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UNSUBSTITUTED POLYAROMATIC HYDROCARBONS IN EXTRACTS OF COAL FLY ASH

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ABSTRACT—Extracts of coal fly ash from the solid waste disposal test cell at Montour, PA, were analyzed by isotope dilution mass spectrometry (IDMS) to detect, identify, and quantify trace amounts of selected, unsubstituted polyaromatic hydrocarbons (PAH's). Isotope dilution experiments using deuterated analogs of PAH's demonstrated that the concentrations of benzo[a]pyrene and anthracene were lower than 1 ng/g of fly ash. Maximum concentrations of fluorene, fluoranthene, pyrene, and chrysene were estimated to be 3 ng/g of fly ash. Phenanthrene concentrations ranged from 6 to 38 ng/g of fly ash with a mean concentration of 14 ng/g of fly ash. Test cell phenanthrene concentrations did not correlate with the position, depth, or time of weathering of fly ash samples. An isotopic carrier was not required for any of the selected PAH's except benzo[a]pyrene.

Coal fly ash, the mixture of aluminosilicates and metal oxides obtained from electrostatic precipitators, is the largest volume of industrial solid waste produced in the United States (45 million metric tons per year, Horn, 1988). The Environmental Protection Agency (US EPA) was charged with classifying fly ash as a hazardous or non-hazardous solid waste by the Solid Waste Disposal Act of 1980, which amended the Resource Conservation and Recovery Act of 1976 (RCRA). In 1993, coal fly ash and three other high-volume combustion wastes were exempted from regulation as hazardous wastes under RCRA Subtitle C (US EPA, 1993).

Analyses of both inorganic and organic components are relevant to the hazardous or non-hazardous nature of fly ash. Analyses of inorganic components of fly ash from coal-fired power plants have been conducted since the mid-1970's. Concentrations of trace metals in fly ash and aqueous leachates of fly ash, adsorption of trace metals by fly ash in the power plant, radioactivity in fly ash, physical classifications of fly ash particles, and the suitability of fly ash for road construction and for revegetation have been reported (Beck and Miller, 1980; Coles et al., 1978; Nakaoka et al., 1984; Fruchter et al., 1988; Fruchter et al., 1990; Horn, 1988; Markowski and Filby, 1985; Ripp and Villaume, 1985; Villaume, 1986). Fisher et al. (1979) demonstrated that coal fly ash was mutagenic by the Ames test. Haas and Macak (1985) demonstrated that vegetables grown in 10 percent fly ash contained toxic levels of boron. In contrast to the analyses of inorganic components, little has been published regarding analyses of concentrations of polyaromatic hydrocarbons (PAH's) in coal fly ash (Table 1).

The goals of this research were to detect, identify, and quantify unsubstituted polyaromatic hydrocarbons in samples of coal fly ash from the Montour test cell using the method of isotope dilution mass spectrometry (IDMS). The analyses require that isotopically labeled internal standards and native polyaromatic hydrocarbons are chemically equivalent in the fly ash before being extracted.

MATERIALS AND METHODS

Chemicals and samples—Phenanthrene, mp 100.0–101.5°C (lit. 101°C) (Weast, 1984) was obtained from Eastman Kodak; all other reagent PAH's except chrysene were obtained from Aldrich and were used as received. Chrysene was obtained from Eastman Kodak and was sublimed to yield fine crystals, mp 258–262°C (lit. 255–256°C) (Weast, 1984). Benzo[a]pyrene-D_{12} was obtained from Cambridge Isotope Laboratories and was used as received. A mixture of deuterated PAH's, including fluorene-D_{10}, anthracene-D_{10}, pyrene-D_{10}, and chrysene-D_{12} at concentrations of 5 mg/mL each in benzene-D_6, was obtained from Merck, Sharp, and Dohme Isotopes, Ontario, Canada. Purities of the deuterated PAH's were verified by capillary gas chromatography-mass spectrometry (GC-MS). Isotopic purity of benzo[a]pyrene-D_{12} was determined by probe mass spectrometry. Standard Reference Material #1647, a mixture of priority pollutants, was obtained from the National Institute of Standards and Technology and was used as received. HPLC-grade solvents were obtained from Burdick and Jackson and from Fisher Scientific. Benzene was distilled twice before use; azeotropes of benzene and methanol were distilled twice more. HPLC-grade tetrahydrofuran was used as received. All glassware was cleaned in chromic acid solution before use.

