrogen to 200 μ L, the appropriate amount of internal standard was added, and the tube was rinsed with the extract. Then the extract was transferred using a Pasteur pipet to an amber GC vial containing a 200- μ L glass insert. The samples were then stored at –20°C in a freezer before GC-MS analysis.

Analysis conditions

When methylene chloride was used as the collection solvent (SFE, EFE, and methylene chloride and methanol ASE), the same GC conditions were used as in the previous extraction study of lignite fly ash (1). Due to the higher boiling point of toluene, the toluene ASE extracts were analyzed using a different set of conditions. First, a new set of PAH standards was prepared using toluene as the solvent. The same GC column was used with a temperature program in which the initial column temperature of 80°C was held for 4 min, increased at 10°C/min to 300°C, and then held for 10 min.

Results and Discussion

The bituminous coal fly ash had a much larger surface area (2,859 m²/g) and a much higher carbon content (15.42 wt% carbon) than the lignite fly ash used in the previous study. The majority of the fly ash particles ranged from 6 to 16 μ m.

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. These solutes were used to measure collection efficiency and

losses during the extract concentration steps as in the lignite fly ash study.

For the bituminous fly ash samples, the collection efficiency of d_{10} -anthracene averaged $69\% \pm 11$, the recoveries for d_{10} -pyrene averaged $72\% \pm 18$, those for d_{12} -benzo[*a*]pyrene averaged $85\% \pm 25$, and those for *p*-terphenyl averaged $68\% \pm 14$ under all the performed extraction conditions.

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 tables are 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 benzofluoranthenes. 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 containing the collection solvent were cooled by placing them in an ice bath prior to use for the extractions done at 150°C . For the high-temperature extractions, the collection efficiencies were 92, 99, 99, and 97% for d_{10} -anthracene, d_{10} -pyrene, d_{12} -benzo[*a*]pyrene, and *p*-terphenyl, respectively. Each replicate set of extractions had a standard deviation less than 7%. It is therefore recommended to cool the collection vessels in order to obtain higher and more reproducible collection efficiencies.

Bituminous coal fly ash

For the SFE, modified SFE, and EFE, only eight PAHs were recovered measurably; no measurable recoveries were found for the PAHs from benzo[*a*]anthracene or those with greater molecular weights. ASE extraction conditions were necessary to extract these higher molecular weight PAHs from bituminous fly ash.

Table I shows the results from several extraction conditions. The extraction efficiencies for the PAHs were compared using an extraction solvent of 40 mol% methanol–60 mol% CO_2 at 238 atm at temperatures of 60 and 150°C . The extractions at 150°C showed higher recoveries for fluorene, phenanthrene, anthracene, fluoranthene, and pyrene. All other PAHs had essentially equivalent recoveries at both temperatures. At this high methanol concentration (EFE conditions), temperature increases enhanced the recovery of the PAHs; this enhancement may have been due to an increase in the vapor pressure of the solutes, thermal disruption of the analyte–matrix interactions, or temperature-dependent solubility changes.

When 100 mol% CO_2 (no modifier) was used at 251 atm and extractions at 60 and 150°C were compared, the only PAH that showed measurable recovery was naphthalene (36%) at 150°C . The naphthalene recovery was comparable to the recoveries obtained using the 40 mol% methanol–60 mol% CO_2 extraction solvent. Therefore, an increase in temperature alone

did not increase the recoveries of the PAHs. The addition of modifier (methanol) was required to increase the extractability of the PAHs.

Extractions done at 150°C and 408 atm while varying the methanol composition of the extraction solvent showed that the methanol composition had little effect on the recovery of naphthalene, acenaphthylene, acenaphthene, fluorene, and anthracene. The extraction efficiency increased with added methanol for phenanthrene, fluoranthene, and pyrene. Although all of the PAHs were not recovered with the SFE or EFE techniques, increases in the recoveries of the selected PAHs could have been due to the methanol increasing the solvating power of the solvents and/or the increased methanol interaction with active sites on the matrix freeing the π -electrons of the PAHs bound to the silanol groups of the matrix (4). Once the temperature was raised to 150°C , increasing the pressure from 238 to 408 atm showed no improvement in extraction efficiency.

