



## Analysis of polynuclear aromatic hydrocarbons from coal fly ash

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### Abstract

The objective of this work is to compare various extraction and quantitation techniques for the determination of adsorbed polynuclear aromatic hydrocarbons (PAHs) on coal ash. Aliquots of a 'clean' fly ash from coal combustion doped with four PAHs have been extracted, using three solvents, three methods and three GC/MS programs. Factorial analysis shows solvent to exert the greatest primary effect:  $\text{CH}_2\text{Cl}_2 > \text{toluene} > > o\text{-xylene}$ . Highest recoveries were obtained using the reflux slurry extraction procedure with  $\text{CH}_2\text{Cl}_2$  and a relatively fast ( $20^\circ/\text{min}$ ) temperature ramp to  $310^\circ$ . With both  $\text{CH}_2\text{Cl}_2$  and toluene solvents, ultrasonic assisted extraction affords the best repeatability. Published by Elsevier Science B.V.

*Keywords:* Polynuclear; Aromatic; Hydrocarbons; Fly ash; Extraction; Ultrasonic

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### 1. Introduction

The release of organic pollutants into the environment by the burning of carbonaceous fuel has been a cause for concern since the industrial revolution. Combustion of coal in particular has presented a major environmental challenge. This challenge has been substantially met with the design of the modern coal-fired boiler, which in normal operation does not discharge significant levels of organic pollutants. However, old boilers which permit localized reducing areas near the points of fuel injection can release a considerable amount of organic compounds [1,2]. Furthermore, any boiler

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operating under abnormal conditions (low temperature, insufficient air supply), such as may occur at startup or shutdown, is likely to release volatile organics [2,3]. In a thorough review of the literature through 1979, Junk and Ford [4] found 48 polynuclear aromatic compounds (PAHs) reported. A recent review [5] found 37 organic compounds which were identified in five or more studies; 28 of the 37 (76%) are PAHs. Some of these sparingly volatile organics are found in stack gases, but all are found as adsorbates on fly ash and other ash [4,5].

There are “no standard or accepted procedures among the many described in the literature for the extraction of organic compounds from particulates [6]”. Soxhlet extraction is the most common method, using benzene [7–11], benzene–methanol [6,12,13], benzene–hexane [14], methylene chloride [14,15], ether [16], toluene [17,18] and toluene–methanol [6,12]. Extraction times, when reported, were between 6 [15] and 48 [11,13,17] h. In addition to the Soxhlet method, stirred slurry [19] and ultrasonic-assisted [6,12,19,20] extractions have been used. Junk et al. [6,12] examined several solvents using both Soxhlet and ultrasonic techniques, and concluded that “no technique resulted in significant improvement in [extraction efficiencies]”.

Analysis of the extracts in some earlier studies was made by column chromatography using ultraviolet detection [7,8]. Later packed GC columns using Dexsil<sup>®</sup> and poly(dimethylsiloxane) were used [15,22]. Most recent studies use GC/mass spectrometry, with separations on capillary columns of poly(dimethylsiloxane) [16,19] or of copolymers of dimethylsiloxane with 5% diphenylsiloxane [11,17,21]. One study has found the minimum detectable limit (MDL) to fall between 1 ppm (naphthalene) and 20 ppm (perylene) [19].

This study, using a standard ash impregnated with known levels of several PAHs and a modern benchtop GC/mass spectrometer fitted with a 60 m × 0.32 mm bonded dimethylsiloxane column, compares the efficiencies of several solvents, extraction techniques and GC/MS analytical programs in the analysis of representative PAHs.

## 2. Experimental

A stock solution was prepared containing 1.140 g each of acenaphthene and fluorene, 0.7125 g anthracene and 0.9975 g pyrene in 100.0 ml of a toluene–methanol solution (69% v/v toluene). From 1.00 ml of this solution a series of dilutions was made, ultimately to 21.5 pg of acenaphthene and fluorene, 18.8 pg pyrene and 13.4 pg anthracene per  $\mu\text{l}$  solution (solution A). A series of GC/MS analyses was then conducted at progressively higher dilutions, to determine the minimum detectable limits (MDL) for these PAHs. Signal response varied linearly with concentration;  $r^2$  of fit exceeded 0.995 for all four analytes. MDL is taken to be that concentration for which the peak signal is three times the height of background noise. In the scan mode (4 Hz, electron multiplier at 1.50 kV) the MDLs for these four PAHs are 0.3–0.5 ng on-column. In SIM mode using in each case the parent ion the MDLs fall to 0.5–3.5 pg on-column. Table 1 shows the results of triplicate determinations. SIM mode analysis monitoring the molecular ions is especially useful with PAHs, since these species are thermodynamically very stable relative to their fragmentation products [23,24].

