

Articles

Polyaromatic Hydrocarbon Emissions in Fly Ashes from an Atmospheric Fluidized Bed Combustor Using Thermal Extraction Coupled with GC/TOF-MS

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Received March 8, 2001. Revised Manuscript Received November 8, 2001

Over 120 polyaromatic hydrocarbons (PAHs) have been identified in urban pollution, of which 16 have been specified by the United States Environmental Protection Agency (EPA) as priority pollutants. Increased urban concentrations from anthropogenic sources are of particular concern because many of them show carcinogenic and/or mutagenic properties. In this study thermal extraction (TE) coupled with GC/TOF-MS and solvent extraction coupled with GC/MS were utilized to determine the PAH concentrations in fly ash samples collected from a bench-scale 0.1 MW_{th} fluidized bed combustor (FBC). In addition to the evaluation of the analysis procedures including conventional solvent extraction and thermal extraction, a comprehensive study of the effect of operating conditions on PAH emissions in fly ashes samples was conducted. The experimental results indicate the majority of PAHs (two and three fused-ring systems) found in the solid phase (fly ash) are derived from breakdown reactions during the combustion and/or pyrolysis processes in an FBC system. The results for PAH analysis obtained with the TE/GC/TOF-MS technique were comparable to or better than the conventional solvent extraction-GC/MS technique.

Introduction

PAHs are a large group of chemicals that are sometimes formed during the incomplete burning of coal, oil and gas, garbage, and other organic substances such as tobacco or charbroiled meat. PAHs can be produced by natural or anthropogenic sources. Natural sources of PAHs include events such as volcanic releases and forest fires. Anthropogenic sources include incomplete fossil fuel combustion, industries, internal combustion and diesel engine exhausts, aviation exhaust, and cigarette smoking. Although cigarette smoke accounts for the highest exposure threat to humans, vehicle exhaust is the main source of PAHs in the environment.¹

PAHs are a group of more than a hundred organic compounds composed of two or more fused carbon rings derived from benzene. They have been identified in soil, surface water, groundwater, sediment, and air. Generally, PAHs are very hydrophobic organic compounds and are relatively insoluble in water. They have a high affinity for organic matter and, when present in soil or sediments, tend to remain bound to solid particles and dissolve slowly in water. Soil, sediment, and suspended

particulate matter represent important media for the transport of these chemicals.²

PAHs produced from combustion sources may be emitted into the surrounding atmosphere through two independent ways. PAHs can be released to the atmosphere in the vapor phase directly from the combustion facility, or emitted with the solid phases (fly ash or bed ash), and then evaporated or dissipated into the environment as well. PAHs associated with solid material is significant due to the physical absorption enrichment inside the solid particle. The concentration of PAHs in ashes is dependent on the fuel type, combustion technology and ash residence time inside the combustion facility.

Exposure to PAHs has long been identified as an environmental concern. Over 120 PAHs have been detected in urban pollution. Of these 120, there are 16 PAH compounds that the U. S. Environmental Protection Agency (EPA) has classified as priority pollutants.³ PAHs are not commonly associated with adverse health effects in humans. However, the U.S. Department of Health and Human Services has determined that some PAHs, particularly 4- and 6-ringed PAHs, can potentially cause cancer.⁴

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(1) Agency for Toxic Substances and Disease Registry (ATSDR). Polycyclic Aromatic Hydrocarbons (PAHs). ATSDR Public Health Statement; U. S. Public Health Service, U. S. Department of Health and Human Services: Atlanta, GA, 1990.

(2) Environment Canada. Toxic Chemicals in Atlantic Canada-Polynuclear Aromatic Hydrocarbons (PAHs). Report EN40-226-1195E, Dartmouth, Nova Scotia, Canada, 1995.

(3) U. S. Environmental Protection Agency. *List of the Sixteen PAHs with Highest Carcinogenic Effect*; IEA Coal Research: London, 1984.

The analysis of complex mixtures of environmental pollutants such as PAHs has in the past involved the extraction of the target compound from the sample matrix with organic solvents.⁵ Ordinarily, the solvent extraction method creates solvent waste that has to be disposed. In addition to the waste, this method usually demands concentration steps and additional cleanup, which can be associated with additional labor and extra time spent in the laboratory. Recently, the EPA has issued a solventless method for extracting semi-volatile organic compounds, such as PAHs, in soils, sludges, and solid wastes by using thermal extraction (TE) coupled with capillary gas chromatography/mass spectrometry (GC/MS).⁶ In theory, the thermal extraction method is a low-temperature technique where the final temperature is 340 °C.^{5,6} By establishing this temperature as a limit, it allows carbon-carbon bonds to remain unaltered while heating. The analytes are extracted from solid samples, such as soil or fly ash, by a process of heating in a stream of inert gas to a final temperature, which is adequate to desorb the semi-volatile organic compounds. Yet, at the same time, this temperature will not degrade the sample matrix itself. The evolved gases are swept through a heated transfer line and trapped for further separation and analysis. The time required is usually less than 1 h.

Fluidized bed combustion (FBC) is one of several advanced approaches for substantially improving the efficiency of coal-fired power systems, while significantly reducing emissions. This reduction in emissions is highly favored due to the increased restrictions that are being imposed on the concentration of gaseous pollutants, such as NO_x and SO₂. The advanced technology employed by FBC systems allows power plants to burn lower rank coals while at the same time addressing environmental and economic concerns. Although technology allows for many evident environmental and economic advances in the FBC system, it cannot be ignored that combustor systems, in general, are one of the major anthropogenic sources of PAH emissions.⁷ With the EPA monitoring 16 PAHs as priority pollutants and their known carcinogenic effect, it is imperative that research is conducted concerning the emission of PAHs from combustor systems to evaluate how the release of these pollutants can be minimized. Therefore, this study was performed to further examine the release of PAHs in the fly ashes of an FBC system.