Increased extraction temperature and methanol concentration caused the largest improvement in analyte recovery. It is well-documented, however, that the PAHs under study are soluble in these fluids under the conditions used (5–10). Therefore, it appears that desorption controls the extraction efficiency and not solubility.

The bituminous coal fly ash used in these experiments had nearly 15.5% carbon, which would strongly adsorb any organic analyte. (This can be compared with National Institute for Standards and Testing [NIST] fly ash standards that have 3–5 wt% carbon [11]). The bituminous matrix along with the analyte spiking procedure used herein clearly represents a very difficult matrix to extract and depicts an almost "worst case scenario."

The difficulty in extracting the spiked analytes from the matrix validates the spiking procedure as a method that imitates a "real-world" sample. If the spiking procedure did not provide matrix–analyte interactions, the PAHs should have been easily extracted from both the lignite and bituminous fly ash matrices. Burford et al. (12) showed that a variety of spiking procedures did not have the same extraction kinetics as native samples. Their spiked samples did not show strong matrix–analyte interactions for PAHs on petroleum waste sludge, urban air particulate matter, or railroad bed soil, where the equilibration time after spiking was 14 h or less. The high-molecular-weight PAHs were very difficult to extract from the fly ashes used in this study, which illustrates that strong matrix–analyte interactions were made during the two-week equilibration period used in the spiking procedure. Only ASE conditions provided extraction recoveries equal to or higher than those found with Soxhlet extraction. Table II shows the recoveries of the PAHs from the different ASE conditions that allowed the successful extraction of all the PAHs from the bituminous coal fly ash.

As with the lignite fly ash samples (1), the same three subgroups within the 16 PAHs (low-, medium-, and high-molecular-weight species) showed similar extraction recovery patterns. The low-molecular-weight species were poorly recovered; all of the extraction procedures had recoveries of 0–70%. (Naphthalene was recovered from the bituminous fly ash due

Table I. Extraction Efficiencies from Different Extraction Procedures Used on the Bituminous Coal Fly Ash

Compound	40% MeOH*	40% MeOH*	0% MeOH*	0% MeOH*	0% MeOH*	10% MeOH*	20% MeOH*	40% MeOH*
	60°C, 238 atm	150°C, 238 atm	60°C, 251 atm	150°C, 251 atm	150°C, 408 atm	150°C, 408 atm	150°C, 408 atm	150°C, 408 atm
Naphthalene	38 (8) [†]	36 (23)	3 (2)	36 (10)	29 (1)	9 (10)	22 (21)	28 (9)
Acenaphthylene	10 (7)	23 (3)	3 (2)	3 (1)	3 (0.2)	8 (3)	7 (2)	10 (3)
Acenaphthene	8 (4)	11 (2)	2 (1)	2 (1)	2 (0.1)	3 (1)	3 (0.5)	2 (1)
Fluorene	49 (1)	65 (3)	6 (10)	9 (3)	11 (1)	27 (3)	25 (4)	23 (6)
Phenanthrene	57 (7)	111 (16)	3 (5)	7 (4)	25 (8)	81 (3)	74 (14)	84 (1)
<i>d</i> ₁₀ -Anthracene [‡]	71 (3)	60 (3)	75 (2)	76 (3)	100 (4)	88 (4)	95 (1)	92 (2)
Anthracene	15 (7)	23 (2)	0 (0)	0 (0)	0 (0)	5 (1)	4 (1)	4 (4)
Fluoranthene	13 (4)	88 (3)	0 (0)	0 (0)	4 (1)	26 (4)	29 (12)	65 (17)
<i>d</i> ₁₀ -Pyrene [‡]	72 (4)	60 (2)	83 (3)	84 (5)	107 (5)	101 (2)	107 (1)	103 (3)
Pyrene	10 (3)	62 (5)	0 (0)	0 (0)	4 (1)	21 (1)	21 (8)	53 (19)
Terphenyl [‡]	94 (4)	52 (7)	68 (6)	67 (7)	114 (5)	97 (2)	105 (1)	113 (3)
Benzo[a]anthracene	0 (0)	8 (2)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	7 (5)
Chrysene	0 (0)	10 (2)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	6 (5)
Benzo[fluoranthenes	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
<i>d</i> ₁₂ -Benzo[a]pyrene [‡]	69 (4)	68 (4)	92 (2)	91 (6)	102 (4)	95 (3)	101 (1)	95 (2)
Benzo[a]pyrene	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
Indeno[1,2,3- <i>c,d</i>]pyrene	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
Dibenzo[<i>a,h</i>]anthracene	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
Dibenzo[<i>g,h,i</i>]perylene	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)