Table 1  
Minimum detectable limits (on-column) for four PAHs<sup>a</sup>

	Scan mode (ng)	SIM mode <sup>b</sup> (pg)
Acenaphthene	0.27 ± 0.05	2.4 ± 0.5
Fluorene	0.37 ± 0.04	3.5 ± 0.3
Anthracene	0.46 ± 0.07	0.9 ± 0.1
Pyrene	0.53 ± 0.05	0.5 ± 0.1

<sup>a</sup>Data are obtained with a Shimadzu QP-5000 GC/mass spectrometer fitted with a 60 m × 0.32 mm × 1.0 μm bonded poly(dimethylsiloxane) column at 100–310° with a constant (temperature-compensated) He linear velocity of 31 cm/s. Detector multiplier voltage is 1.50 kV. These data are averages of triplicate determinations using the 3σ criterion.

<sup>b</sup>Data are from runs with selected *m/z* values of 154 and 166 to 17 min (acenaphthene and fluorene), then 178 and 202 (anthracene and pyrene).

A 'clean' fly ash was obtained from a cascading FBC system being evaluated by the University. Its composition is shown in Table 2. The amorphous carbon phase provides high-affinity sites for PAH adsorption. Portions of the ash were extracted with methanol, methylene chloride, toluene and 1,2-dichloroethane. No traces of PAHs were detectable by GC/MS.

Two PAH-impregnated ashes were prepared. Ash A was made by combining 99.0 ml of solution A with 308.5 g. of the dry ash. An additional 25 ml of toluene was added to obtain uniform incipient wetness. The wetted ash was air dried for 48 h, then vacuum-dried at 50° for 6 h. Ash B was similarly prepared, using a solution of anthracene 250.3 mg and pyrene 250.4 mg in 33 ml toluene, with 100.0 g of the clean dry ash.

Table 2  
Chemical composition of raw fly ash

Analysis	As determined (%)	Dry basis (%)
Moisture	0.78	—
Ash	70.12	70.67
Volatile matter	6.17	6.22
Carbon	27.44	27.66
Hydrogen	0.39	0.31
Nitrogen	0.21	0.21
Heating value, kJ/g	9.95	10.03
Btu/lb	4280	4310
SiO <sub>2</sub>	—	36.86
SO <sub>3</sub>	—	0.24
K <sub>2</sub> O	—	2.42
CaO	—	37.46
TiO <sub>2</sub>	—	1.47
Fe <sub>2</sub> O <sub>3</sub>	—	15.76
Na <sub>2</sub> O	—	1.66
MgO	—	1.31
Al <sub>2</sub> O <sub>3</sub>	—	2.02
MnO <sub>2</sub>	—	0.81

Table 3  
GC programs used<sup>a</sup>

Prog.	Initial <i>T</i> (°C)	Ramp (°/min)	Final <i>T</i> (°C)	Final hold (min)
A	100°	20	310°	17.5
B	150°	5–7	310°	26.4
C	100°	5	310°	48.0

<sup>a</sup>For each run helium pressure was adjusted in three steps during the temperature ramp to maintain a flow rate of 1.5 ml/min. Detection is by selected ion monitoring, *m/z* 154 and 166 (acenaphthene and fluorene) and 178 and 202 (anthracene and pyrene).

In the preliminary study a series of extractions of Ash A was made, using three physical methods, a 48-h standard Soxhlet extraction, a 6-h reflux slurry extraction (flat-bottom flask fitted with reflux condenser and Teflon<sup>®</sup> clad stir bar; contents stirred at moderate reflux), and a 2-h ultrasonic-assisted extraction, using the toluene–methanol azeotrope in a medium-power (173 W, 47 kHz) ultrasonic bath. In each case 5.00 g of doped ash was treated with 50–150 ml of solvent; the extract was then reduced using a Kuderna–Danish concentrator [25] to 4.0 ml, then subjected to GC/MS analysis using three different analytical programs. This exploratory block was then repeated with toluene, methylene chloride and *o*-xylene as extractants.

The three GC programs used are shown in Table 3. For all runs the GC/MS (Shimadzu model QP-5000) was fitted with a 60 m × 0.32 mm × 1.0 μm Rtx-1 (bonded poly(dimethylsiloxane)) column, split ratios were varied between 15 to 100, and the electron multiplier was operated at 1.3–1.5 kV. Scan rate was 4 Hz. For the scanning runs the mass range was 50–350 amu. Analysis of a set of solutions containing both analytes present in Ash B (as well as the internal standard) provided a reasonably good linear calibration (Table 4).

