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THE KINDS & QUANTITIES OF ORGANIC COMBUSTION PRODUCTS IN SOLID & LIQUID WASTES FROM A COAL FIRED POWER STATION (NTIS) - (USED AS A REFERENCE IN OU 1 RI)

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The Kinds and Quantities of Organic Combustion Products in Solid and Liquid Wastes from a Coal-Fired Power Station

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THE KINDS AND QUANTITIES OF ORGANIC COMBUSTION PRODUCTS IN SOLID AND LIQUID WASTES FROM A COAL-FIRED POWER STATION

ABSTRACT

Organic compounds recovered from solid and liquid wastes from the Four Corners Coal-Fired Power Station at Fruitland, New Mexico, were analyzed. Total organic carbon, total extractable hydrocarbons, and identities and quantities of aliphatic and aromatic hydrocarbons are reported. Organic constituents in water and particulate samples were extracted into organic solvents and characterized by gas chromatography (GC) and gas chromatography, mass spectrometry (GC MS). In addition, concentrations of inorganic elements and ions present in the scrubber water and in the acid-soluble fraction of particulate material in and nearby the Four Corners Plant were determined.

Organic compounds in acidic, basic, and neutral fractions of extracts of liquid waste were low in molecular weight and included alkanes, alcohols, ketones, and phthalates. Organic constituents in extracts of solid waste included large numbers of aliphatic and aromatic compounds. A series of normal C_{15} to C_{30} paraffins was found in the aliphatic fractions. The aromatic fractions contained compounds of one, two, three, and four rings. No compounds containing more than four rings were identifed. However, our studies on recovery of radiolabeled naphthalene and benzo(a)pyrene added to scrubber fly ash indicate that polynuclear aromatic hydrocarbons containing more than four rings are poorly recovered, and absence of these compounds in the GC MS analysis does not imply that they are not present in the sediment.

Comparison of organic constituents in extracts of fly ash from the wet scrubber and the electrostatic precipitator was made. Large numbers of compounds were identified; few were common to both extracts.

INTRODUCTION

The Power Plant and Industrial Fuel Act of 1979 is designed to minimize the use of petroleum and natural gas and to emphasize the use of coal. Implementation of this act will increase the pollutant load to local environments from the combustion products of coal. Fly ash and bottom ash will be produced in greater amounts. This is of concern because these ashes are enriched in trace metals and contain potentially carcinogenic organic combustion products such as polynuclear aromatic hydrocarbons (PAHs). The

amount of unsubstituted PAHs has decreased in soil sediments in the last 30 y, probably because of the change from coal to fuel oil (Wakeham and Farrington, 1960).

The organic by-products of coal combustion are commonly grouped into three classes: acidic, basic, and neutral compounds. The acidic compounds include phenols, which are generally water soluble and toxic but not mutagenic. The basic compounds constitute a small percentage of the total, but include a group of highly toxic and potentially mutagenic compounds such as aromatic amines and heterocyclic nitrogen compounds. The neutral compounds constitute the largest percentage of the combustion products and include the PAHs, many of which are carcinogenic.

Emission-control devices are effective in reducing the total suspended solids discharged from the stack. Generally, $<5\%$ of the airborne particles produced are released in the plume. Because each type of emission-control device captures some particle sizes more effectively than others, the size distribution of particles remaining in the plume differs for electrostatic precipitators (ESPs) and wet scrubbers (WSs). A greater proportion of the mass of aerosols from WSs occurs in particles of respirable size than those from ESPs (Ondov et al., 1979a).

The availability to adjacent ecosystems of the organic and inorganic pollutants associated with fly ash depends on the discharge pathway of the pollutants. Plume particles are dry- or wet-deposited on aquatic and terrestrial ecosystems, both on and adjacent to the station. Fly ash collected by ESPs and WSs is deposited in holding ponds or pits. Fly ash collected by WSs is of special interest because these devices are designed to remove both gaseous and particulate material, require large volumes of water, and operate at relatively low temperatures. The large surface area and temperature drop provided by scrubbers may result in effective capture of fly ash particles, SO_2, PAHs, and other organic combustion products.

Our objective was to characterize the kinds and quantities of organic combustion products in solid and liquid wastes released from a coal-fired power station. We analyzed WS and ESP fly ash and waters collected from different components of the WS fly-ash disposal system. The information obtained will be used to determine the impact on man and the environment of potentially hazardous organic combustion products released in power production.

MATERIALS AND METHODS

DESCRIPTION OF POWER STATION

The Four Corners Coal-Fired Power Station, located in northwestern New Mexico, consists of five steam electric-generating units that burn pulverized coal and have a combined power capacity of 2170 MW. Coal burned at the plant comes from the nearby Navajo Mine. The coal is classified as subbituminous with an average heat content of 9000 BTU/lb, an average ash content of 22.5%, and an average sulfur content of 0.67%. Daily coal consumption averages 18,500 ton (28,000 ton maximum at peak output). Atmospheric emissions from the plant are controlled by Venturi WSs with rated efficiencies of 99.6% (Units 1 through 3) and by ESPs with rated efficiencies of 97.6% (Units 4 and 5). Two of the units fitted with WSs contain 180-MW generators; the third unit has a 240-MW generator. Each of the units fitted with ESP collectors has a 750-MW capacity. Water for the WSs is obtained from Morgan Lake, a 1260-acre man-made reservoir fed via aqueduct from the San Juan River.

Ash material from coal combustion is handled in one of two ways. Ash collected by ESPs is trucked to the Navajo Mine and buried in the scar left from the mining operation. Ash material collected by the Venturi WSs is pumped to the distribution tank where slaked lime (calcium hydroxide) is added. The slurry is pumped next to the thickener tank where water is continuously removed and recycled to the Venturi WSs (Fig. 1). The slurry from the thickener tank is pumped through a trench to ash settling ponds located adjacent to the power plant; these ponds support little or no life. Water overflows from the ash ponds into the duck pond and ultimately into Chaco Wash. Water leaving the plant site ultimately returns to the San Juan River via groundwater and surface water systems. Considerable vegetation is found in and around the duck pond and Morgan Lake.

COLLECTION OF SAMPLES

Samples were collected at the Four Corners Power Station on March 7 and December 12, 1979. Samples collected in December were greater in number and larger in size than those taken in March (Table 1).

Water samples were filtered through precombusted glass-fiber filters, preserved by the addition of 25 mL of methylene chloride per liter, and stored in 4-L amber glass bottles at room temperature. Particulate material was taken from the top 5 cm with a

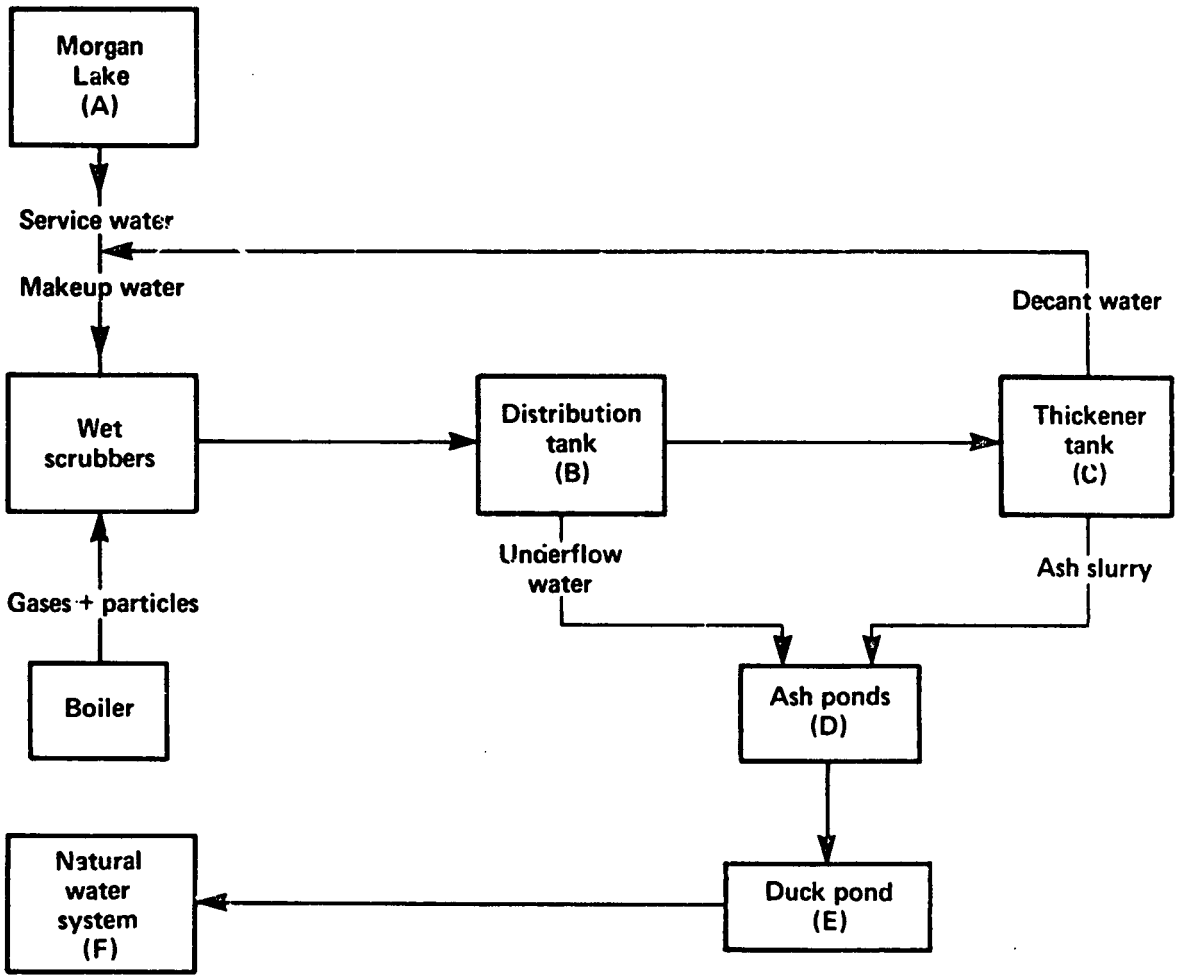

Figure 1. The input and output of water to the Venturi wet scrubbers with locations of sampling sites (A-F).