* The solvent compositions are in mol%.
[†] Numbers in parentheses are absolute standard deviations.
[‡] Surrogates.

Table II. Extraction Efficiencies from the Different Extraction Procedures Used on the Bituminous Coal Fly Ash

Compound	Soxhlet	Methylene chloride	Methylene chloride	Toluene ASE*
		ASE*	ASE with static step*	
Naphthalene	29 (2) [†]	16 (18)	31 (1)	70 (13)
Acenaphthylene	1 (0)	7 (2)	6 (1)	5 (1)
Acenaphthene	0 (0)	1 (0)	1 (0)	1 (0)
Fluorene	22 (1)	12 (1)	10 (1)	16 (2)
Phenanthrene	57 (3)	85 (1)	80 (2)	121 (8)
<i>d</i> ₁₀ -Anthracene [‡]		116 (1)	124 (4)	80 (3)
Anthracene	5 (0)	4 (0)	5 (0)	6 (0)
Fluoranthene	61 (2)	87 (1)	93 (1)	132 (8)
<i>d</i> ₁₀ -Pyrene [‡]		124 (4)	119 (5)	84 (2)
Pyrene	52 (1)	78 (2)	71 (3)	99 (3)
Terphenyl [‡]	79 (2)	120 (2)	120 (5)	86 (2)
Benzo[a]anthracene	60 (13)	62 (2)	58 (2)	101 (2)
Chrysene	56 (2)	76 (2)	71 (3)	120 (4)
Benzo[fluoranthenes	53 (1)	56 (6)	77 (11)	110 (14)
<i>d</i> ₁₂ -Benzo[a]pyrene [‡]		122 (1)	118 (2)	97 (1)
Benzo[a]pyrene	3 (1)	15 (10)	11 (3)	5 (7)
Indeno[1,2,3- <i>c,d</i>]pyrene	27 (2)	35 (3)	55 (3)	95 (22)
Dibenzo[<i>a,h</i>]anthracene	28 (2)	39 (3)	57 (9)	108 (27)
Dibenzo[<i>g,h,i</i>]perylene	26 (2)	34 (1)	53 (2)	83 (22)

* ASE conditions: 136 atm at 150°C.
[†] Numbers in parentheses are absolute standard deviations.
[‡] Surrogates.

to the higher retentivity of the bituminous fly ash [1].) The recoveries of acenaphthylene and acenaphthene were close to zero for all extraction conditions of the bituminous fly ash. The reasons for these extremely low recoveries are discussed below.

The ASE methods recovered the medium-molecular-weight PAHs better than the Soxhlet extraction technique. Extraction efficiencies with the ASE technique ranged from 56 to 132% (except for anthracene, and the reasons for low recoveries of this analyte are discussed below). The toluene ASE conditions showed the highest overall recoveries for these analytes.

Although the high-molecular-weight species appear to have been best recovered with the toluene ASE technique (83–108%, except benzo[*a*]pyrene), the high standard deviations for the toluene ASE (> 20%) made all three ASE techniques statistically equivalent (using the Student's *t*-test with a 95% confidence interval). The methylene chloride ASE with the static step showed the most consistent recoveries (53–57%), and the largest standard deviation was only 9%.