In an FBC combustor, a bed of combustible and noncombustible materials is fluidized using air blown upward. Using dolomite or limestone as the noncombustible material, it is possible to have fuel combustion and flue gas desulfurization taking place simultaneously in the same combustion vessel. The height of the bed materials suspended above the bottom of the combustor is a function of the fluidizing velocity of the combustion

air entering below the bed. The amount of coal fed into the bed is approximately 2–3% of the total weight of the bed material. The fluidization of the bed and the relatively small amount of coal present in the bed at any one time causes good heat transfer, and good particle and oxygen mixture throughout the bed material. The temperatures usually encountered in FBC units are 800–950 °C. Moreover, because of lower combustion temperatures and high erosion, no melting layer can be formed on the outside surface of the particle. Study of the morphology of ashes from FBC systems indicates that the ash has a highly porous structure. The active surface area of the ash from FBC systems is much higher than that produced from high temperature pulverized coal combustion. A typical metal analysis of the fly ashes and bed ashes from FBC systems indicates that the major compounds in the ashes are calcium compounds, which comes from limestone, the SO_x sorbent. In the WKU FBC system, the average particle size of bed ash is 1.24 mm with a range from 0 to 3.5 mm. The carbon content in the bed ash is less than 0.7%. The average particle size of the fly ash is 0.23 mm with a range from 0 to 0.56 mm, and the carbon content is in the range from 5 to 15%.

The purposes of the study reported in this paper was to examine how the content of PAHs in the fly ash varied with different combustion parameters and to compare a developed thermal extraction method with the conventional solvent extraction method.

Experimental Section

Collection of Fly Ash Samples. The fly ash samples were collected using a high efficiency cyclone attached to one of the sampling ports along the freeboard section of the combustor. This same port was used for monitoring individual test conditions. By means of a vacuum, flue gas with suspended particles was drawn from the freeboard of the combustor through the sampling port and into the cyclone. The flow rate was approximately 1.79 L/s. The average sampling time was approximately thirty minutes. Sampling for the fly ash began 8 h after changing the test conditions when the combustor had stabilized.

Reagents. Reagents used in this study that were obtained from SUPELCO, Inc. (Bellefonte, PA) include the standard PAH mixture, 2000 µg/mL each in methylene chloride:benzene (50:50) (catalogue no. 48905-U); naphthalene-*d*₈, 2000 µg/mL in methylene chloride (catalogue no. 48715-U); anthracene-*d*₁₀, 2000 µg/mL in methylene chloride (catalogue no. 48863); and benzo[*a*]anthracene-*d*-12, 2000 µg/mL in methylene chloride (catalogue no. 48789). Methanol (purge and trap grade, catalogue no. 48093) and methylene chloride (capillary GC grade, catalogue no. 41475-1) were purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI).

Coals and Limestone. Two high volatile bituminous coals (WKU numbers 97025 and 99626) were used in the study. The analytical values for the coals are listed in the Table 1.

Apparatus. Two types of extraction apparatuses were used in this study. One type was a Tecator Soxhlet 1045 extraction system and the other was a ThermEx thermal extraction system. The ThermEx Inlet system has several accessories that were needed to operate this system. A muffle furnace tray holder was required to hold the porous fused quartz sample crucibles while they were being cleaned in the furnace. The crucibles were handled with stainless steel forceps and stored in quartz Petri dishes inside a desiccator. A 100-mesh (150 µm) sieve was used to prepare the fly ash.

Combustion Runs. The experiments were conducted with Western Kentucky University's 0.1 MW_{th} bench-scale bubbling

(4) Knopp, D.; Seifert, M.; Vaananen, V.; Niessner, R. *Environ. Sci. Technol.* **2000**, *34*, 2035.

(5) Snelling, R.; King, D.; Belair, B. Analysis of PAHs in Soils and Sludges Using Thermal Extraction-GC/MS. Application Note 228; Hewlett-Packard Company: Wilmington, DE, June 1993.

(6) U. S. Environmental Protection Agency. *Method 8275: Semivolatile Organic Compounds (PAHs and PCBs) in Soil/Sludges and Solid Wastes Using Thermal Extraction/Gas Chromatography/Mass Spectrometry*; U.S. Government Printing Office: Washington, DC, December 1996.

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Table 1. Analytical Values^a for the Coals Used in the Study

	97025	99626
proximate analysis		
% moisture	4.56	6.96
% ash	10.97	13.81
% volatile matter	36.25	34.14
% fixed carbon	52.78	52.05
ultimate analysis		
% ash	10.79	13.81
% carbon	74.69	69.53
% hydrogen	4.95	4.49
% nitrogen	1.63	1.55
% sulfur	3.06	4.48
% oxygen	4.50	5.73
miscellaneous analysis		
chlorine (ppm)	2070	4080
btu/pound	13152	12406

^a Moisture is as-received; all other values are reported on a dry basis.