stainless steel scoop. Obvious organic matter (leaves, twigs, and grass) as well as large stones were discarded. The material was then packed into 1-L amber glass bottles and stored at 0 to 4°C.

REAGENTS AND PREPARATION PROCEDURES

All reagents were used as received. Methylene chloride (distilled in glass) was obtained initially from Burdick and Jackson (Muskegon, MI) and later from MCB Manufacturing Chemists, Inc. (Cincinnati, OH) (LiChrosolv). Pentane and hexane (distilled in glass) were supplied by Burdick and Jackson. Methanol, toluene, scintillation cocktail

Table 1. Water and particulate material collected at the Four Corners Power Station.

Sample[a]	March 7, 1979 Volume (L)	March 7, 1979 pH	December 12, 1979 Volume (L)	December 12, 1979 pH
Morgan Lake water	3.8	8.2	23	8.1
Scrubber water (distribution tank)	52.9	5.6[b]	23	8.2
Ash pond inlet water	3.7	6.1	23	8.6
Duck pond outlet water	7.6	8.5	23	8.2
Seepage water through ash pond levee	3.8	8.2	--	--
Electrostatic precipitator fly ash	1	--	15	--
Scrubber fly ash (distribution tank)	1	--	1.9	--
Ash pond bottom sediment	1	--	1.9	--
Duck pond bottom sediment	1	--	1.9	--
Ash pond levee sediment	--	--	1.9	--
Morgan Lake sediment	--	--	1.9	--

[a] All water samples were filtered through glass fiber.

[b] Sample collected from intake area where no addition of lime had occurred.

(Universe LSC), hydrochloric acid (Ultrex), and sodium hydroxide (Ultrex) were purchased from J. T. Baker Chemical Company (Phillipsburg, NJ) (Baker Analyzed Reagent). The ^{14}C-labeled phenol, naphthalene, and benzo(a)pyrene (BaP) were purchased from Amersham Corporation (Arlington Heights, IL).

All glassware and other implements were washed thoroughly with detergent and rinsed repeatedly with tap water, distilled water, methanol, and finally methylene chloride. All bottles were fitted with Teflon-lined screw caps.

Glass-fiber filters of nominal 1-μm pore size (Gelman Instrument Co., Ann Arbor, MI) were used in all filtering procedures. Alumina CC-10, 100 to 200 mesh, activity grade 4 was purchased from Mallinckrodt Inc. (Paris, KY). Silica Gel 60, 70 to 230 mesh ASTM came from MCB Manufacturing Chemists, Inc.

ANALYSES FOR ORGANIC CARBON

Analyses for organic carbon were performed with an Oceanography International Corporation Carbon Analyzer (College Station, TX) by the standard persulfate oxidation method (Strickland and Parsons, 1972). Untreated water samples were analyzed for total organic carbon content. In addition, samples filtered in the field through glass-fiber filters were analyzed for soluble and particulate organic carbon. To determine organic carbon content of sediment, 50-mg predried triplicate samples were analyzed in the carbon analyzer.

ANALYSES OF EXTRACTABLE HYDROCARBONS

Water samples collected in March were placed in a 12-L separatory funnel at room temperature and extracted at pH 5.6, the pH of the sample at collection. Total extractable hydrocarbons were removed with three 100-mL portions of methylene chloride. The combined extracts were dried over sodium sulfate and concentrated by rotary evaporation and then further condensed to 0.1 mL with a stream of cooled nitrogen gas.

The water samples collected in December were separated into acidic, basic, and neutral fractions by the procedure outlined in Fig. 2. Each of the three dried methylene chloride extracts was condensed to 0.1 mL.

All samples of wet sediment and fly ash were freeze-dried (Unitrap II, Virtis, Gardiner, NY) before treatment. Three different analysis regimes were followed. The samples collected in March were extracted for 120 h in a Soxhlet thimble (33- x 80-mm cellulose) using refluxing methanol-toluene (72:28). This procedure resulted in the esterification of organic acids. Because the peaks of some esters could mask those of PAHs, this procedure was discontinued.

The first group of samples collected in December was extracted by rotary shaking using a model 6150 Eberback Shaker (Ann Arbor, MI). Samples included fly ash and sediment collected from different components of the WS fly-ash disposal system. The 25-g aliquots of particulate material were shaken with 100 mL of methylene chloride-toluene (1:1) at 220 rev/min for 5 h. Particles were separated from the supernatant by centrifugation at 2500 rpm and the supernatant decanted into amber bottles. The decanted liquid was used to extract a new sediment sample and fresh solvent was used to reextract the remaining sediment. This was repeated three times. All extracts were filtered through glass-fiber filters, concentrated to 25 to 50 mL by rotary evaporation, and further condensed to 100 to 500 µL under cooled nitrogen gas.

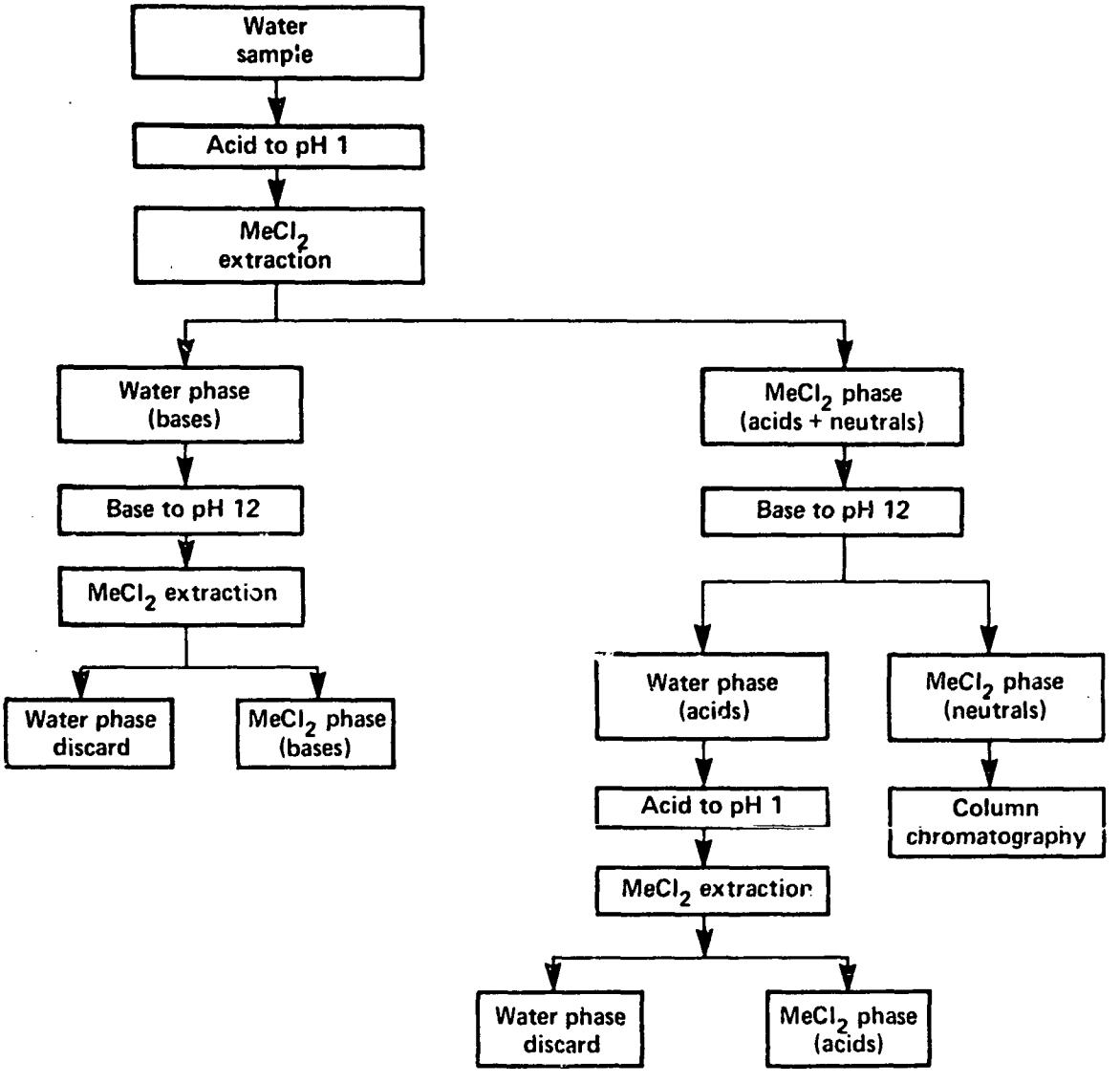

Figure 2. Flow diagram for acid-base-neutral extraction.