Samples of fly ash were obtained from the Pennsylvania Power and Light Company from the twin, coal-fired, 800 megawatt power plants at Montour, PA, which produce 320,000 metric tons per year of fly ash from electrostatic hoppers. These two units burn medium sulfur coal (1.2% S) from western Pennsylvania by pulverization and tangential firing with 5% excess air at temperatures near 1300°C. The ash content of the coal was 12.5%. The coal-fired units were constructed by Combustion Engineering in 1971 and 1973. The electrostatic precipitators were designed to achieve 99.5% collection efficiency of fly ash particles by mass. Heat exchangers are present in the stack gas stream to preheat combustion air and to cool the stack gas to 140°C

TABLE 1. Published concentrations of polyaromatic hydrocarbons in coal fly ash[a].

Report	Several PAH's[b]	Phenanthrene	Benzo[a]pyrene	Method
Griest and Guerin (1979)	8 to 37	18	35	HPLC
Griest and Guerin (1979)	0.03 to 0.9	0.5	0.03	GC-FID
Harrison et al. (1985)	16 to 93	N/D[c]	N/D	GC-FID
Avery et al. (1986)	0.2 to 10[d]	0.2 to 40	N/D	GC-FID
Morselli and Zappoli (1988)[e]	9 to 69	38	53	GC-FID
Mangani et al. (1987)	0.5 to 3.2	N/M[f]	N/D	GC-MS
Funcke et al. (1988)	0.02 to 0.99	0.4 to 3.1	N/D	GC-MS
Zupancic-Kralj et al. (1991)	0.1 to 10	40	0.2	HPLC

[a] Concentrations in ng/g of fly ash.
[b] Not including phenanthrene and benzo[a]pyrene.
[c] Not detected.
[d] Data from Table 7 of Avery et al. (1986).
[e] "Light ash".
[f] Not measured.

before passing through the electrostatic precipitators. Sulfur trioxide was added to the stack gas to improve collection efficiency of fly ash; sodium salts were not used. Fly ash was conditioned, before being landfilled on site, by addition of waste water from the power plants to achieve 15 volume % water and give maximum stability to the fly ash pile. Moist fly ash was transported by truck, dumped, and rolled into layers 0.3 m high. Fly ash samples were taken from a "test cell," which was designed and built in 1984 for research on fly ash (Fruchter et al., 1988; Fruchter et al., 1990; Ripp and Villaume, 1985; Villaume, 1986). Samples were collected in 1985 and 1986 with coring devices from depths as great as 3 m. In addition to samples from the fly ash test cell, a sample of fly ash was collected in 1986 with a PVC pail from the hopper of the electrostatic precipitator.

Capillary gas chromatography-mass spectrometry (GC-MS)—A Finnigan 4000 quadrupole mass spectrometer with an electron impact/chemical ionization source and INCOS software was used for data acquisition and integration of ion abundances. The gas chromatographic column was an SPB-1 methyl polysiloxane fused silica column (WCOT, Supelco, Inc., State College, PA), 15 m, 0.25 mm i.d., 0.25 μm stationary phase. This column was protected by a 1 m, uncoated guard column (Supelco, Inc.). To obtain reproducibly shaped chromatographic bands and reproducible ion abundances, the guard column was replaced after 20 or 30 injections of fly ash extracts. A Grob-type splitless injector with silylated glass injection liner was used.

Procedures—Three standard stock solutions were prepared. Stock solution I contained 120 μg/mL of fluorene, 120 μg/mL of anthracene, 108 μg/mL of pyrene, 112 μg/mL of chrysene, and 125 μg/mL of benzo[a]pyrene in tetrahydrofuran. Stock solution II contained 114 μg/mL of benzo[a]pyrene-D_{12} in tetrahydrofuran. Stock solution III contained 20 μg/mL each of fluorene-D_{10}, anthracene-D_{10}, pyrene-D_{10}, and chrysene-D_{12} in tetrahydrofuran. Calibration standards were prepared by diluting aliquots of stock solutions.

Samples of 40 g of fly ash were slurried with 30 mL of methanol. Slurried samples of fly ash were doped with aliquots of stock solutions II and III containing 0.96 μg each of fluorene-D_{10}, anthracene-D_{10}, pyrene-D_{10}, and chrysene-D_{12} and 5.6 μg of benzo[a]pyrene-D_{12}. The methanol was then removed from the fly ash by rotary evaporation at 45°C. Doped samples of fly ash were transferred to cellulose Soxhlet thimbles, 33 mm deep by 94 mm high, and extracted with 200 mL of benzene:methanol azeotrope for 42 hours using cycle times between 6 and 14 minutes. Extracts were concentrated by rotary evaporation to approximately 50 mL, dried over 3 g of anhydrous sodium sulfate, and concentrated to approximately 0.5 mL for fractionation.