Table 2. Shimadzu GC Temperature Program for PAH Analysis

rate (°C/min)	temp. (°C)	time (min)
	70	1.00
8.00	150	0.00
5.00	250	5.00
7.00	300	5.00

fluidized bed combustor. It has a 0.3-m i.d. and a 4.0-m effective height. The freeboard zone in the combustor is 2.5 m high. Coal was fed into the system by means of an underbed auger, which is under positive pressure. Primary air was injected into the combustor from the bottom and secondary air was injected into the combustor in the freeboard zone, 1 m above the bed. Six active heat exchange tubes were used to control the temperature of the bed. A 1000-h run was made with each of the coals.

Analysis Procedure. *Solvent Extraction Followed by GC/MS.* The fly ash samples collected under specific operating conditions during the first run were extracted using a Tecator Soxtec 1045 extraction system. Then for each condition, 6–15 g of the 100-mesh ash was placed in the extraction thimble with dichloromethane. The extractor was then heated to 120 °C in order to extract materials from the ash for a period of 1 h. Once heated, the thimble and the ash were removed from the apparatus and the extract was heated with the refluxing dichloromethane (80 mL) for five more hours. After 5 h, the extracted solution was then condensed and placed in a 10-mL volumetric flask.

Once the extraction was completed, a Shimadzu QP 5000 system with a NIST/EPA/NIH 62,000 compound database was used for GC/MS analysis. Two microliter aliquots of the samples were injected, using the splitless mode, into the RTX-5 fused silica capillary column (60 m × 0.32 mm and a stationary phase thickness (5%-phenyl)methylpolysiloxane of 1 μm). Helium was the carrier gas. The surrounding temperature for the interface, injector, and detector was 230 °C. The mass spectrometer was operated in two modes, the scan mode and the selected ion monitoring (SIM) mode. The scan mode was used for determining the PAH retention times and the SIM mode was used for the analysis of the PAHs. The temperature program for the Shimadzu GC is listed in Table 2. Quantitative analysis was performed using calibration data from the PAH standard, which contained the sixteen PAHs specified by the EPA. The range of detection limits for these sixteen PAHs using the GC/MS SIM mode is 1–10 ppb, depending on the boiling point of the individual PAHs. However, the GC approach to molecular information is often hampered by lack of volatility and is generally limited to aromatic systems of five or six condensed rings with molecular weights up to about

Table 3. Operating Parameters for the ThermEx Inlet System for PAH Analysis

start (°C)	rate (°C/min)	end (°C)	time (min)
Temperature Program for Thethermex Inlet System			
60	hold	60	0.5
60	35	280	6.3
280	hold	280	30.0
280	35	340	1.7
340	hold	340	3.0
340	100	60	2.8
Temperature Program for the Cryogenic Focusing System			
-50.0	hold	-50.0	44.3
-50.0	step	315	1.5
315	hold	315	6.5
315	step	-50.0	1.5
GC Temperature Program			
rate (°C/min)	temp (°C)	time (min)	
	35	44.3	
35.0	315	2.0	

300. For samples with average molecular weights over 300, the molecular information available from GC/MS analysis is limited.

Thermal Extraction Followed by GC/TOF-MS. A sample of about 100-mg fly ash was loaded into a quartz crucible, which was then placed into the ThermEx pyrocell and heated. The evolved gases formed from heating were then swept by helium to the cryogenic focusing system (CFS) cryocell. In the cryocell, the gases were trapped using liquid nitrogen, desorbed onto the GC capillary column, and then analyzed by the GC/TOF-MS. The LECO Pegasus II GC/TOF-MS is equipped with a 60000-compound NIST database, which was used for the analysis of the samples. Helium was the carrier gas. The capillary column used was a HP-5 (30 m × 0.32 mm × 0.25 μm). The surrounding temperature for the transfer line was 300 °C. The mass spectrometer was operated in the selected ion mode for each of the 16 PAHs specified by the EPA. The temperature programming parameters for the ThermEx Inlet system, cryogenic focusing system, and the GC are listed in Table 3. Quantitative analysis was carried out using calibration curves of the PAH standard, which contained the sixteen PAHs specified by the EPA. The range of detection limits for these sixteen PAHs using the Thermal-Ex GC/TOF-MS is 0.1–1 ppm.

Standards Preparation. Blank fly ashes (100-mesh material, preheated to be organic free) were used for the preparation of the calibration standard ash and internal standard ash. A given amount of PAH-free ash blank was weighed into a 2-mL amber vial, and spiked with the standard PAH mixture. Methanol and methylene chloride were also added to the sample vial just above the sample surface, to assist in distributing the standard compounds homogeneously throughout the ash. The vial was sealed and shaken frequently. The sample was left at room temperature for more than 5 days to allow the PAHs to distribute thoroughly, then the vial was opened in order to completely evaporate the solvent. Each standard sample was stored at -10 to -20 °C and protected from exposure to light and moisture. Two standard ash samples were made with the concentrations of 38.24 and 19.90 μg/g. By using the same procedure, the internal standard ash samples containing naphthalene-*d*₈, anthracene-*d*₁₀, and benzo[*a*]anthracene-*d*₁₂ were also prepared. The concentration of each internal standard ash sample was 50.08 μg/g.