After storage for 1-1/2 y, a second group of the samples collected in December was extracted using a combination of solvents and equipment found to be effective in recovering naphthalene and BaP that were added separately to fly ash in different experiments (Appendix A). Rotary shaking and sonication methods were compared as to their effectiveness in removing these compounds from the ash. A model W185E Branson Sonifier (Danbury, CO) fitted with a model H419 microtip (Heat Systems, Plainview, NY) was used as the ultrasonic generator. Samples extracted included WS fly ash from the distribution tank, ESP fly ash from the hopper, and sand that had been ashed at 500°C for

2 d. Before the samples were extracted, they were spiked with internal standards of d_{10}-anthracene and 1-chloronaphthalene that were dissolved in acetone. The mixture was homogenized using the sonifier without a microtip, rotary evaporated, and then freeze-dried. The 25-g aliquots were shaken with 100 mL of methylene chloride at 220 rev/min for 5 h, centrifuged at 2500 rpm, and then the supernatant was decanted and filtered. Each aliquot was extracted 3 times, and a total of 12 aliquots (300 g) was processed. The supernatants from all aliquots were combined and rotary evaporated to approximately 25 mL. The volume was reduced to 0.5 mL by evaporation with cooled nitrogen gas and then stored in Teflon-lined screw cap vials at -30°C until analysis.

All aliquots of each sample were further extracted using the ultrasonic generator. We added 50 mL of dried toluene-methanol (80:20) to the residue from the methylene chloride extractions. The sample was sonicated with a microtip at >100 W for 3 min; the mixture centrifuged; and then the supernatant removed, filtered, and rotary evaporated to approximately 25 mL. Three extractions were again performed. Because methanol is undesirable for gas chromatography (GC) and gas chromatography, mass spectrometry (GC MS) analysis, the rotary-evaporated samples were carefully evaporated to dryness and then reconstituted to 0.5 mL with methylene chloride before storage at -30°C.

COLUMN CHROMATOGRAPHY

Different classes of compounds in extracts of particulate materials from samples obtained in March were separated by alumina-silica-gel column chromatography using a procedure similar to that of Giger and Blumer (1974). Alumina (100 to 200 mesh) and silica gel (100 to 200 mesh) were activated for 24 h at 400 and 125°C, respectively. The 8-g portions of each adsorbent were deactivated with water (1.5%) and allowed to equilibrate for a minimum of 24 h before use.

The glass columns were 1 cm (i.d.) x 30 cm with a glass frit, Teflon stopcock, and 100-mL solvent reservoir. Silica gel was packed into the column first, followed by alumina. The total bed volume ranged from 25 to 28 mL. Mixtures of standards were separated in four fractions and identified by GC.

All chromatography columns were eluted in four steps.

Fraction 1. One bed volume of 100% n-hexane. Aliphatic hydrocarbons are eluted in this fraction.

Fraction 2. Two bed volumes of 40% methylene chloride in n-hexane. One- and two-ring aromatic hydrocarbons are eluted in this fraction.

Fraction 3. One bed volume of 100% methylene chloride. Esters and PAHs with three or more rings are eluted in this fraction.

Fraction 4. Two bed volumes of 100% methanol. The asphaltenes and polar components are eluted in this fraction.

Extracts of particulate material from samples collected in December were chromatographed on smaller columns (12.5 mm) that contained only silica gel. Fractions 2 and 3 were combined and analyzed as the aromatic fraction.

GAS CHROMATOGRAPHY

Quantitative separations of hydrocarbon mixtures were performed on Hewlett-Packard model 5840A and 5880 gas chromatographs (Palo Alto, CA). The instruments were fitted with fused silica, wall-coated 25-m SP2100 and 25-m DB-5 columns (0.25-mm i.d.), respectively, from J. and W. Scientific (Rancho Cordova, CA). The oven was programmed to hold at 35°C for 5 min, then increase from 35 to 260°C at 3°C/min, and hold at 260°C for 20 min. The carrier gas was helium and the flow rate was 3.2 cm^3/min. Quantitative information is calculated from response factors determined by analysis of known standard compounds. Four different groups of standards were used to establish response factors for quantifying compounds extracted from the sediment samples. The first group of standards was a mixture of nine PAHs that ranged in size from that of naphthalene to benzo(a)pyrene. A chromatogram of this standard appears in Appendix B. Repeated injections of these standards in the gas chromatograph produced coefficients of variation of ≤ 0.04. The second group of standards was a mixture of eight phthalates ranging in molecular weight from 194 to 390. The coefficient of variation after several injections was also ≤ 0.04. A mixture of four paraffins ranging from C_{16} to C_{22} comprised the third group; these produced coefficients of variation of ≤ 0.03. The final standard was 1-chloronaphthalene, used also as an internal standard by adding known concentrations to the sediments before extraction. Coefficient of variation for this compound was ≤ 0.03. An average response factor was determined from all of the groups of standards and used in the Hewlett-Packard model 3350 Laboratory Automation System to quantify GC peaks. Because the response to a column for a given concentration of a compound is not the same for compounds of different molecular weight, the use of an average response factor generates bias in the data. The average response factor value used would tend to underestimate the concentration of high molecular-weight compounds by up to 18% and overestimate some low molecular-weight compounds by approximately 10%. All chromatograms and data reported in tables list quantities based on average response factors.

GAS CHROMATOGRAPHY, MASS SPECTROMETRY

Major components in the Four Corners samples were identified using the Hewlett-Packard 5985B GC MS system. The GC conditions and column type were the same as for the 5880 system described above. The mode of ionization was by electron impact--70-eV. The ion-source temperature was 200°C, and the scan cycle time was 1.5 s.

Compounds were identified by comparing mass spectra acquired during a run with reference spectra contained in a library. The Wiley and National Bureau of Standards libraries we have on file contain over 40,000 different spectra for organic compounds. The computer searches these libraries for the spectra that best match those contained in the run. Visual comparisons of the unknown and reference spectra allows the analyst to identify most of the major components in the sample.

A technique known as reverse searching allows the analyst to search the entire run for specific compounds. Alteration of the search parameters allows the components to be detected in the presence of contaminants or noise.

The molecular ion of a compound may be plotted against run time to determine the presence or absence of a compound at a particular time in the run. The presence of a particular ion is only a fair indicator of the presence of a given compound, but the absence of the ion is strong evidence against the presence of that compound. This technique was used to detect the presence of trace levels of some PAHs in a sample.

The relative quantities of a group of PAHs required for detection by GC and GC MS were examined (see Appendix B). The amounts of the individual compounds needed for detection differed by a factor of 20.

ELEMENT AND ION ANALYSES

The elements in the scrubber water were analyzed by Inductively Coupled Plasma, Optical Emission Spectroscopy (ICP OES). Acidified samples in duplicate were subjected to the automated system consisting of a model 975 Jarrell-Ash Atomcomp spectrometer with a PDP-81E minicomputer and a plasma source (Peck et al., 1979).

The anions in the scrubber water were measured by ion chromatography on a Dionex model 10 ion chromatograph (Sunnyvale, CA). The principle of ion chromatography is described by Mulik and Sawicki (1979).

RESULTS

QUANTITY AND IDENTITY OF ORGANIC COMPONENTS

Organic Carbon

Concentrations of organic carbon in water samples collected from different sampling sites in December were similar; the greatest differences with site were found in concentrations of particulate organic carbon (Table 2). These concentrations are in the range reported for water from many natural sources.

The total organic carbon content in sediment samples ranged from 170 to 440 ppm. The lowest concentration was found in fly ash collected from the ESP, the highest in sediment collected from a levee near the ash pond.

Extractable Hydrocarbons in Water Samples

Neutral extractable hydrocarbons were measured in samples of water collected from different sites of the WS fly-ash disposal system in March and December (Table 3). Although values are similar during the two collection periods, factors that could contribute to some differences include coal combustion rate and water flow rate in the waste-disposal system.