Preparative thin layer chromatography (TLC) was used to fractionate the concentrated extracts and to obtain polyaromatic hydrocarbons using either of two types of TLC plates: polyethylene terephthalate sheets with 100 μm of silica gel (Eastman Kodak #13181) or glass plates with 1000 μm of silica gel (Analtech silica gel GF). TLC plates were developed with 1:1 benzene:methanol. Bands were visualized by fluorescence during irradiation at 366 μm. The band, which contained polyaromatic hydrocarbons, was removed from the TLC plate, loaded into a 2-cm column, and eluted with tetrahydrofuran under nitrogen pressure. The resulting eluate was concentrated to less than 0.5 mL for analysis.

A reagent blank was prepared by the same procedure used for processing fly ash samples, except that an empty Soxhlet thimble was used. Before extraction of a reagent blank, a 200-mL portion of benzene:methanol azeotrope was doped with aliquots of stock solutions II and III containing deuterated polyaromatic hydrocarbons.

Capillary GC-MS was used to separate and quantify individual polyaromatic hydrocarbons present in samples. The ion source of the mass spectrometer was operated at 300°C and 10^{-6} torr in the electron impact mode at 70 eV. The quadrupole was programmed in three subroutines for analysis of each sample by selected ion monitoring of molecular ions for each polyaromatic hydrocarbon and deuterated analog (Table 2). The cycle time for each subroutine was 1 second. The electron multiplier of the mass spectrometer was operated at 1400 volts, and the amplifier was operated at 1×10^{-8} amps/volt.

The temperature program for the gas chromatograph oven was 50°C isothermal for 2 min, then 50°C to 150°C at 25°C/min, then 150°C to 290°C at 10°C/min, followed by 290°C isothermal for 1.2 min. Calibration standards, reagent blanks, and extracts of fly ash samples (4 μL) were injected in the splitless mode (30

TABLE 2. Ions monitored by GC-MS during Selected Ion Monitoring analysis of coal fly ash extracts.

Subroutine[a]	Ion [m/z]	Dwell time [s]	Analytes
First	113	0.005	paraffins
	149	0.001	phthalates[b]
	166	0.1	fluorene
	176	0.1	fluorene-D_{10}, phenanthrene, anthracene, and diethyl phthalate[b]
	178	0.1	phenanthrene and anthracene
	188	0.1	anthracene-D_{10}
	202	0.1	fluoranthene and pyrene
	212	0.1	pyrene-D_{10}
Second	113	0.005	paraffins, chrysene, and bis(2-ethylhexyl) phthalate[b]
	149	0.001	phthalates[b]
	228	0.4	chrysene and isomers
	240	0.4	chrysene-D_{12}
Third	113	0.005	paraffins and benzo[a]pyrene
	252	0.4	benzo[a]pyrene and isomers
	264	0.4	benzo[a]pyrene-D_{12} and benzo[k]fluoranthene-D_{12}

[a] Selected Ion Monitoring subroutines were called up in consecutive order by the INCOS software for GC-MS analysis of each injected sample.

[b] Diethyl phthalate, di-n-butyl phthalate, and bis(2-ethylhexyl) phthalate were identified in chromatograms of extracts of fly ash. Di-n-butyl phthalate was identified in chromatograms of calibration standards and was present in the septum of the GC injector (Personal communication, T. Rendl. 1989. Alltech Associates, Inc. Applied Science Laboratories at Deerfield, Illinois).

s transfer time at 275°C), and eluted with He carrier gas at 140 kPa (55 cm/s).

Chromatographic bands of individual polyaromatic hydrocarbons were identified from reconstructed ion chromatograms. Bands of polyaromatic hydrocarbons were tentatively identified by absolute elution time and by m/z values. Band assignments were confirmed by comparison with elution times of corresponding deuterated internal standards, which preceded bands of protonated polyaromatic hydrocarbons by 2 to 4 s, or by spiking samples with calibration standards.

Bands observed in reconstructed ion chromatograms were selected for integration when band heights were more than 10 standard deviations above background. Ion abundances were obtained by integrating band areas with INCOS software. Concentrations of selected polyaromatic hydrocarbons in samples of fly ash were calculated from ratios of ion abundances of polyaromatic hydrocarbons and deuterated internal standards.

The accuracy of measurements was verified by GC-MS analysis of NIST Standard Reference Material #1647 using benzo[a]pyrene-D_{12} as an internal standard.