Results and Discussions

Method Development. A total of 60 g of fly ash (Fly Ash C) collected from the run burning Coal 97025 was used for most of the method development investigations including thermal extraction and solvent extraction. The

Table 4. The Heating Program Trials for Investigation of Optimum Thermal Extraction Conditions

heating condition	step	initial temp. (°C)	rate (°C/min)	final temp. (°C)	isothermal	total time (min)
1	1	45	-	45	0.5	43.0
	2	45	10	340	10.0	
	3	340	100	45	0	
2	1	45	-	45	0.5	83.0
	2	45	10	200	25.0	
	3	200	100	45	0.0	
	4	45	100	200	0.0	
	5	200	10	340	24.5	
	6	340	100	45	0.0	
3	1	45	-	45	0.5	130.5
	2	45	10	200	70.0	
	3	200	100	45	0.0	
	4	45	100	200	0.0	
	5	200	10	340	24.5	
	6	340	100	45	0.0	
4	1	60	-	60	0.5	45.3
	2	60	35	280	30.0	
	3	280	35	340	3.0	
	4	340	100	280	1.0	
	5	280	100	60	0.0	

ash was ground to 100 mesh, well mixed, split into eight vessels, and stored in a refrigerator for further study. All samples used in the Thermal Extraction investigation came from the same vessel. The samples used in the Solvent Extraction experiments came from different vessels.

Preliminary Test for PAHs in Fly Ash. A sample of fly ash weighing approximately 100 mg was analyzed according to the recommended conditions in EPA Method 8275: Semivolatile Organic Compounds (PAHs and PCBs) in Soil/Sludges and Solid Wastes Using Thermal Extraction/Gas Chromatography/Mass Spectrometry (TE/GC/MS). The thermal extraction profile was set as follows: Hold at 60 °C for 2 min, raise the temperature from 60 °C to 340 °C in 8 min, hold at 340 °C for 3 min, and cool from 340 °C to 60 °C in 4 min. The National Institute of Standards and Technology (NIST) electronic library picked four possible PAHs with molecular weights of 128 (naphthalene), 152 (acenaphthylene), and 178 (phenanthrene and anthracene) from the GC/TOFMS chromatogram of the sample. However, after reheating the sample, compounds with m/z 128 and 178 were still present. After another 10-min isothermal heating period at 340 °C, compounds with m/z 128 and m/z 202 were found which may be due to the weak chemical bonds between PAHs and carbon in the ash. These results indicated that the matrix of fly ash is different from Soil/Sludges or Solid Wastes for which EPA Method 8275 was developed. Consequently, the thermal extraction conditions had to be modified such that the PAHs in the fly ash sample could be effectively extracted.

Investigation of Optimum Thermal Extraction Conditions. Four different heating programs were examined in order to set up optimized experimental conditions for thermal extraction, as summarized in Table 4. A longer isothermal step was applied at the high final temperature (°C) in Condition 1. To investigate the effect of temperature, heating rate and the heating process on PAHs released from ash samples, an intermediate temperature between initial and final temperature was chosen for the other three test conditions. A manually chosen holding step at a temperature of 200 °C was used in Condition 2, and the isothermal time at the high final

temperature was about 15 min longer than that in the Condition 1. Condition 3 had a longer holding time at the medium temperature (200 °C) than that in Condition 2. In Condition 4 a holding step at 280 °C was chosen (which is 80 °C higher than Condition 1, but is close to the boiling points of acenaphthylene and acenaphthene and higher than that of naphthalene) while the other parameters remained as those in EPA Method 8275. There were no significant peaks identified as PAHs when an additional postheating of 15 min was applied to each condition after the analysis process was over.

For comparison, the peak area-to-sample weight ratio for each PAH identified by the NIST library was calculated. The results listed in Table 5 showed that all conditions could be used for PAH analysis in the ash samples. The peak area-to-sample weight ratio for all PAHs calculated from each condition is relatively close. The discrepancy between each condition is in the range of $\pm 10\%$ except for phenanthrene (first m/z 178). The majority of the small molecules are released at low temperatures, for instance, 74.6% of naphthalene is emitted at 200 °C as shown in Condition 2. However, the larger molecules are only released at higher temperatures. As illustrated in Table 5, the larger molecules [such as phenanthrene, anthracene, fluoranthrene, pyrene and higher molecular weight compounds (if any)] cannot be detected during the low temperature heating process used in Conditions 2 and 3. In this study condition 4 was preferred since it showed relatively high peak area-to-sample weight ratios and required a shorter overall time as well.

Mean Recoveries Using the TE/GC/TOFMS Technique. Three different standard ash samples with different PAH amounts (49.71, 53.54, and 57.36 ng) were tested on three different days to determine the recovery rate of the TE/GC/TOFMS technique for analyzing fly ashes. The ions used for the SIM analysis mode and the boiling points of the sixteen PAHs are listed in Table 6. Also listed are original concentrations, the measured concentrations, the mean recoveries, and the relative standard deviations (RSDs). The data in Table 6 shows that the percent recoveries varied from 83.1 to 96.1 for different PAHs. Generally, PAHs with higher molecular weights have relatively lower recoveries due to their higher boiling points. Another reason might be larger PAHs were adsorbed more tightly by ash particles. By comparison, the solvent extraction method resulted in lower recoveries for lower molecular weight PAHs and higher recoveries for higher molecular weight PAHs. When the fly ash sample from the same source was extracted by the Soxhlet extraction procedure, the recoveries for the three internal standards were 83.4% for naphthalene- d_8 , 87.7% for anthracene- d_{10} , and 90.1% for benz[*a*]anthracene- d_{12} , respectively. The PAHs with low molecular weights may be lost during solvent extraction because they are more volatile and more difficult to keep in the solution during solution transfer and concentration. However, in the thermal extraction procedure, the evolved gases were trapped directly on the head of GC column without external transferring procedures, thus avoiding loss of PAHs.