The final block of extractions was carried out using Ash B (doped with anthracene and pyrene), with the two most promising solvents, toluene and methylene chloride, both containing the internal standard 4-bromophenyl ether, the two preferred extraction methods, reflux slurring and ultrasonic, and the two most effective GC programs. All extractions in this 2 × 2 × 2 block were made in duplicate. Data in this block was then examined by 2<sup>3</sup> factorial analysis [26].

Table 4  
Coefficients for calibration curves<sup>a</sup>

Analyte	Program	<i>a</i>	<i>b</i>	<i>r</i> <sup>2</sup> of fit
Anthracene	A	+ 5.20E – 2	+ 1.68E – 7	0.9992
Pyrene	A	+ 1.16E – 2	+ 1.97E – 7	0.9999
4-Bromophenyl ether	A	+ 6.87E – 2	+ 2.975E – 7	0.9995
Anthracene	B	-- 3.11E – 3.	+ 5.189E – 8	0.9986
Pyrene	B	+ 8.942	+ 3.756E – 8	0.988
4-Bromophenyl ether	B	-- 2.456E – 3	+ 9.443E – 8	0.9999

<sup>a</sup>Linear fits for concentration (mg/ml) = *a* + *b* × counts, for the range 1 to 25 mg/ml.

### 3. Results and discussion

At a detector multiplier voltage of 1.50 kV the minimum detectable limits of the analytical system in the scan mode are in the range  $0.27 \pm 0.05$  (acenaphthene) to  $0.53 \pm 0.5$  (pyrene) ng on-column. In the SIM mode using molecular ions the MDLs are in the range  $0.5 \pm 0.1$  (pyrene) to  $3.5 \pm 0.3$  (fluorene) pg on-column.

Preliminary extractions were carried out using Ash A with methylene chloride, toluene and *o*-xylene as solvents. Toluene appeared to be most effective for the light PAHs (acenaphthene and fluorene). Methylene chloride was more effective for the higher PAHs. *o*-Xylene was the least effective of the three solvents, for all PAHs and for both ultrasonic and reflux slurry procedures. On this basis *o*-xylene was dropped from further study.

Further preliminary data with toluene as extractant indicate that the reflux slurry and Soxhlet procedures are comparable in efficiency. Since the reflux slurry method (6 h) is much faster than the classical Soxhlet (48 h), the latter procedure was dropped from further study.

Using the same column in the same instrument, three heating programs were used (Table 3). In these preliminary tests 12 analyses by each program were compared. The analytical running times for programs A, B and C are 28, 55 and 90 min, respectively. Program C provided no improvement in precision and a moderate loss in sensitivity, owing to diffusional effects. Accordingly, program C was dropped from further study.

The final block of tests was conducted in duplicate. Table 5 shows the pattern of extraction recoveries of anthracene and pyrene, for the two solvents, two extraction procedures and two GC programs. Where the high value of a pair is more than two-fold

Table 5  
Comparison of extraction efficiencies

	GC method A		GC method B	
	Slurry	Ultrasonic	Slurry	Ultrasonic
Anthracene				
Toluene	37.2	32.5	61.8	43.0
	25.2	31.9	[23.1]	[1.4]
Avg.	31.2	32.2	61.8	43.0
CH <sub>2</sub> Cl <sub>2</sub>	53.6	33.8	68.2	81.0
	71.3	35.7	106.7	62.5
Avg.	62.5	34.8	87.4	71.8
Pyrene				
Toluene	32.8	30.3	43.4	46.7
	21.4	31.9	[19.4]	[s]
Avg.	27.1	31.1	43.4	46.7
CH <sub>2</sub> Cl <sub>2</sub>	49.5	28.2	76.9	68.3
	31.6	31.2	[37.5]	40.9
Avg.	40.6	29.7	76.9	54.6

<sup>a</sup>s = single datum. Averaging uses the 2 × criterion (see text).