RESULTS AND DISCUSSION

Extraction of polyaromatic hydrocarbons from coal fly ash—The most frequently used methods for extracting polyaromatic hydrocarbons from coal fly ash are Soxhlet extraction, sonication of slurries of fly ash, and liquid extraction under subcritical or supercritical conditions (Avery et al., 1986; Burford et al., 1993; Funcke et al., 1988; Griest and Guerin, 1979; Griest et al., 1986; Harrison et al., 1985; Janssen and Kanij, 1984; Junk and Richard, 1986; Lopez-Avila et al., 1994; Mangani et al., 1987; Morselli and Zappoli, 1988; Soltys et al., 1986; Zupancic-Kralj et al., 1991). Sonication of slurries of fly ash is not quantitative when samples are doped at concentrations from 10 to 6,000 ng/g of fly ash, even when using benzene, toluene, or pyridine (Griest and Guerin, 1979; Griest et al., 1986; Harrison et al., 1985; Janssen and Kanij, 1984; Junk and Richard, 1986). Liquid extraction using toluene is quantitative for polyaromatic hydrocarbons as large as pyrene when samples are doped at concentrations from 2 to 57 ng/g of fly ash. Liquid extraction using benzene is also quantitative when samples are doped at concentrations of 64,500 ng/g of fly ash (Mangani et al., 1987; Soltys et al., 1986). Soxhlet extraction of polyaromatic hydrocarbons using the preferred solvents benzene, toluene, or pyridine is not quantitative when samples are doped at concentrations of 100 ng/g of fly ash or less. Soxhlet extraction is improved and nearly quantitative when samples are doped with polyaromatic hydrocarbons at concentrations of 250 and 1000 ng/g of fly ash (Junk and Richard, 1986). Therefore, Soxhlet extraction of polyaromatic hydrocarbons into benzene, toluene, or pyridine should be quantitative for samples of fly ash doped with chemical surrogates at concentrations >100 ng/g of fly ash.

Deuterated polyaromatic hydrocarbons as chemical surrogates—In this study, deuterated polyaromatic hydrocarbons were used as internal standards during extraction and GC-MS analysis. Deuterated polyaromatic hydrocarbons were assumed to mimic native polyaromatic hydrocarbons during all procedural steps, including equilibration during doping of the fly ash, Soxhlet extraction, TLC fractionation, chromatographic separation, and detection. Several authors have reported concerns, including nonuniform mixing of doped compounds with native polyaromatic hydrocarbons, more complete extraction of doped compounds

TABLE 3. Analytical limits of detection determined by GC-MS analysis of reagent blanks.

Compound	Number of blanks	Mean response [ng/g]	Standard deviation	Limit of detection[a]
Fluorene	4	0.6	0.3	1.6
Phenanthrene	6	2.2	0.9	3.8
Anthracene	8	0.1[b]	0.1	0.4
Fluoranthene	8	0.5[b]	0.3	1.3
Pyrene	8	0.5	0.3	1.3
Chrysene	8	0.5[b]	0.4	1.5
Benzo[a]pyrene	7	0.1[b]	0.1	0.4

[a] Analytical limit of detection at 95 percent confidence level (LOD), equivalent to 40 g of fly ash: LOD = 2 ($t_{0.05,\phi}$) (SD).
[b] Includes one or more blank responses of 0.0 ng/g.

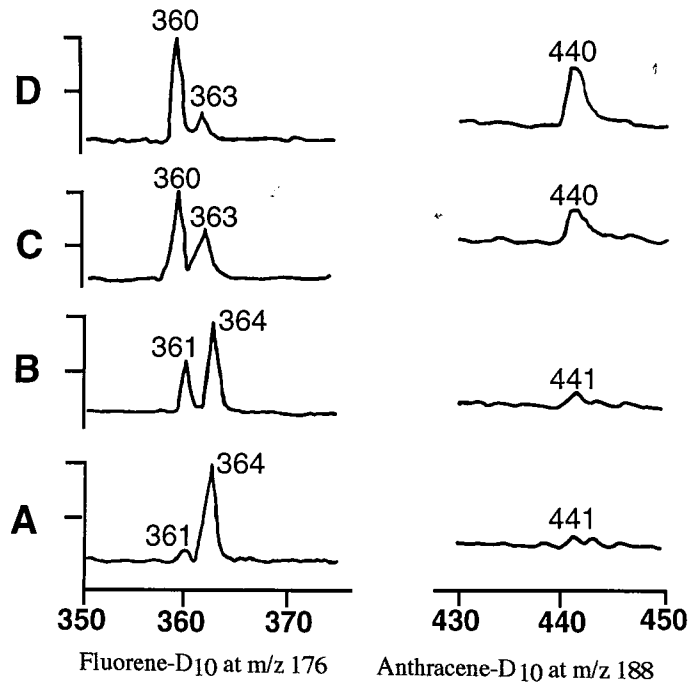

FIG. 1. Mass Chromatograms of deuterated polyaromatic hydrocarbons, doped at concentrations of 1, 3, 10, and 30 ng/g of fly ash. Numbers above chromatographic bands are elution times (s). Chromatographic bands at 360 and 361 s were from molecular ions of fluorene-D_{10}. Bands at 363 and 364 s were attributed to fragment ions of diethyl phthalate. Bands at 440 and 441 s were from molecular ions of anthracene-D_{10}. (A) 1 ng/g, (B) 3 ng/g, (C) 10 ng/g, and (D) 30 ng/g.