Analysis of Fly Ash Samples. Comparison of the Two Methods. Fly ash samples collected from the FBC

Table 5. The Analysis Results Illustrating Effect of Different Heating Conditions on Peak Area-to-Sample Weight Ratios

	heating condition	mass-to-charge ratios (<i>m/z</i>)							
		128	152	154	165	178	178	202	202
1	45–340 °C	90579	5821	2791	1825	12218	14220	35711	28917
2	45–200 °C	63943	2944	1510	902	n.d.	n.d.	n.d.	n.d.
	200–340 °C	26912	2663	1182	1040	10654	16570	37772	27873
	total	90855	5607	2692	1942	10654	16570	37772	27873
3	45–200 °C	66956	2434	1441	980	2837	n.d.	n.d.	n.d.
	200–340 °C	22743	3182	1200	1031	8788	15870	36175	27105
	total	89699	5616	2641	2011	11625	15870	36175	27105
4	60–340 °C	92013	6089	2935	1903	16005	17370	34810	30012
av		90787	5783	2765	1920	12626	16008	36117	28477
max deviation (%)		1.35	5.29	6.16	4.73	26.77	8.51	4.58	5.39

Table 6. Mean Recovery and RSDs Obtained from TE/GC/TOF-MS Experiments

peak no.	compound	selected ions ^a	analysis content in sample (ng)			mean recovery (%)	RSD (%)	bp (°C) at 1 atm
1	naphthalene	<i>128</i> , 102	48.34	49.43	53.34	94.2	2.7	218
2	acenaphthylene	<i>152</i> , 153, 76	44.98	48.83	53.40	91.6	1.3	280
3	acenaphthene	<i>153</i> , <i>154</i> , 155, 76	48.26	51.79	54.21	86.1	1.4	279
4	fluorene	<i>166</i> , 165, 139, 83	41.81	43.51	49.75	84.0	2.7	298
5	phenanthrene	<i>178</i> , 89, 76, 152	44.74	47.46	51.11	89.2	0.7	340
6	anthracene	<i>178</i> , 89, 76	41.26	44.30	48.76	83.6	1.2	na
7	fluoranthene	<i>202</i> , 101, 100, 88	41.76	42.97	48.54	82.9	2.3	384
8	pyrene	<i>202</i> , 101, 100, 88	42.80	44.71	48.81	84.9	0.8	na
9	benz[<i>a</i>]anthracene	<i>228</i> , 229, 114, 101	42.05	43.88	47.67	83.2	1.3	438
10	chrysene	<i>228</i> , 229, 113, 101	42.75	44.89	49.04	85.1	1.1	448
11	benz[<i>b</i>]fluoranthene	<i>252</i> , 253, 126, 125	44.24	44.92	50.48	87.0	2.7	na
12	benz[<i>k</i>]fluoranthene	<i>252</i> , 250, 125, 111	43.10	45.33	49.47	85.9	1.1	na
13	benz[<i>a</i>]pyrene	<i>252</i> , 253, 228, 149	42.00	43.33	48.12	83.1	1.9	495
14	indeno[1,2,3- <i>cd</i>]pyrene	<i>276</i> , <i>277</i> , 138, 137	42.50	44.12	46.63	83.1	2.2	na
15	dibenzo[<i>a,h</i>]anthracene	<i>278</i> , 279, 250, 139	43.05	44.86	48.18	84.8	1.7	524
16	benz[<i>ghi</i>]perylene	<i>276</i> , <i>277</i> , 138, 137	42.23	43.02	48.96	83.6	2.8	> 500
			49.71 ^b	53.54 ^b	57.36 ^b			

^a The italicized ion is the base (or molecular) ion of each PAHs. ^b Original values used for each compound.

Table 7. Analysis of PAHs in Fly Ash Sample A

compound	thermal extraction (mg/kg)	solvent extraction (mg/kg)
naphthalene	138.3	109.2
acenaphthylene	53.3	58.1
acenaphthene	28.4	18.3
fluorene	14.6	16.6
phenanthrene	50.3	46.3
anthracene	36.9	21.1
fluoranthene	33.8	22.2
pyrene	39.4	35.0
total PAHs	395.0	326.8

Table 8. Analysis of PAHs in Fly Ash Sample B

compound	thermal extraction (mg/kg)	solvent extraction (mg/kg)
naphthalene	149.8	70.9
acenaphthylene	49.5	60.3
acenaphthene	50.3	24.5
fluorene	22.7	19.7
phenanthrene	27.0	43.2
anthracene	21.0	25.0
fluoranthene	16.7	29.8
pyrene	27.3	53.2
benz[<i>a</i>]anthracene	2.5	n.d. ^a
chrysene	8.9	8.8
benzo[<i>b</i>]fluoranthene	44.2	47.5
benzo[<i>k</i>]fluoranthene	3.9	n.d. ^a
total PAHs	423.8	382.9

^a n.d.: not detected.

system were repeatedly analyzed using the solvent extraction method followed by GC/MS and the thermal extraction method followed by GC/TOF-MS. Tables 7 and 8 list the results obtained from analyzing two fly

ash samples (Samples A and B) using the two methods. For sample A, the amounts used in thermal extraction were 19.8 mg and 29.5 mg, while the amounts used in solvent extraction were 6.0 and 6.9 g. The amounts used for thermal extraction of sample B were 6.8 mg and 11.6 mg, while 2.8 and 3.0 g were taken for the duplicate solvent extractions.