Table 6  
Analysis of data in Table 5

GC	Solvent	Extraction	PAH <sup>a</sup>	Detn 1 (%)	Detn 2 (%)	$\Delta^2$
A	toluene	slurry	A	37.2	25.2	144.0
A	toluene	slurry	P	32.8	21.4	130.0
A	toluene	ultrasonic	A	32.5	31.9	0.4
A	toluene	ultrasonic	P	30.3	31.9	12.6
A	CH <sub>2</sub> Cl <sub>2</sub>	slurry	A	53.6	71.3	313.3
A	CH <sub>2</sub> Cl <sub>2</sub>	slurry	P	49.5	31.6	320.4
A	CH <sub>2</sub> Cl <sub>2</sub>	ultrasonic	A	33.8	35.7	3.6
A	CH <sub>2</sub> Cl <sub>2</sub>	ultrasonic	P	28.2	31.2	9.0
B	toluene	slurry	A	61.8	[23.1]	–
B	toluene	slurry	P	43.4	[19.4]	–
B	toluene	ultrasonic	A	43.0	[1.4]	–
B	toluene	ultrasonic	P	46.7	–	–
B	CH <sub>2</sub> Cl <sub>2</sub>	slurry	A	68.2	106.7	1482.3
B	CH <sub>2</sub> Cl <sub>2</sub>	slurry	P	76.9	[37.5]	–
B	CH <sub>2</sub> Cl <sub>2</sub>	ultrasonic	A	81.0	62.5	342.3
B	CH <sub>2</sub> Cl <sub>2</sub>	ultrasonic	P	68.3	40.9	750.8
Global	Average (%)	$\Sigma \Delta^2$	<i>n</i>	SD (%)		
GC A	36.1	923.2	16	7.6		
GC B	63.6	2575.3	6	20.7		
Slurry	52.3	2389.9	10	15.5		
Ultrasonic	42.7	1108.5	12	9.6		
Toluene	36.5	276.9	8	5.9		
CH <sub>2</sub> Cl <sub>2</sub>	56.0	3221.6	14	15.2		
<i>With GC program A only</i>						
Slurry	40.3	907.7	8	10.7		
Ultrasonic	31.9	15.5	8	1.4		
Toluene	36.5	276.9	8	5.9		
CH <sub>2</sub> Cl <sub>2</sub>	41.9	646.3	8	9.0		

<sup>a</sup>A = anthracene; P = pyrene.

greater than the low value, we have arbitrarily dropped the low value from the averaging process. An analysis of the data in Table 5 is shown in Table 6.

### 3.1. GC/MS Programs A and B

The standard deviation of eight pairs of analyses using program A is  $\pm 7.6\%$ , compared with that for three pairs using program B of  $\pm 20.7\%$ . Inclusion of all seven paired data from program B raises this standard deviation to  $\pm 23.8\%$ . Program A thus shows superior repeatability.

The slurry reflux method affords higher average recoveries (54%) than the ultrasonic method (43%), and with higher average standard deviations between pairs (15.5% vs. 9.6%).

Methylene chloride provides higher average recoveries (57%) than toluene (40%). Average standard deviations are also higher with methylene chloride (15.2% vs. 5.9%).

### 3.2. Program A data only

When program A data are examined separately, the average recovery from methylene chloride extractions (42%) is greater than that from toluene extractions (30%). The average spread between replicate analyses is in line with these figures (methylene chloride 10.1%, toluene 6.4%). The average from reflux slurry (40%) is moderately higher than the average from ultrasonic extraction (32%). However, a sharp difference in repeatability emerges. The average spread between replicate analyses is 14.8% for reflux slurry data, and 1.8% for ultrasonic data.

## 4. Conclusions

Factorial analysis for each of the PAHs shows solvent to exert the largest primary effect (methylene chloride is favored). The largest interaction effect is that between extraction method and GC program (favoring ultrasonic extraction and program A).

Toluene (dielectric constant  $\epsilon = 2.37$ , Hildebrand  $\delta = 8.9$  H) and *o*-xylene ( $\epsilon = 2.57$ ,  $\delta = 8.8$  H) should have similar solvent properties. The significantly higher boiling point of *o*-xylene (144° compared with 111°) might suggest that under atmospheric reflux conditions (reflux slurry and Soxhlet extraction) xylene would prove to be a superior extracting solvent. The opposite was found: toluene is consistently superior to *o*-xylene as an extractant. Furthermore, the lower boiling but more polar methylene chloride (b. 40°,  $\epsilon = 9.08$ ,  $\delta = 9.9$  H) is a still better extractant.

The use of a fairly high temperature ramp (program A, 20°C/min) in the GC/MS analysis does not hurt the analysis; in fact it improves repeatability over parallel analyses at 5–7°C/min (programs B and C).

The reflux slurry procedure provides somewhat higher recoveries (8 to 10% higher with GC method A) than ultrasonic assisted extraction. Hot slurring is the one procedure which may entail mechanical grinding.

Ultrasonic extraction appears to provide the best repeatability. When program A is used to examine the subset of eight pairs of extractions (four pairs using the reflux slurry method and four using the ultrasonic method) the average relative error of the ultrasonic method is 4.4%; that of the reflux slurry method is 26.6%.

Sonication—which deaggregates fly ash clusters and thus appears to provide the most rigorously uniform solvent-particle contact of these methods—is on this basis to be preferred over Soxhlet or slurry methods.

## 5. Future work

In future work we hope to compare these extraction efficiencies with those obtainable using newer technology: supercritical fluid extraction [27], microwave-assisted extraction [28] and automated mechanical soak-and-rinse procedures such as provided by the Soxtec<sup>®</sup> apparatus [29].

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