Organic compounds in the scrubber water collected in March from the distribution tank were identified (Table 4). Total extractable hydrocarbons were low (7.9 ppb) and analysis of the extract by GC showed that a large number of the compounds were present at concentrations less than one part per trillion (ppt). Compounds present that are on the Environmental Protection Agency Priority Pollutant List are naphthalene, diethyl phthalate, di-n-butylphthalate, and dioctylphthalate.

The quantities of extractable hydrocarbons in the acidic, basic, and neutral fractions of the water samples collected in December differed with the sampling site (Table 5 and Fig. 3). The neutral fraction contained phthalates, some aliphatic compounds, and derivatives of cyclohexane (Table 6). Many neutral compounds were found also in the acidic and basic fractions because factors other than pH affect the separation. The acidic fraction contained mostly phthalates (Table 7), whereas the basic fraction contained the oxide, alcohol, and ketone of cyclohexene as well as xylenes and phthalates (Table 8). No PAHs larger in molecular weight than naphthalene were detected in any of the water samples. The 4-L water samples were probably insufficient in size to permit identification of compounds present in very small quantities.

Table 2. Mean organic carbon concentration in ppm in water and particulate material collected at the Four Corners Power Station on December 12, 1979.[a]

Sample and site	DOC[b]	POC[c]	DOC + POC	TOC[d]
Water				
Scrubber water (filtered in the field)	2.8	--	--	--
Scrubber water (filtered at lab)	2.2	--	--	--
Ash pond	3.3	2.4	5.7	4.4
Duck pond	3	2	5	4.9
Morgan Lake	3.4	0.8	4.2	4.7
Particulate material				
Electrostatic precipitator fly ash	--	--	--	170
Scrubber fly ash (from distribution tank)	--	--	--	260
Ash pond	--	--	--	330
Duck pond	--	--	--	400
Levee	--	--	--	440
Control soil	--	--	--	360

[a] Values given are means of three samples. Fractional standard deviation $\leq$ 0.03.

[b] Dissolved organic carbon (DOC) is the organic carbon in the filtrate.

[c] Particulate organic carbon (POC) is the organic carbon captured on the filter.

[d] Total organic carbon (TOC) is the organic carbon in the untreated water that was determined in a separate analysis and should be equal to the sum of the DOC and POC.

Table 3. Neutral extractable hydrocarbons in water samples collected from the Four Corners Power Station in March and December 1979.

Sample site	Hydrocarbons (ppb) March	Hydrocarbons (ppb) December
Scrubber water (from distribution tank)	7.9	16
Ash pond inlet	23	16
Duck pond outlet	19	23
Seepage from levee	17	NA[a]
Morgan Lake	15	22

[a] Not analyzed.

Table 4. Organic compounds identified in extracts of scrubber water collected from the distribution tank at the Four Corners Power Station on March 7, 1979.

Molecular weight	Formula	Name
82	C_6H_{10}	Cyclohexene
92	C_7H_8	Toluene
98	$C_6H_{10}O$	Cyclohexene oxide
106	C_7H_{10}	Ethylbenzene
106	C_7H_{10}	o-Xylene
104	C_8H_8	Styrene
96	C_6H_8O	2-Cyclohexenone
120	C_9H_{12}	1,2,4-Trimethylbenzene
120	C_9H_{12}	Isopropylbenzene
128	$C_{10}H_8$	Naphthalene
222	$C_{12}H_{14}O_{14}$	Diethylphthalate
--	--	(Alkane)[a]
278	$C_{16}H_{22}O_4$	Isobutylphthalate
--	--	(Alkane)[a]
278	$C_{16}H_{22}O_4$	Di-n-butylphthalate
266	$C_{16}H_{26}O_3$	Epi-juvabione
390	$C_{24}H_{38}O_4$	Dioctylphthalate

[a] Alkane tentatively identified by ion pattern, but exact molecular weight and formula not determined.

Extractable Hydrocarbons in Farticulate Material Samples

Total extractable hydrocarbons measured in samples of particulate material collected from different parts of the WS fly-ash disposal system differed greatly with site (Table 9). The duck pond sediment was obtained from an area of heavy vegetation, resulting in significantly higher hydrocarbon concentrations.

Organic compounds recovered in the aromatic fractions from the ash pond fly ash collected in March were identified by GC MS (Tables 10 and 11). Samples from the December collection that were extracted included material from the distribution tank and downstream sites. The concentrations and kinds of organic compounds in the extracts

Table 5. Total extractable hydrocarbons (neutral, acidic, and basic fractions) in water samples collected at the Four Corners Power Station on December 12, 1979.

Sample site	Extracted fraction	Water samples: Hydrocarbons (ppb)	Water samples: Number of compounds > 250 ppt
Scrubber water (from distribution tank)	Neutral	16	20
	Acidic	17	32
	Basic	12	8
Ash pond inlet	Neutral	16	31
	Acidic	19	23
	Basic	12	26
Duck pond outlet	Neutral	23	30
	Acidic	19	34
	Basic	19	8
Morgan Lake outlet	Neutral	22	38
	Acidic	13	14
	Basic	20	19

obtained by rotary shaking differed with the collection site (Table 12). Large numbers of normal paraffins, a group of phthalates, and a few PAHs were found.

Extracts of scrubber fly-ash sediment collected in December from the distribution tank were separated by column chromatography into aliphatic, aromatic, and polar fractions. Compounds identified by GC MS in these fractions are large in number and diverse in structure (Tables 13-15).

Comparison of Organic Compounds in Electrostatic Precipitator and Wet Scrubber Fly Ash

Large numbers of compounds were extracted from WS and ESP fly ash by a combination of shaking and sonicating (Table 16, Figs. 4 and 5). Some compounds were extracted easily by just shaking whereas others were removed better by sonicating. Characteristic of the GC scan of the scrubber fly-ash extract was a hump at retention times between 45 and 60 min (Fig. 5a). These terpene-type compounds (molecular weight 268 to 274), which are not present in the ESP fly ash, comprise about one third of the total concentration of hydrocarbons extracted from WS fly ash.

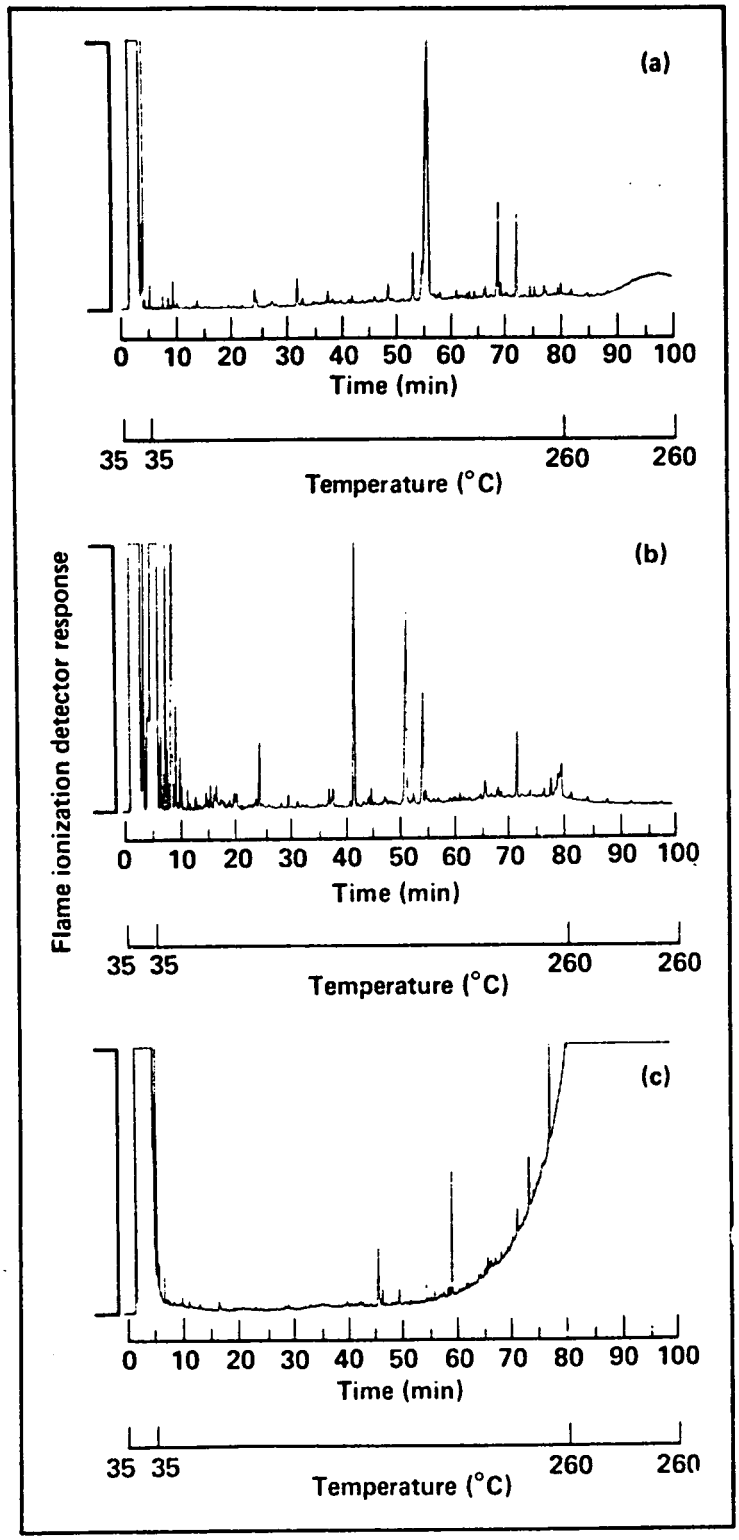

Figure 3. Gas chromatograms of the extract of scrubber water collected at the Four Corners Power Station on December 12, 1979: (a) neutral fraction, (b) basic fraction, and (c) acidic fraction.