The results indicate that the thermal extraction method developed is comparable with the traditional solvent extraction method when observing the total amount of PAHs in a single sample. However, the concentrations of the individual PAHs varied in the two methods since the compounds may have different behavior in thermal extraction versus solvent extraction. Specifically, naphthalene showed substantial differences, which may be attributed to the higher volatility of naphthalene.

The Effect of Sample Size on PAH Analysis. Fly ash sample C was used to investigate the sample size effects comparing the Soxhlet extraction and thermal extraction methods. The sample was extracted with CH₂Cl₂ for 6 h for the Soxhlet extraction process. The results of this experiment are shown in Table 9. The data in this table implies a sample size of approximately 1–10 g is appropriate for the Soxhlet extraction procedure, which would give an average total PAH concentration of about 0.6 ppm. As for the thermal extraction procedure, a sample size of approximately 100 mg shows good reproducibility and would give an average total PAH concentration of about 1.2 ppm. Smaller sample sizes gave higher values, probably due to increased efficiency in the extraction process.

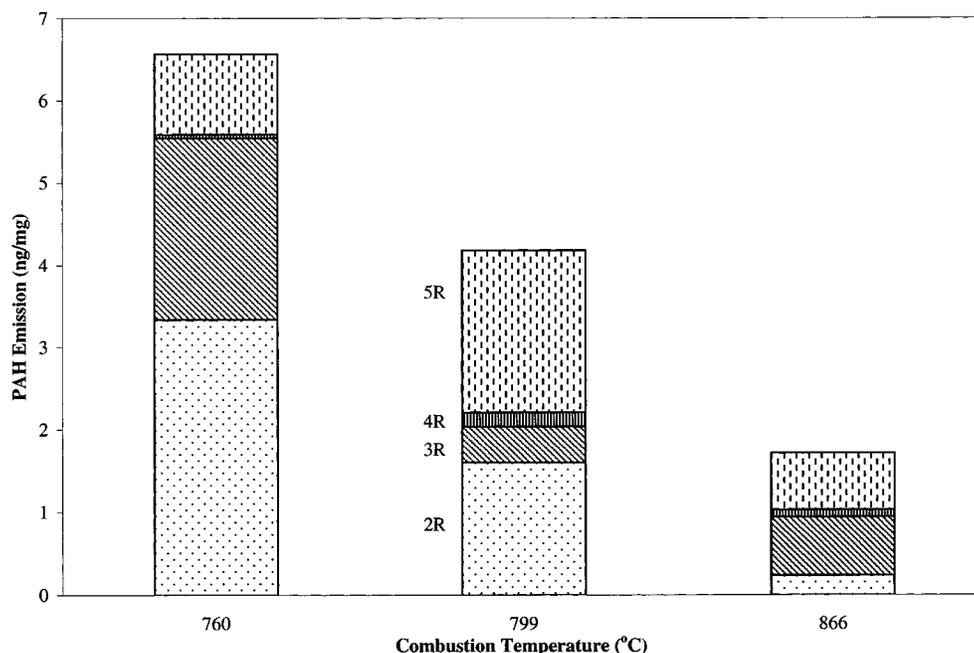


Figure 1. The distribution of PAHs in the fly ash at different temperatures in an FBC system.

Table 9. Sample Size Effects upon Soxhlet Extraction and Thermal Extraction Methods

soxhlet extraction method		thermal extraction method	
sample size (g)	total PAHs in sample concentration (ppm)	sample size (g)	total PAHs in sample concentration (ppm)
20.0000	0.8	0.3433	0.8
10.0300	0.4	0.1004	1.3
9.9700	0.2	0.1000	1.2
0.9970	0.1	0.0940	1.0
0.9960	1.8	0.0155	3.8
0.0975	n.d. ^a		
0.0117	n.d. ^a		

^a n.d.: not detected.

Limitations of the Thermal Extraction Method. In general, changing the sample size or the GC split ratio can make the on-column weight of the target PAH fall into the linear calibration range for the analysis. Less sample (less than 20 mg) and high GC split ratio (20:1 or above) are preferred for fly ash samples with high PAH concentrations, while large sample sizes and low GC split ratios are preferred for fly ash samples with low PAH contents. However, given the limitation in the volume of the quartz crucible, the size of the ash sample should not exceed half the size of the crucible. There are various reasons for this limitation, including efficiency of extraction and the simple fact that the sample may be blown from the crucible by the sweeping gas. Therefore, if the PAH content in the fly ash were too low, the thermal extraction method may not give satisfactory results. In this respect, the solvent extraction method should be taken into consideration if the sample was over 6 g. It is worth noting that the particle sizes of fly ash after grinding were almost identical, but the distributions of PAHs in the particulate still may not be homogeneous. Thus, small sample sizes may not be truly representative of the whole sample.

Effect of Operating Parameters. *Effect of Combustion Temperature.* When considering the effect the combustion temperature has on the number of rings in

the PAHs in the fly ash, the most significant reduction was seen in the two and three fused-ring PAHs, as illustrated in Figure 1. This decrease could result from the smaller ringed species being more completely combusted at elevated temperatures. Yet, these smaller ringed species were still present in the fly ash at elevated temperatures. The presence of these rings in the fly ash could be attributed to the apparent, but mild, decrease in five and four fused-ring PAHs. The larger ringed species may have decomposed at the higher temperatures and produced the smaller ringed species that were detected. This indicates that higher temperatures may provide the energy needed to break the macromolecular structure of the PAHs during coal pyrolysis, resulting in the smaller ringed PAHs.