than native polyaromatic hydrocarbons, and exchange of hydrogen isotopes from internal standards on fly ash (Griest et al., 1986; Janssen and Kanij, 1984; Soltys et al., 1986). In this study, uniform doping of fly ash was enhanced by adding deuterated polyaromatic hydrocarbons to a slurry of fly ash in methanol, which was removed by rotary evaporation. Even though the methanol was removed slowly and quantitatively, it was not possible to show that doped and native polyaromatic hydrocarbons were in chemical equilibrium because of the heterogeneous nature of the fly ash. Similarly, it was not possible to show that doped and native polyaromatic hydrocarbons were extracted with equal efficiencies.

Several authors have reported biases in which deuterated polyaromatic hydrocarbons were extracted more completely than native polyaromatic hydrocarbons from contaminated soils, marine sediments, and urban particulate matter (Burford et al., 1993; Langenfeld et al., 1995; Lopez-Avila et al., 1994). If there were a bias during the extraction of polyaromatic hydrocarbons from fly ash, the concentrations of native polyaromatic hydrocarbons would be understated. Exchange of hydrogen isotopes has been reported for both tritium-labeled benzo[a]pyrene and deuterium-labeled polyaromatic hydrocarbons on fly ash (Griest et al., 1986; Bolt, 1995). If deuterium exchange were to occur during doping of internal standards, then detection of internal standards would be biased and concentrations of native polyaromatic hydrocarbons would be overstated.

TLC fractionation of the concentrated extracts—Barbas et al. (1996) described the oxidation of phenanthrene on silica gel. Even so, TLC fractionation was used by Karimi-Loftabad et al. (1996) for two-dimensional separations on Eastman Kodak #13181 silica gel. Column chromatography is the preferred method for fractionating polyaromatic hydrocarbons from aliphatic hydrocarbons, phenols, nitrogen-, and sulfur-containing aromatics. Gel permeation chromatography also has been used to remove high molecular weight compounds and lipid fractions (Chui et al., 1984; Fernandez and Bayona, 1992).

Detection of selected polyaromatic hydrocarbons—GC-MS limits of detection of individual polyaromatic hydrocarbons ranged from 12 pg (72 fmol) of fluorene to 120 pg (500 fmol) of chrysene or benzo[a]pyrene, as determined from injections of calibration standards, based on a minimum ion intensity of 3 standard deviations above background. These limits of detection are equivalent to concentrations of fluorene at 0.003 ng/g of fly ash and chrysene or benzo[a]pyrene at 0.03 ng/g of fly ash. Greater sensitivity toward fluorene is attributed to analytical biases in favor of compounds with lower molecular masses. Biases may occur during transfer of dissolved polyaromatic hydrocarbons from the syringe tip to the capillary column (Grob, 1994) or during quadrupole filtration and detection of molecular ions (Message, 1984).

GC-MS limits of detection also were determined for experiments involving the use of deuterated polyaromatic hydrocarbons. Stock solution III, containing deuterated internal standards, was analyzed by GC-MS using selected ion monitoring of molecular ions. The ratio of ion intensities of molecular ions of fluorene-D_{10} to fluorene-$^1H_{10}$ was >700; anthracene-D_{10} to anthracene-$^1H_{10}$ > 740; pyrene-D_{10} to pyrene-$^1H_{10}$ > 840; and chrysene-D_{12} to chrysene-$^1H_{12}$ > 360. Based on these ratios, aliquots of stock solution III, used to dope each sample of 40 g of fly ash, could contain concentrations of fluorene, anthracene, or pyrene equivalent to 0.03 ng/g of fly ash and a concentration of chrysene equivalent to 0.07 ng/g of fly ash. Stock solution II, containing internal standard benzo[a]pyrene-D_{12}, was analyzed by probe insertion; the ratio of ion intensities from molecular ions of benzo[a]pyrene-D_{12} to benzo[a]pyrene-$^1H_{12}$ was >560. Based on this ratio, aliquots of stock solution II, used to dope each sample of 40 g of fly ash, could contain a concentration of benzo[a]pyrene equivalent to 0.3 ng/g of fly ash.