Table 6. Organic compounds identified in the neutral fraction of extracts of scrubber water collected at the Four Corners Power Station on December 12, 1979.[a]

Molecular weight	Formula	Name
98	$C_6H_{10}O$	(Cyclohexene oxide)
134	$C_6H_{11}ClO$	(Chlorocyclohexanol)
196	$C_6H_{10}BrCl$	(Bromo-chloro-cyclohexane)
162	$C_{10}H_7Cl$	1-Chloronaphthalene[b]
180	$C_{11}H_{16}O_2$	(Butylatedhydroxyanisole)
168	$C_{12}H_{24}$	(Cyclododecane)
278	$C_{16}H_{22}O_4$	Dibutylphthalate
390	$C_{24}H_{38}O_4$	Dioctylphthalate
400+	C_nH_{2n+4}	Alkane
400+	C_nH_{2n+2}	Alkane

[a] Compounds tentatively identified are shown in parentheses. No polynuclear aromatic hydrocarbon compounds were identified.

[b] Internal standard.

The total quantities of aromatic compounds and the quantities of those of each ring size were greater in ESP than in WS fly ash (Table 17). Among the nonaromatic compounds, a greater number of low molecular-weight compounds (< 170) were extracted from the ESP fly ash than from the WS fly ash.

Ondov et al. (1979b) compared the efficiency of WSs and ESPs in a coal fuel plant and found the WS system to be less efficient in removing respirable-size particles. Natusch (1978) reports that potentially carcinogenic compounds condense or adsorb onto the surface of these respirable-sized fly-ash particles. Consequently, some of the PAHs generated in coal-fired plants fitted with WS devices would be more likely to escape through the stack by their association with the respirable-sized particles than in plants using ESP devices.

Table 7. Organic compounds identified in the acidic fraction of extracts of scrubber water collected at the Four Corners Power Station on December 12, 1979.[a]

Molecular weight	Formula	Name
116	$C_6H_{12}O_2$	(Cyclohexanediol type)
112	$C_7H_{12}O$	(Dimethylpentadienol type)
112	$C_7H_{12}O$	(Dimethylpentadienol type)
112+	$C_7H_{12}O$	(Dimethylpentadienol type)
194	$C_{10}H_{10}O_4$	Methylphthalate
222	$C_{12}H_{14}O_4$	Diethylphthalate
198	--	--
250	$C_{14}H_{18}O_4$	Dipropylphthalate
278	$C_{16}H_{22}O_4$	Dibutylphthalate
306	$C_{18}H_{26}O_4$	Phthalate type
390	$C_{24}H_{38}O_4$	Dioctylphthalate
450	$C_{32}H_{66}$	Dotriacontane type
450	$C_{32}H_{66}$	Dotriacontane type

[a] Compounds tentatively identified are shown in parentheses. These extracts were extremely dilute and some compounds identified could be contaminants in the scrubber water and not coal derived. The phthalates, which are ubiquitous plasticizers, are especially suspect.

IDENTITY AND QUANTITY OF INORGANIC COMPONENTS

Wet Scrubber Water Samples

Filtered scrubber water was analyzed for cations and anions. Sulfate was the predominate anion and was present in concentrations greater than 2000 ppm. Chloride-ion concentration was close to 170 ppm, and large amounts of nitrate and fluoride ions were also present. Sodium and calcium ions were present in concentrations greater than 100 ppm and boron, magnesium, potassium, and silicon in concentrations greater than 10 ppm. All of the 22 cations sought were present in scrubber water at concentrations greater than the minimal detectable limits of our ICP OES system (Table 18).

Table 8. Organic compounds identified in the basic fraction of extracts of scrubber water collected at the Four Corners Power Station on December 12, 1979.[a]

Molecular weight	Formula	Name
98	$C_6H_{10}O$	(Cyclohexene oxide)
106	C_8H_{10}	Ethylbenzene
106	C_8H_{10}	m- and p-xylene
98	$C_6H_{10}O$	Cyclohexenone
98	$C_6H_{10}O$	Cyclohexenol
96	C_6H_8O	Cyclohexenone
120	C_9H_{12}	Isopropylbenzene
135	C_7H_5NS	Benzothiazole
∿180	$C_{11}H_{16}O_2$	--
∿194	$C_{12}H_{18}O_2$	--
222	$C_{12}H_{14}O_4$	Diethylphthalate
244	$C_8H_{16}OS$	(Butylthiolbutyrate)
236	--	--
278	$C_{16}H_{22}O_4$	Diisobutylphthalate
278	$C_{12}H_{22}O_4$	Butylisobutylphthalate
278	$C_{16}H_{22}O_4$	Dibutylphthalate
∿314	$C_{12}H_{34}O_4$	(Dibutylsebacate)
240	--	--
206	$C_{18}H_{22}O_4$	(Diamylphthalate)
390	$C_{24}H_{38}O_4$	Dioctylphthalate

[a] Compounds tentatively identified are shown in parentheses. These extracts were extremely dilute and some compounds identified could be contaminants rather than coal derived. The phthalates, which are ubiquitous plasticizers, are especially suspect.

Wangen and Wienke (1976) reported on the chemical composition of the scrubber's water source, Morgan Lake, and the scrubber water destination, Chaco River, as well as various waters and soils near the Four Corners Plant. Their data shows dramatic increase in lithium and strontium content between the intake and the final outflow. Our measurements also show an increase in these elements in the scrubber water over the Morgan Lake intake. However, our scrubber concentration is similar to that of the river water. These elements are likewise in high concentration in the remainder of the waters

Table 9. Total extractable hydrocarbons in particulate material collected from the Four Corners Power Station in December 1979.[a]

Sample	Hydrocarbons (ppb)
Distribution tank fly ash	5,700
Ash pond fly ash	4,400
Duck pond sediment	47,000
Levee sediment	9,800
Morgan Lake sediment	7,700

[a] Samples extracted by rotary shaking.

and sediments between the distribution tank and the Chaco River (Wangen and Wienke, 1976). The system appears near saturation for these elements. The occurrence of other elements increases dramatically between the intake and the distribution tank and then reduces in concentration before the Chaco River. Molybdenum, boron, arsenic, and selenium appear to be produced from the coal burning process but are mostly deposited before the Chaco River outflow.

Particulate Material Samples

Concentrations of elements in acid-soluble extracts of fly ash and sediment samples were wide ranging (Table 19). Concentrations of elements were similar in ESP fly ash, scrubber fly ash, and ash pond sediment. Only calcium and magnesium were present in different concentrations. This was expected because lime is added to the fly ash in the distribution tank. Sediment collected from the levee appeared to be enriched in iron and magnesium. Movement of water through these sediments may have resulted in enrichment of some of the more soluble elements that were originally associated with the fly ash.

Table 10. Major organic compounds identified in an aromatic fraction (2 and 3 rings) of ash pond fly ash collected at the Four Corners Power Station on March 7, 1979.[a]

Molecular weight	Formula	Name
106	C_8H_{10}	Ethylbenzene
106	C_8H_{10}	m- and p-Xylene
106	C_8H_{10}	o-Xylene
120	C_9H_{12}	1,2,4-Trimethylbenzene
156	$C_{11}H_{24}$	m-Undecane
128	$C_{10}H_8$	Naphthalene
142	$C_{11}H_{10}$	2-Methylnaphthalene
142	$C_{11}H_{10}$	1-Methylnaphthalene
156	$C_{12}H_{12}$	1,2-Dimethylnaphthalene
168	$C_{12}H_8O$	Dibenzofuran
182	$C_{13}H_{10}O$	4-Methyldibenzofuran
198	$C_{15}H_{18}$	1,6-Dimethyl-4-isopropylnaphthalene
∿268	∿$C_{19}H_{40}$	Alkane
178	$C_{14}H_{10}$	Anthracene or phenanthrene
208	$C_{15}H_{12}O$	3-Methoxyphenathrene
192	$C_{15}H_{12}$	2-Methylanthracene
270	$C_{17}H_{34}O_2$	Methyl-n-hexadecanoate
284	$C_{18}H_{36}O_2$	Methylheptadecanoate
202	$C_{16}H_{10}$	Pyrene
296	$C_{19}H_{36}O_2$	Methyloleate
298	$C_{17}H_{38}O_2$	Methylstearate
312	$C_{20}H_{40}O_2$	Methyl-n-nonadecanoate
300+	C_nH_{2n+2}	Alkane
326	$C_{21}H_{42}O_2$	Methylarachidate
300+	C_nH_{2n+2}	Alkane
354	$C_{23}H_{46}O_2$	Methylbehenate
300+	C_nH_{2n+2}	Alkane
382	$C_{25}H_{50}O_2$	Methyllignocerate
300+	C_nH_{2n+2}	Alkane
300+	C_nH_{2n+2}	Alkane

[a] Samples were extracted in a Soxhlet.