These speculations, which are based on the data collected, of how the PAHs vary in distribution and concentration, are very plausible explanations of the sources of PAHs that are released during coal combustion. However, when it is well-known that there are three major mechanisms for the formation and release of PAHs in coal combustion, the other two mechanisms should be considered as well. Based on the results of this study, at lower temperatures the combustion was less efficient. It is known that the breakdown reaction is a mechanism that occurs during inefficient combustion conditions and results in the release of PAHs that were initially part of the coal matrix.^{8,9} Observations made at 760 °C, as shown in Figure 1 are characteristic of breakdown reactions. At lower temperatures, there was an increase in the amount of two and three fused-ring PAHs when compared to the concentration of the four or five fused-ring PAHs. The breakdown reaction could result in this increased release of the two- and three-fused ring PAHs that were initially part of the coal matrix.

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(9) Zimmerman, R.; Heger, H. J.; Kettrup, A.; Nikolai, U. *Fresenius' J. Anal. Chem.* **2000**, *366*, 368.

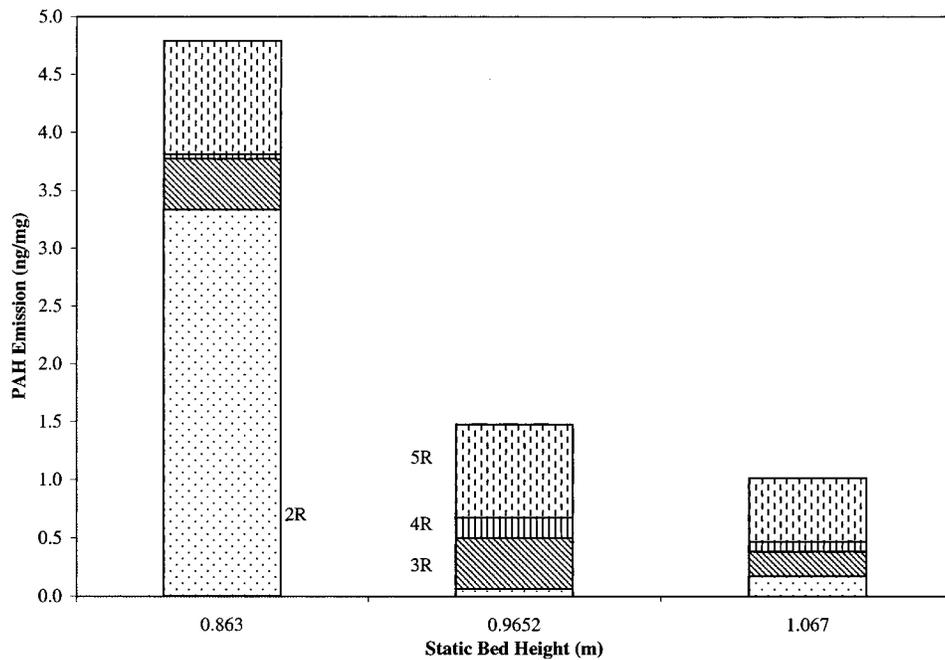


Figure 2. The distribution of PAHs in the fly ash at different bed heights in an FBC system.

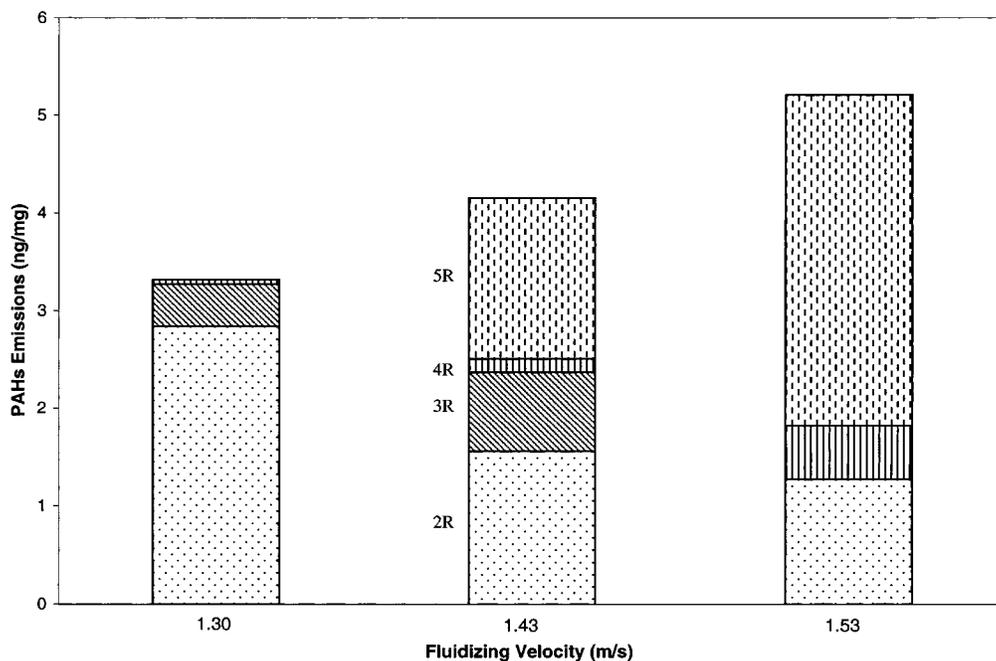


Figure 3. The distribution of PAHs in the fly ash at different fluidizing velocities in an FBC system.