Analytical limits of detection were determined from analyses of reagent blanks, and were equivalent to concentrations of phen-

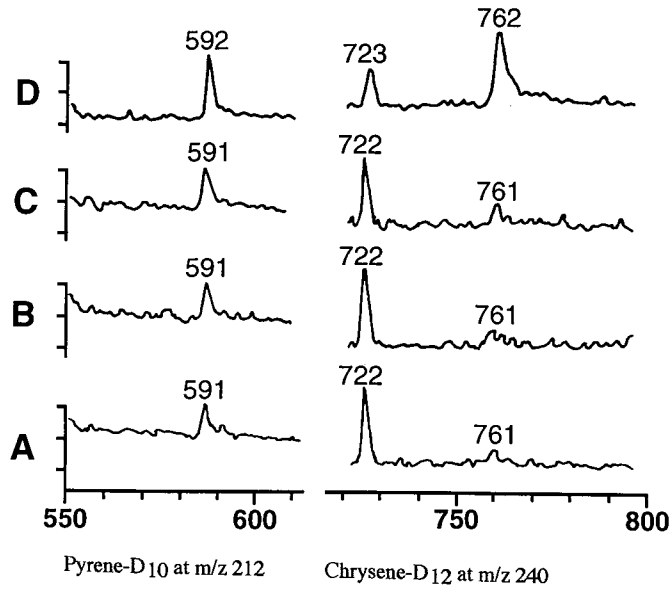

FIG. 2. Mass Chromatograms of deuterated polyaromatic hydrocarbons, doped at concentrations of 1, 3, 10, and 30 ng/g of fly ash. Numbers above chromatographic bands are elution times (s). Chromatographic bands at 591 and 592 s were from molecular ions of pyrene-D_{10}. Bands at 760–762 s were from molecular ions of chrysene-D_{12}. Bands at 722 and 723 s were not identified. (A) 1 ng/g, (B) 3 ng/g, (C) 10 ng/g, and (D) 30 ng/g.

anthrene at 3.8 ng/g of fly ash and concentrations of other polyaromatic hydrocarbons at 0.4 to 1.6 ng/g of fly ash (Table 3).

Analytical limits of detection also were demonstrated by an alternative method. Fly ash was doped with deuterated polyaromatic hydrocarbons as low as 1 ng/g of fly ash, and analyzed by GC-MS to obtain chromatograms with bands of deuterated polyaromatic hydrocarbons having ion intensities greater than 10 standard deviations above background.

Fluorene-D_{10}, anthracene-D_{10}, pyrene-D_{10}, and chrysene-D_{12} were detected in extracts of fly ash doped at concentrations from 1 ng/g up to 30 ng/g of fly ash. It was not necessary to dope the fly ash with any carriers, such as fully protonated polyaromatic hydrocarbons, to detect fluorene-D_{10}, anthracene-D_{10}, pyrene-D_{10}, and chrysene-D_{12} in extracts of fly ash that had been doped at a concentration of 1 ng/g. Figures 1–3 show selected mass chromatograms of molecular ions from bands of internal standards eluted from extracts of fly ash. The analytical method used for analysis of fluorene, anthracene, pyrene, and chrysene would permit detection of these compounds if present at concentrations as high as 1 ng/g of fly ash (Figs. 1 and 2).

Benzo[a]pyrene-D_{12} was not detected in extracts of fly ash doped with benzo[a]pyrene-D_{12} alone at concentrations from 1 ng/g up to 60 ng/g of fly ash. Benzo[a]pyrene-D_{12} was detected in the extract of fly ash doped at 90 ng/g (Fig. 3). Benzo[a]pyrene-D_{12} also was detected in extracts of samples of fly ash doped with both benzo[a]pyrene-D_{12} at a concentration of 1 ng/g and benzo[a]pyrene at 125 ng/g. In the presence of benzo[a]pyrene carrier, the band for benzo[a]pyrene-D_{12} was detected at a concentration of 1 ng/g of fly ash (Fig. 4). In the absence of a carrier, benzo[a]pyrene-D_{12} could not be detected at concentrations as high as 60 ng/g of fly ash. The analytical method used for analysis of benzo[a]pyrene in fly ash, in which stock solution