The recoveries for acenaphthylene, anthracene, and benzo[*a*]pyrene were close to zero for all the extraction conditions used. Other researchers (13–15) showed that these particular PAHs may decompose after adsorption onto fly ashes. The extent of the decomposition also varied among fly ash types studied (16). Chuang et al. showed that these analytes can degrade on various matrices to the point where they are no longer detected (14). In the study described herein, another possible source of analyte loss was the spiking step. Evaporation or inhomogeneous sampling of the spiked fly ashes could have caused this result. Evaporative loss seems highly unlikely because these solutes were readily recovered from the lignite fly ash when using the same spiking procedure; inhomogeneous sampling is also unlikely because a large quantity of spiked bituminous fly ash was used in this study, and the extraction yields were low for these analytes. It was therefore concluded that the most likely cause of the low recoveries of these three PAHs was decomposition.

A two-way analysis of variance (ANOVA)

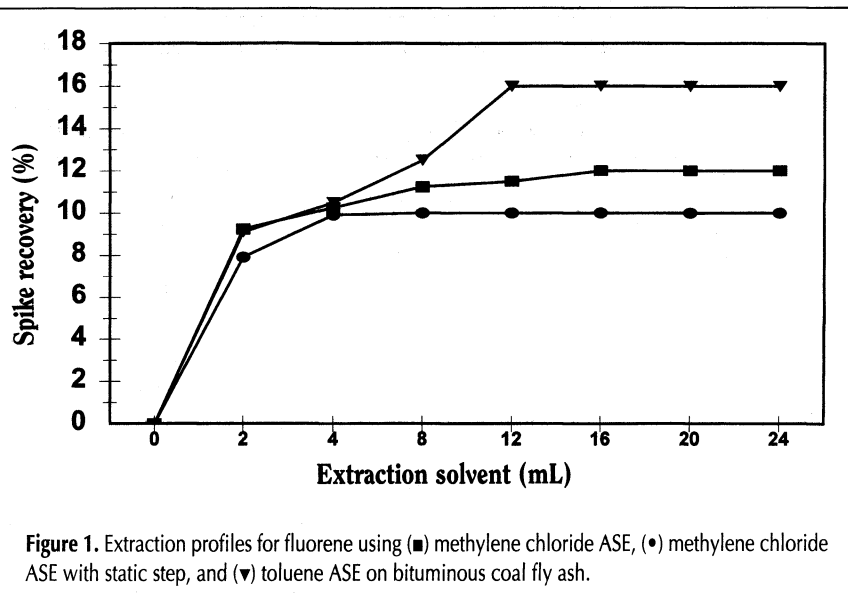


Figure 1. Extraction profiles for fluorene using (■) methylene chloride ASE, (●) methylene chloride ASE with static step, and (▼) toluene ASE on bituminous coal fly ash.