000022

Table 11. Organic compounds identified in an aromatic fraction (3 or more rings) of ash pond fly ash collected at the Four Corners Power Station on March 7, 1979.[a]

Molecular weight	Formula	Name
214	$C_{13}H_{26}O_2$	Methyldodecanoate
228	$C_{14}H_{28}O_2$	Methyltridecanoate
242	$C_{15}H_{30}O_2$	Methylmyristate
242	$C_{15}H_{30}O_2$	Methyl-n-tetradecanoate
256	$C_{16}H_{32}O_2$	Methyl-n-pentadecanoate
256	$C_{16}H_{32}O_2$	(Methyl-12-methyltetradecanoate)
194	$C_{14}H_{10}O$	Anthrone
256	$C_{16}H_{32}O_2$	(Methylpentadecanoate isomer)
268	$C_{18}H_{36}O$	(Hexahydrofarnesylacetone)
266	$C_{17}H_{30}O_2$	(Methyl-7,10-hexadecanoate)
268	$C_{17}H_{32}O_2$	Methylpalmitoleate
270	$C_{17}H_{34}O_2$	Methyl-n-hexadecanoate
284	$C_{18}H_{36}O_2$	(Methyl-n-heptadecanoate)
~284	$\sim C_{18}H_{36}O_2$	(Methyl ester type)
284	$C_{18}H_{36}O_2$	Methylheptadecanoate
294	$C_{19}H_{34}O_2$	(Methyl-12,15-octadecadienoate)
296	$C_{19}H_{36}O_2$	Methyloctadec-8-enoate
298	$C_{19}H_{38}O_2$	Methyloctadecanoate
312	$C_{20}H_{40}O_2$	Methyl-n-nonadecanoate
324	$C_{21}H_{40}O_2$	Methyl-11-eicosenoate
326	$C_{21}H_{42}O_2$	Methylarachidate
230	$C_{17}H_{10}O$	Benzanthrone
~354	$C_{23}H_{46}O_2$	(Mixture including a methyl ester)

[a] Compounds tentatively identified are shown in parentheses. Samples were extracted in a Soxhlet.

Table 12. Concentrations in ppb of some of the organic compounds identified in extracts of particulate material sampled at different collection sites at the Four Corners Power Station on December 12, 1979.[a]

Compound	Sample site				
	Distribution tank	Ash pond	Levee	Duck pond	Morgan Lake
a-Hydroxytoluene	1700	240	430	340	1600
Methylphenol isomer	9	20	--	300	--
n-Undecane	9	--	<50	<100	--
Naphthalene	21	--	--	<100	250
2-Methylnaphthalene	9	8	<100	<90	--
1-Methylnaphthalene	--	8	--	<90	--
n-Tridecane	11	38	--	<90	trace
Dimethylnaphthalene	41	9	<100	110	trace
Dimethylphthalate	48	88	--	130	--
C_{15} alkane	19	18	--	--	--
Trimethylnaphthalene	79	--	<50	200	trace
Diethylphthalate	41	17	110	--	--
Octylphenol isomer	190	--	--	270	<55
Indan isomer and dimethylisobutylnaphthalene	130	--	190	310	110
Anthracene or phenanthrene	170	--	430	250	<55
(Aromatic type compound)	190	6	710	--	<40
C_{17} alkane	140	43	--	330	--
C_{18} alkane	160	10	--	930	--
C_{19} alkane	200	13	--	--	110
C_{20} alkane	190	15	650	400	37
C_{21} alkane	150	13	520	1700	trace
C_{22} alkane	84	31	1000	510	160
C_{23} alkane	520	43	860	--	130
C_{24} alkane	80	58	980	1600	160
C_{25} alkane	72	110	920	700	170
C_{26} alkane	28	95	820	890	270
C_{27} alkane	15	220	590	210	330

Table 12. (Continued)

Compound	Sample site				
	Distribution tank	Ash pond	Levee	Duck pond	Morgan Lake
C_{28} alkane	24	130	510	--	130
C_{29} alkane	11	360	300	200	280
C_{30} alkane	7	170	200	17	150

[a] Samples were extracted by rotary shaking.

Table 13. Organic compounds identified in the aliphatic fraction of extracts of wet scrubber fly ash collected at the Four Corners Power Station on December 12, 1979.[a]

Molecular weight	Formula	Name
162	$C_{10}H_7Cl$	1-Chloronaphthalene (internal standard)
226	$C_{16}H_{34}$	Hexadecane type
196	$C_{10}H_6Cl_2$	1,2-Dichloronaphthalene (from internal standard)
240	$\sim C_{17}H_{36}$	(Heptadecane type)
254	$C_{18}H_{38}$	Hexadecane type
254	$C_{18}H_{38}$	Hexadecane type
268	$C_{19}H_{40}$	Nonadecane type
268	$C_{19}H_{40}$	Nonadecane type
282	$C_{20}H_{42}$	Eicosane type
282	$C_{20}H_{42}$	Phytane type
296	$C_{21}H_{44}$	Tetramethylheptadecane
310	$C_{22}H_{46}$	Heneicosane type
324	$C_{23}H_{48}$	Tricosane type
324	$C_{23}H_{48}$	(Tricosane type)
338	$C_{24}H_{30}$	Tetracosane type
352	$C_{25}H_{52}$	Pentacosane type
352	$C_{25}H_{52}$	(Pentacosane type)
422	$C_{30}H_{62}$	(Squalene type)

[a] Compounds tentatively identified are shown in parentheses. Samples were extracted by rotary shaking.

Table 14. Organic compounds identified in the aromatic fraction of extracts of wet scrubber fly ash collected at the Four Corners Power Station on December 12, 1979.[a]

Peak number	Molecular weight	Formula	Name
1	120	C_9H_{12}	n-Propylbenzene
2	106	C_7H_6O	Benzaldehyde
3	120	C_9H_{12}	Trimethylbenzene
4	120	C_9H_{12}	Methylethylbenzene
5	120	C_9H_{12}	Trimethylbenzene
6	120	C_9H_{12}	Trimethylbenzene
7	108	$C_7H_{10}O$	α-Hydroxytoluene
8	132	$C_{10}H_{12}$	Methylindan
9	128	$C_{10}H_8$	Naphthalene
10	142	$C_{11}H_{10}$	Methylnaphthalene
11	162	$C_{10}H_7Cl$	1-Chloronaphthalene (internal standard)
12	152	$C_{12}H_{12}$	Dimethylnaphthalene
13	220	$C_{14}H_{20}O_2$	Di-tert-butylbenzoquinone
14	154	$C_{12}H_{10}$	Acenapthene
15	218	$C_{15}H_{22}O$	--
16	168	$C_{12}H_8O$	Dibenzofuran
17	220	$C_{15}H_{24}O$	Methyl-di-tert-butylphenol
18	182	$C_{14}H_{14}$	Methyldiphenylmethane
19	182	$C_{14}H_{14}$	Dimethylbiphenyl
20	166	$C_{13}H_{10}$	(Fluorene)
21	248	$C_{16}H_{24}O_2$	(Di-tert-amylquinone)
22	248	$C_{16}H_{24}O_2$	(Di-tert-amylquinone)
23	248	$C_{16}H_{24}O_2$	Di-tert-amylquinone
24	236	$C_{18}H_{20}$	Trimethylphenylindan
25	178	$C_{14}H_{10}$	Phenanthrene or anthracene
26	236	$C_{18}H_{20}$	(Methyldiphenylpentene)
28	192	$C_{15}H_{12}$	Methylanthracene
29	278	$C_{16}H_{22}O_4$	Di-n-butylphthalate
30	206	$C_{16}H_{14}$	Dimethylphenanthrene
31	202	$C_{16}H_{13}$	(Fluoranthrene)
32	202	$C_{16}H_{10}$	(Pyrene)
33	--	--	(Phthalate)

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Table 14. (Continued)

Peak number	Molecular weight	Formula	Name
34	370	$C_{22}H_{24}O_4$	Dioctyladipate
35	390	$C_{24}H_{38}O_4$	Dioctylphthalate
36	410	$C_{30}H_{50}$	Squalene
37	$\geq$390	$C_{10}H_{20}O_4$	(Di-iso-octylphthalate)

[a] Compounds tentatively identified are shown in parentheses. Samples were extracted by rotary shaking.