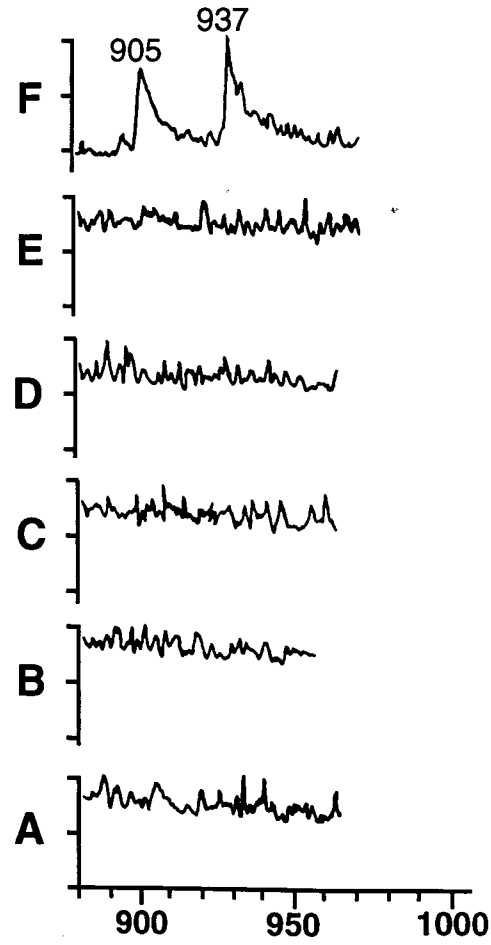

FIG. 3. Mass Chromatograms of deuterated polyaromatic hydrocarbons, doped at concentrations of 1, 3, 10, 20, 30, 60, and 90 ng/g of fly ash. Numbers above chromatographic bands are elution times (s). Chromatographic bands at 905 and 937 s were from molecular ions of benzo[k]fluoranthene-D_{12} and benzo[a]pyrene-D_{12}, respectively. (A) 1 ng/g each, (B) 3 ng/g each, (C) 10 ng/g each, (D) 30 ng/g each, (E) 10 ng/g b[k]f-D_{12} and 60 ng/g b[a]p-D_{12}, and (F) 20 ng/g b[k]f-D_{12} and 90 ng/g b[a]p-D_{12}.

II was used to dope samples at a concentration of 140 ng/g of fly ash, would permit detection of native benzo[a]pyrene if it were present at concentrations as high as 1 ng/g of fly ash.

Quantitation of selected polyaromatic hydrocarbons—Concentrations of selected polyaromatic hydrocarbons were determined by isotope dilution of extracts of nine samples of fly ash from the Montour test cell (Table 4). The precision of phenanthrene analysis was determined to be ±1 ng/g of fly ash, based on analysis of extracts of four identical fly ash samples from the Montour test cell. Precisions achieved for fluorene, fluoranthene, pyrene, and chrysene were apparently less than ±1 ng/g of fly ash, but their concentrations were below analytical limits of detection. Concentrations of anthracene and benzo[a]pyrene also were below analytical limits of detection.

The results of fluorene, anthracene, fluoranthene, pyrene, chrysene, and benzo[a]pyrene analyses by IDMS were consistent with the model of Natusch et al. (1978), in which polyaromatic

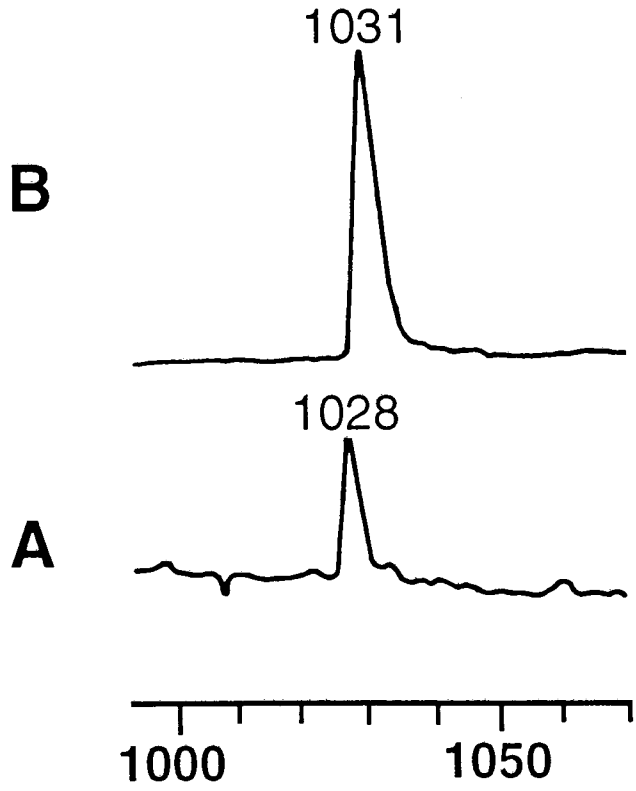

FIG. 4. Mass chromatograms of benzo[a]pyrene-D_{12}, doped at a concentration of 1 ng/g of fly ash, in the presence of benzo[a]pyrene, doped at 125 ng/g. Numbers above chromatographic bands are elution times (s). (A) benzo[a]pyrene-D_{12} at m/z 264, (B) benzo[a]pyrene at m/z 252.

TABLE 4. Summary of concentrations of selected polyaromatic hydrocarbons determined by IDMS analysis of fly ash from the Montour test cell.