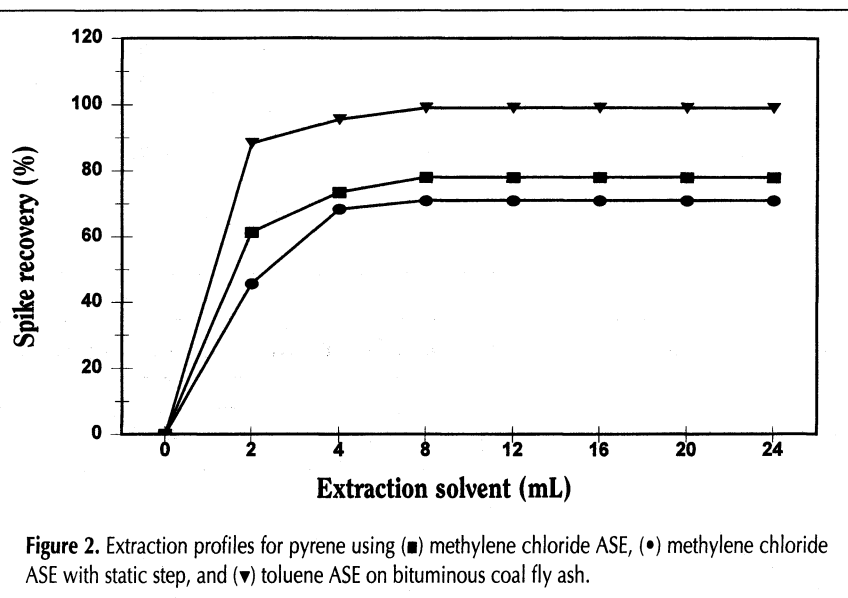


Figure 2. Extraction profiles for pyrene using (■) methylene chloride ASE, (●) methylene chloride ASE with static step, and (▼) toluene ASE on bituminous coal fly ash.

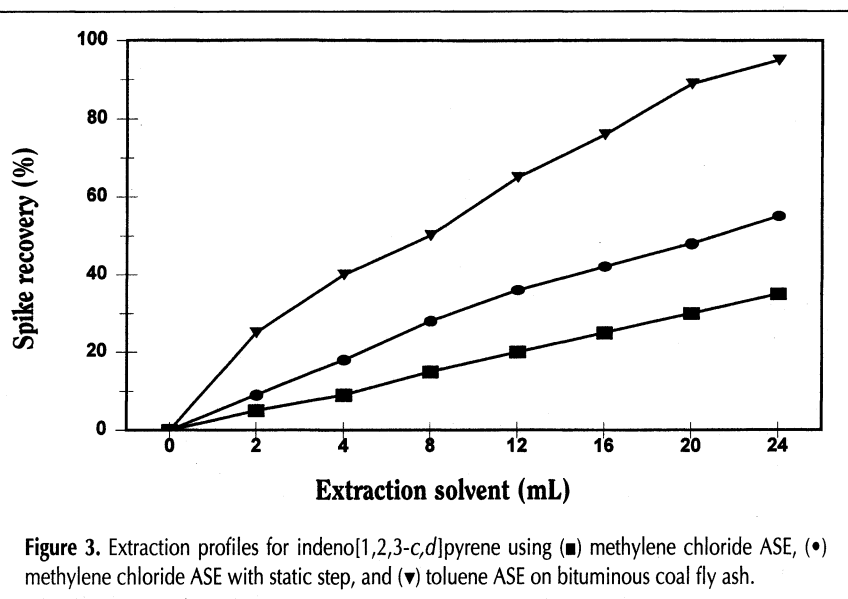


Figure 3. Extraction profiles for indeno[1,2,3-*c,d*]pyrene using (■) methylene chloride ASE, (●) methylene chloride ASE with static step, and (▼) toluene ASE on bituminous coal fly ash.

at the 95% confidence interval (17) was used to evaluate the differences in recoveries among the individual PAHs (first factor) and differences in recoveries between extraction procedures (second factor). Results showed that there was a significant difference between the recovery of all the analytes (thus trends observed for low-, medium-, and high-molecular-weight species) and that all three ASE extraction procedures were significantly better than the Soxhlet procedure for the medium- and high-molecular-weight PAHs. Using the Student's *t*-test at the 95% confidence level and comparing the overall recovery means, there was little difference among all of the ASE procedures. However, extraction with methylene chloride with a static step ASE was slightly better than the other two methods, due to the higher precision observed using the static step.

Figures 1–3 show the rate of extraction for fluorene, pyrene, and indeno[1,2,3-*c,d*]pyrene, respectively, where each represents a low-, medium-, and high-molecular-weight species for the three "best" extraction conditions from the bituminous coal fly ash as a function of extraction volume. The shapes of the curves show that, for fluorene and pyrene, all of the recoverable PAHs were extracted within the first 8 mL. Pyrene was recovered quantitatively, but fluorene was only recovered to approximately 14% of the spiked level. (The Soxhlet extraction only recovered fluorene at 22% of the spiked level.) The small slopes of the indeno[1,2,3-*c,d*]pyrene curves in Figure 3 indicate that the desorption of the analyte from the matrix was slow and was the rate-limiting step in the extraction. Longer extraction times would be necessary to quantitatively extract the higher molecular weight species from the matrix. An increase in temperature may aid in a faster extraction as well. The extraction was stopped after 24 mL (approximately 30 min), and the extract was collected. Hence, it does not represent an exhaustive extraction for each solvent.