Effect of Residence Time. Combustion residence times for particles can be very different, depending on their nature. In a bubbling bed coal particle residence times are of the order of seconds to minutes. This is essentially their burnout time, although there can be various complications depending on whether the particles shrink in the process or undergo fragmentation. Small fragments will be subject to elutriation. The residence time of particles in the dense fluidized zone (high temperature region) of the FBC system depends on two factors, the solid bed height, and fluidizing velocity. Long residence times for particles always corresponds to higher bed height and low fluidizing velocity based on primary air flow. The distribution of PAHs in the fly ash at different bed heights is shown in Figure 2. The

figure clearly illustrates that as the bed height increased, the overall concentration of PAHs found in the samples decreased. However, upon closer observation of the actual distribution of PAHs in both types of coals, it should be noted that at the lower bed heights the smaller (2R and 3R) PAHs were detected in higher concentrations than the larger (4R and 5R) PAHs. This is the same trend as that shown in Figure 1 for the temperature variation. Therefore, the mechanism that was responsible for the formation and release of the PAHs may be the same as that observed with the temperature changes. A plausible explanation of these observations is that when the efficiency of the combustor was low (at 0.863-m bed height), breakdown reactions probably occurred, which would release two- and three-

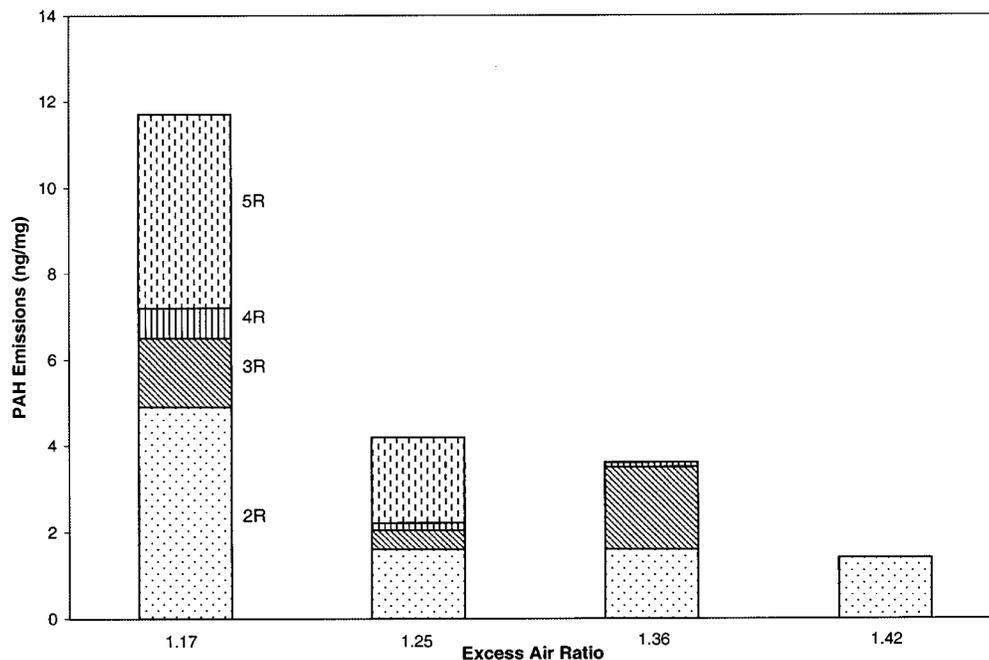


Figure 4. The distribution of PAHs in the fly ash at different excess air ratio in an FBC system.

ring PAHs that were initially part of the complex coal matrix. As the bed height increased, the operating conditions of the combustor are much more efficient, which yields a dramatic reduction in the two and three-ring PAHs. Despite this substantial decline, the four- and five-ring PAHs were still detected at virtually the same concentrations until the highest efficiency was attained at 1.067 m bed height.

Figure 3 shows the distribution of PAHs at different fluidizing velocities for coal 99626. As the flow rate decreased, the total amount of two- and three-ringed PAHs substantially increased. However, the larger PAHs (4R and 5R) were completely gone at the 1.30 m/s condition. This extreme increase in two fused-ring PAHs can be attributed to the decomposition of four- and five-ring PAHs. Yet, it must also be considered that as the combustion efficiency decreased, there is a trend for four- and five-ring PAHs to increase. This trend has been observed in the previous parameters investigated, and is indicative of the occurrence of the breakdown reaction, which favors the release of the smaller PAHs.

Effect of Excess Air Ratio. The relationship between the excess air ratio and the content of PAHs in the fly ash is shown in Figure 4. This figure illustrates that during the first plotted excess air ratio (1.17), two- and

five-ring PAHs exist in large concentrations. This observation is directly related to those previously made relating the distribution of PAHs as a function of other parameters. As the excess air ratio increased and the combustion efficiency increased, the larger PAHs significantly decreased in concentration. The smaller PAHs also decreased in concentration as the excess air ratio increases. No PAHs with more than four fused rings were detected after the excess air ratio exceeded 1.36.

Conclusions

1. The TE/GC/TOF-MS technique is comparable to, or even more effective, than the conventional solvent extraction-GC/MS technique for PAH analysis.
2. The concentration of PAHs in the fly ash will decrease in an FBC system when the combustor is operated at relatively high temperatures, increased static bed heights (>0.7 m), low fluidizing velocities, and increased excess air ratios.
3. Smaller PAHs (two- and three-ring systems) are produced as a result of breakdown reactions during inefficient combustion conditions in FBC systems.

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