Year sampled	Core	Sample depth [m]	Phenanthrene [ng/g of fly ash]	Polyaromatic hydrocarbons other than phenanthrene[a] [ng/g of fly ash]
1985	B	0.6	9	<3[b]
	B	1.5	6	<3
	A	1.5	38	<3
	A	3.0	12	<3
1986	B	1.2	8[c]	<3
	B	1.2	10[c]	<3
	B	1.2	10[c]	<3
	B	1.2	9[c]	<3
	B	3.0	28	<3

[a] Fluorene, anthracene, fluoranthene, pyrene, chrysene, and benzo[a]pyrene.

[b] Maximum concentrations at the 95 percent confidence level were 2.9 ng/g for fluorene, 2.3 ng/g for anthracene, 3.0 ng/g for fluoranthene, 2.7 ng/g for pyrene, 2.9 ng/g for chrysene, and 2.3 ng/g for benzo[a]pyrene.

[c] Replicate samples were used to obtain the precision of the method, which was ± 1 ng/g of fly ash for phenanthrene.

hydrocarbons were calculated to be too volatile to condense onto fly ash particles in the stack of the power plant. At a temperature of 140°C, the model of Natusch et al. (1978) predicted that less than 50 percent of the pyrene would be adsorbed onto particulates. These results also were consistent with the results of Funcke et al. (1988), in which 97 percent of polyaromatic hydrocarbons were found in the gas phase in electrostatic precipitators at temperatures between 105°C and 131°C. For the present samples at Montour, the effluent temperature in the exhaust train was at least 140°C prior to electrostatic precipitation.

The concentrations of fluorene, anthracene, fluoranthene, pyrene, chrysene, and benzo[a]pyrene determined by IDMS in extracts of fly ash from the Montour test cell were most similar to the data reported by Mangani et al. (1987), who found concentrations between 0.5 and 3.2 ng/g of fly ash and to data reported by Funcke et al. (1988), who found concentrations between 0.02 and 0.99 ng/g of fly ash. Griest and Guerin (1979) also found low concentrations of polyaromatic hydrocarbons when using GC-FID. Avery et al. (1986) and Zupancic-Kralj et al. (1991) found concentrations between 0.1 and 10 ng/g of fly ash. The only exception was the concentration of fluorene found by Zupancic-Kralj et al. (1991), which was 1300 ng/g of fly ash. Concentrations of polyaromatic hydrocarbons analyzed by Harrison et al. (1985) and Morselli and Zappoli (1988) were one or two orders of magnitude higher than those found by the other authors (Table 1).

Concentrations of phenanthrene ranged from 6 to 38 ng/g in extracts of 9 fly ash samples from the Montour test cell, and always were higher than the analytical limit of detection for phenanthrene, with a mean concentration of 14 ng/g of fly ash. In the present study, no correlations were found between concentrations of phenanthrene in the Montour test cell and descriptive features of the test cell, including location of the core, depth of the sample taken from the core, the time elapsed between building the test cell and coring, and whether or not the samples were dried to constant weight before analysis. There was no evidence of a concentration gradient for phenanthrene, which might have suggested movement of phenanthrene through the test cell. In previous studies, other authors found concentrations of phenanthrene from 0.2 to 40 ng/g (Avery et al., 1986; Funcke et al., 1988; Griest and Guerin, 1979; Morselli and Zappoli, 1988; Zupancic-Kralj et al., 1991).

Results of analyses of phenanthrene by IDMS were not consistent with the model of Natusch et al. (1978) described above. Phenanthrene, with mp 101°C and bp 340°C, is more volatile than pyrene, with mp 156°C and bp 393°C (Weast, 1984); therefore, it is unlikely that phenanthrene would condense onto particulates in the absence of pyrene and other, heavier polyaromatic hydrocarbons. Selective survival of only one polyaromatic hydrocarbon during fossil fuel combustion has not been reported in the literature. Funcke et al. (1988) found concentrations of phenanthrene from 0.4 to 3.1 ng/g of fly ash, along with fluoranthene, pyrene, chrysene, and benzofluroene isomers. Schmidt (1987) and Grimmer and Pott (1983) have described mixtures of polyaromatic hydrocarbons that were commonly produced during combustion, including phananthrene, anthracene, fluoranthene, pyrene, and chrysene.

Deposition of phenanthrene onto fly ash must occur at some processing step after combustion. Analysis of a single sample of

fly ash taken directly from the hopper of the electrostatic precipitator yielded a concentration of 34 ng/g of fly ash, similar to concentrations of phenanthrene in extracts of fly ash from the test cell. This suggests that any deposition of phenanthrene onto fly ash occurred before or during electrostatic precipitation.

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