Conclusion

Due to the difficulty in extracting the PAHs from the bituminous fly ash, the sample "spiking" procedure was shown to be acceptable for measuring extraction efficiencies. For the bituminous fly ash, the non-ASE extraction techniques could not recover any of the PAHs with molecular weights greater than pyrene. An increase in the methanol content of the extraction solvent did increase the extraction efficiency for phenanthrene, fluoranthene, and pyrene for the non-ASE techniques. Increasing the temperature to 150°C alone did not increase the extraction efficiencies.

None of the ASE techniques could quantitatively extract the low-molecular-weight PAHs from the bituminous fly ash. The medium-molecular-weight PAHs were best recovered with toluene ASE. The high-molecular-weight PAHs were best recovered with the toluene ASE technique (> 80%), but high standard deviations (of the order of 25%) affected overall extraction precision. Methylene chloride ASE with a static step recovered the high-molecular-weight PAHs with the next highest efficiency (approximately 55%) and had standard devi-

ations less than 10%. Longer extraction times should increase the recoveries of these analytes because the shape of the recovery versus extraction volume curve did not level off.

Comparison of lignite and bituminous fly ash extractions

Comparing both fly ash matrices, the PAHs were recovered better from the lignite fly ash than from the bituminous fly ash. This is most likely due to the large differences in the carbon content (0.2% versus 15%) of the fly ashes. The non-ASE extraction solvents that were used to quantitatively extract the PAHs from the lignite fly ash were ineffective in extracting the same analytes from the bituminous fly ash. The low carbon content of the lignite was not as adsorptive a surface as the high-carbon-content bituminous ash, thus requiring less desorption energy and solvents of lesser strength to extract the PAHs. A more rigorous extraction procedure was required to extract the PAHs from the bituminous fly ashes. ASE methods were the only methods that could extract the higher molecular weight PAHs, incorporating high temperature and high solvent strength to obtain the higher recoveries. Except for naphthalene, the lower molecular weight PAHs were not recovered from the high-carbon bituminous fly ash when using the toluene ASE. This inefficient extraction was probably due to the high adsorptivity of the PAHs and the increased reactivity of the adsorbed lower-molecular-weight PAHs (12).

The poor quantitative recoveries of PAHs from fly ashes noted by other researchers from fly ash (18) indicate that significant surface-analyte interactions must be overcome in some fly ash extractions. Because the ASE techniques were more capable of extracting the PAHs from the high-carbon fly ash, it is clear that the ASE solvents weakened the interactions between the fly ash surface and the adsorbed PAHs more readily than did the other solvents studied.

This study illustrates the difficulty in developing and adapting analyte-specific extraction methods for different matrices. The two matrices studied herein and in the previous paper (1) (lignite fly ash and bituminous fly ash) were similar (moisture percentage, particle sizes, elemental composition, etc.) except for the carbon composition percentage, yet much more rigorous extraction conditions were required to extract the PAHs from the bituminous fly ash. When analyte-specific extraction procedures are developed in the laboratory, great care must be taken to quantitatively assess the effect of the matrix on the efficiency of the extractions performed (proper spike recovery studies) or misleading results may occur.

Of the extraction techniques studied, ASE was used to achieve the largest recoveries for the medium- and high-molecular-weight PAHs from the bituminous fly ash in this study and from the lignite fly ash in the previous study (1). The ASE technique showed the advantages of universal extractions and required much shorter extraction times than other universal extraction techniques, such as Soxhlet extraction. The use of methylene chloride required a less elaborate extract concentration procedure than the toluene ASE technique, but it also yielded lower recoveries than when toluene was used in the solvent.

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