Table 15. Organic compounds identified in the polar fraction of extracts of wet scrubber fly ash collected at the Four Corners Power Station on December 12, 1979.[a]

Molecular weight	Formula	Name
122	$C_7H_6O_2$	Benzoic acid
135	$C_7H_5N_5$	Benzothiazole
194	$C_{10}H_{10}O_4$	Dimethylphthalate
200	$C_{12}H_{24}O_2$	Lauric acid mixture
222	$C_{12}H_{14}O_4$	Diethyl-o-phthalate
236	$C_{13}H_{16}O_4$	Methylbutylphthalate
228	$C_{14}H_{28}O_8$	Tetradecanoic acid
278	$C_{16}H_{22}O_4$	(Diisobutyl)phthalate
278	$\sim C_{16}H_{22}O_4$	(Phthalate type)
278	$\sim C_{16}H_{22}O_4$	(Phthalate type)
256	$C_{16}H_{32}O_2$	(Palmitic acid)
278	$C_{16}H_{22}O_4$	Dibutylphthalate
266	$C_{16}H_{26}O_3$	Epi-juvabione
278	$\sim C_{16}H_{22}O_4$	(Phthalate type)
284	$C_{18}H_{36}O_2$	(Stearic acid)
322	$C_{18}H_{26}O_5$	Butyl(butoxyethyl)phthalate
370	$C_{22}H_{42}O_4$	Dioctyladipate
240	$C_{15}H_{12}O_3$	(Methylbenzoylbenzoate type)
240	$C_{15}H_{12}O_3$	(Methylbenzoylbenzoate type)

[a] Compounds tentatively identified are shown in parentheses. Samples were extracted by rotary shaking.

Table 16. Concentrations in ppb of organic compounds identified in wet scrubber and electrostatic precipitator fly ash collected from the Four Corners Power Station on December 12, 1979, and extracted after 1-1/2 y of storage.

Compound	GC[a] retention time (min)	Molecular weight	Wet scrubber fly ash			Electrostatic precipitator fly ash		
			Shaker	Sonic	Total	Shaker	Sonic	Total
Isopropylbenzene	11.2	120	150	--	150	--	--	--
Propylbenzene	11.7	120	--	14	14	--	--	--
Ethylmethylbenzene	13	120	13	--	13	--	--	--
n-Propylbenzene	13.1	120	6	10	16	--	--	--
Ethylmethylbenzene	13.4	120	--	4	4	--	--	--
Methylnonane	13.6	142	--	9	9	--	--	--
Methylstyrene	14	118	29	--	29	46	23[b]	69
Trimethylbenzene	14.6	120	--	--	--	36	37	74
Decane	14.8	140	--	19	19	--	--	--
Decane	14.9	142	--	120	120	--	390	390
Trimethylbenzene	15.4	120	--	--	--	11	--	11
Dimethylphenol	16	122	--	12	12	--	--	--
Methylbutylacetate	16.2	130	12	--	12	--	--	--
(Methylheptanol)	16.4	130	12	--	12	--	--	--
α-Hydroxytoluene	16.5	108	--	--	--	14	--	14
(Methylcyclohexenone)	16.6	110	--	--	--	300	--	300
Decalin	16.7	138	9	--	9	--	--	--
Methylcyclohexeonone	17.4	110	--	--	--	--	66	66
(Methyldecanes)	17.4-18.1	156	--	74	74	--	--	--
Trimethylbenzene	17.6	120	--	--	--	--	34	34
Cresol	18.2	108	13	--	13	--	--	--
Phenylpropanol	18.6	136	21	--	21	--	--	--
Undecane	19.2	152	--	--	--	35	94	129
Dimethylheptadienone	19.6	138	--	8	8	53	180	233
Isophorone	20.1	138	--	--	--	87	403	490
Artemisa ketone	21.1	152	--	--	--	--	32	32
Hydroxymethyltetrahydrofuran	22	128	--	--	--	--	90	90
Naphthalene	22.6	128	9	trace	9	13	81	93
Dodecane	23.3	170	--	--	--	22	72	94
Dimethylhydroxyheptene	23.7	142	--	--	--	34	93	127
Trimethylcyclohexenone	24.2	138	--	--	--	42	--	42
Decanol	24.2	168	9	44	53	--	--	--
(Decanol type)	24.9	168	9	--	9	--	--	--
Dimethyl-t-butyl phenol	25.5	--	--	--	--	--	60	60
(Acetoxyphenol)	27	--	--	--	--	--	83	83
2-Methylnaphthalene	27.1	142	--	--	--	24	12	36
1-Methylnaphthalene	27.6	142	--	--	--	37	32[b]	69
(Butylmethylenedioxybenzene)	27.6	--	--	--	--	--	32	32
Tridecane	28.2	184	--	--	--	95	170	265
Diisopropylphenol	29.3	178	--	--	--	31[b]	110	141
(Diisopropylphenol)	30	178	--	--	--	--	140	140
(Cyclictetrahydroadipate type)	30-0.4	200	67	--	67	--	--	--
(Diisopropyl phenol)	30.6	178	--	--	--	47	--	47

Table 16. (Continued)

Compound	GC[a] retention time (min)	Molecular weight	Wet scrubber fly ash			Electrostatic precipitator fly ash		
			Shaker	Sonic	Total	Shaker	Sonic	Total
Tetradecane	31.2	198	--	--	--	poss[c]	42	42
(Amylanisole)	31.5	--	--	--	--	--	41	41
Dimethylheptahydronaphthalene	31.8	178	--	--	--	--	62	62
Dimethylnaphthalene	31.8	156	--	--	--	19	--	19
Dimethylphthlate	32.8	156	--	--	--	26[b]	20	46
(2,6-Di-t-butylbenzoquinone)	33	220	--	--	--	130	--	130
Acenaphthene	33.6	154	--	--	--	--	16	16
Pentadecane	33.8	212	7	--	7	--	--	--
Triphenylpropane	--	--	--	--	--	--	16	16
t-Butylmethoxyphenol	33.9	180	34	39	63	--	--	--
(Dimethyl biphenol)	34.2	182	--	--	--	--	16	16
(Aristolone)	34.8	218	--	--	--	29[b]	92	121
Methyldiphenylmethane	35.2	182	--	--	--	8[d]	22	30
(Aristolone)	35.3	218	--	--	--	18[d]	32	52
Trimethylnaphthalene	35.6	170	--	--	--	24	--	24
Fluorene	36.7	166	--	--	--	--	72	72
Diethylphthalate	37.1	222	900	46	946	190	97	287
Diphenylamine	37.8	169	20	4	24	--	--	--
Substituted naphthalene	39.3	198	--	--	--	13	--	13
Heptadecane	39.9	240	21	--	21	--	--	--
Heptadecane	40	240	--	--	--	31	--	31
Pristane	40.2	268	--	--	--	28	--	28
Styrene dimer	40.2	208	--	--	--	--	68	68
Methylbutylphthalate	40.6	236	--	--	--	9[d]	95	104
Thunbergene types:	41.5-48	--	1400	--	1400	--	--	--
(Dihydrosilarene)	--	274	--	--	--	--	--	--
(Podocarpene)	--	272	--	--	--	--	--	--
(Anhydroretinol)	--	268	--	--	--	--	--	--
(Dehydroabietane)	--	270	--	--	--	--	--	--
(Kaurene)	--	272	--	--	--	--	--	--
Phenyltetrahydronaphthalene	41.8	236	--	--	--	9[d]	180	189
Phenanthrene	42.6	178	--	--	--	poss	poss	poss
Anthracene	42.8	178	--	poss	poss	poss	poss	poss
Octadecane	42.9	254	poss	--	poss	poss	poss	poss
Donadecane	45.5	268	85	--	85	13[d]	20	33
Dibutylphthalate	47.5	278	65	18	83	46	94	140
Eicosane	48.1	282	30	1	31	--	--	--
(Vinyldecanate)	48.6	--	--	2	2	--	--	--
Juvabione	48.8	234	--	--	--	7[b]	21	28
Di-n-pentylphthalate	49.8	306	--	--	--	13[b]	94	107
Fluoranthrene	50	202	--	--	--	--	23	23
Heneicosane	50.5	296	34	--	34	19	--	19
Pyrene	51.4	202	poss	--	--	--	20	20
Docosane	52.9	310	13	--	13	22	--	22
Tricosane	55.1	324	24	--	24	43[b]	3	46
Butyl(butoxyethyl)phthalate	55.6	336	97	100	197	400	440	840

Table 16. (Continued)

Compound	GC[a] retention time (min)	Molecular weight	Wet scrubber fly ash			Electrostatic precipitator fly ash		
			Shaker	Sonic	Total	Shaker	Sonic	Total
Tetracosane	57.4	338	--	--	--	38	--	38
(Substituted phenol)	58.3	312	--	28	28	--	--	--
Benzophenanthradine	58.9	229	57	--	57	--	--	--
(Carbomethoxybenzophenone)	59	312	--	--	--	40	40	80
Pentacosane	59.4	352	24	--	24	47	--	47
(Methyldiphenylcyclopropane-phenylsulfides)	59.1-59.4	316	--	--	--	--	10	10
Dioctylphthlate	60.6	390 & 330	25	6	31	13	32	45
Hexacosane	61.5-61.6	336 & 366	15	--	15	45	57	102
(Substituted phenol)	63.7	312	--	--	--	--	33	33
Heptacosane	64.5-64.2	380	38	--	38	46	--	46
Octacosane	67.3	394	20	--	20	--	--	--
Triphenylbenzene	68.5	306	55	--	55	--	--	--
Nonacosane	71.2	408	--	--	--	27	--	27
Tricontane	76.1	422	7	2	9	26	--	26

NOTE: Compounds tentatively identified are shown in parentheses. All organic compounds in the fly ash have been corrected for amounts in the sand.

[a] Gas chromatography.

[b] Peak seen on gas chromatogram but not identified by gas chromatography, mass spectrometry.

[c] Possible occurrence. The gas chromatography, mass spectrometry showed some ions in reverse ion search.

[d] The gas chromatography peaks found in this region had the molecular weight indicated but were not identified as the compound shown.

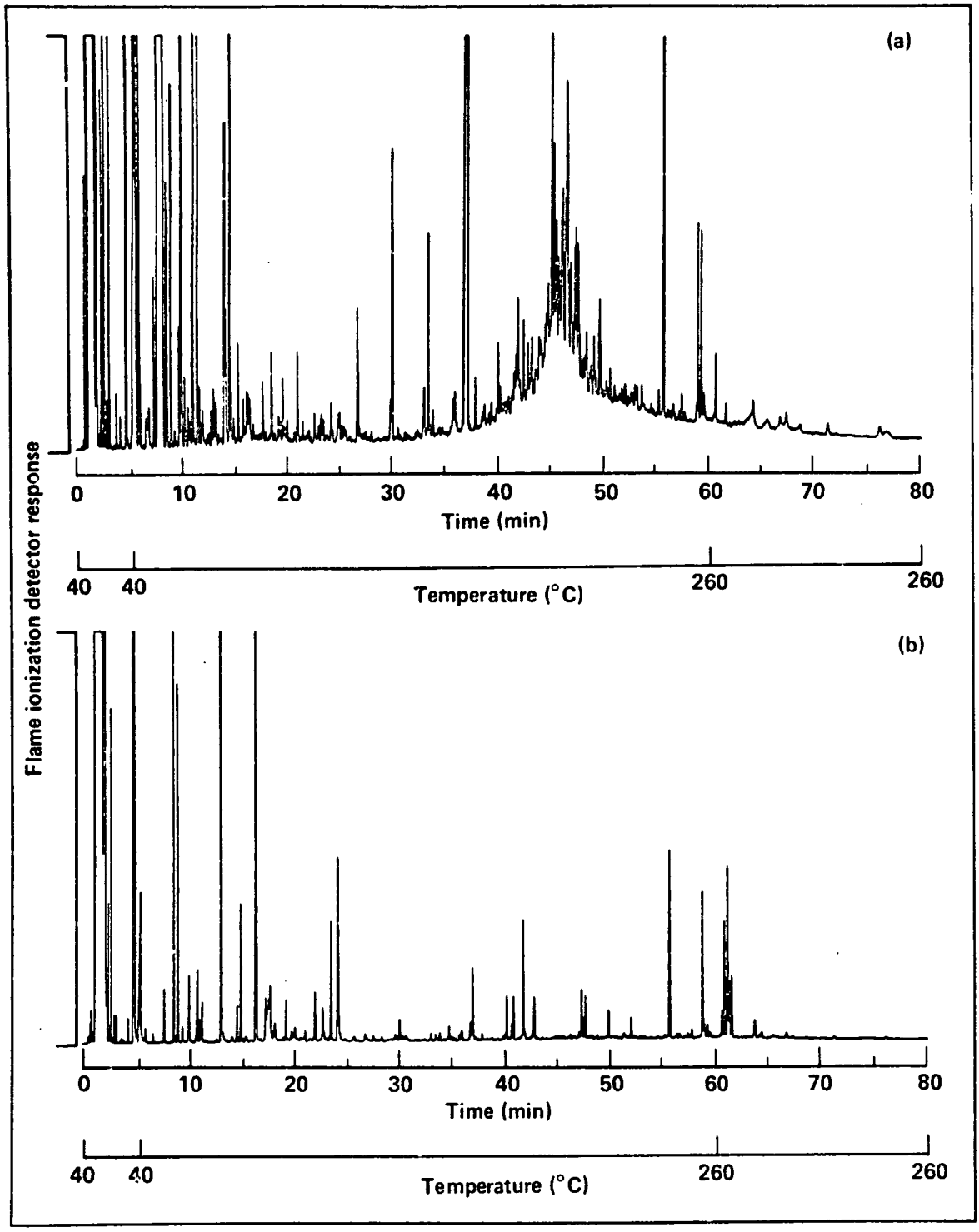

Figure 4. Gas chromatograms of (a) the rotary shaker extracts of fly ash from the Venturi wet scrubber collected at the Four Corners Power Station on December 12, 1979; and (b) the sonicated extracts of fly ash from the Venturi wet scrubber collected at the Four Corners Pow[illegible]tation on December 12, 1979.

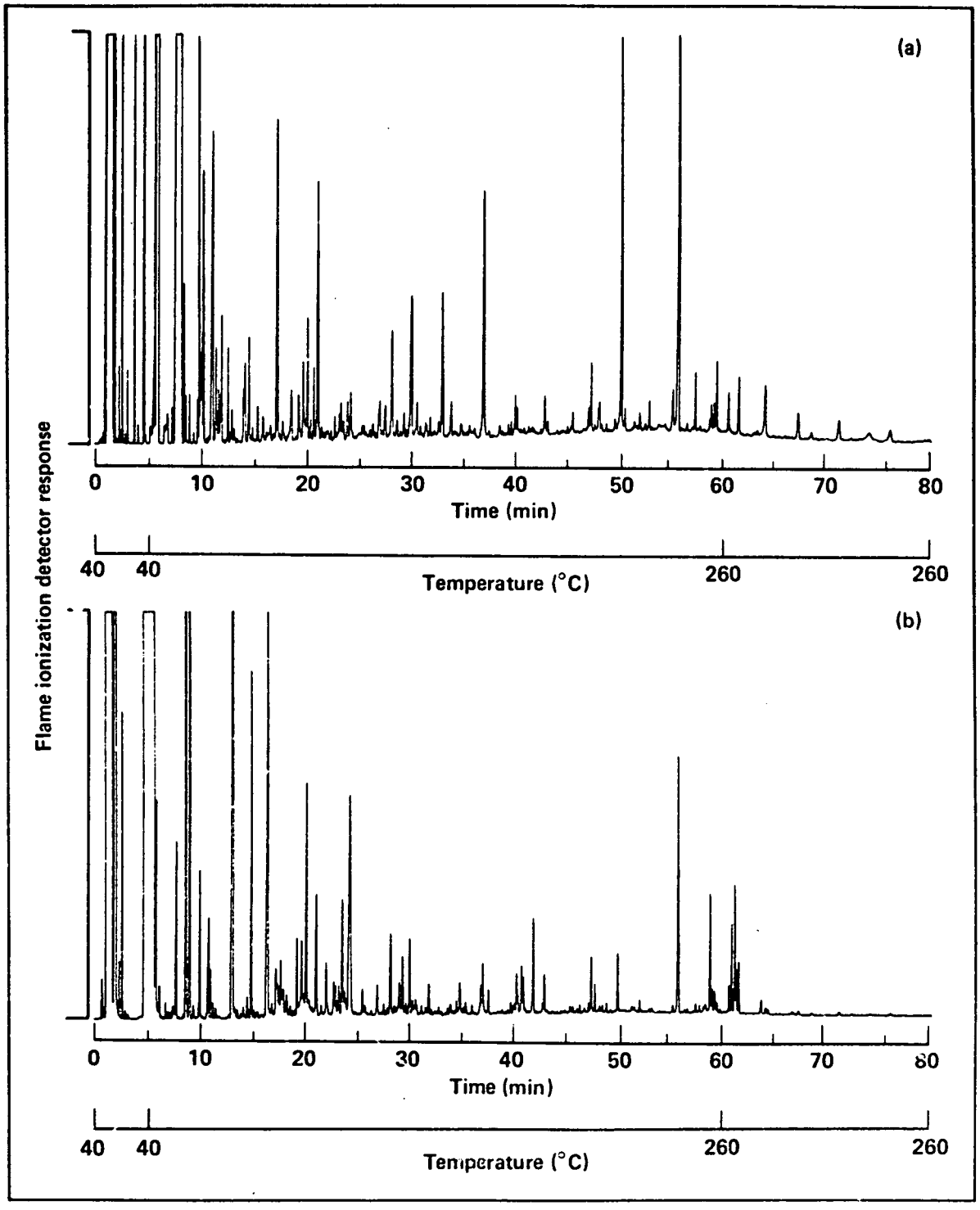

Figure 5. Gas chromatograms of (a) the rotary shaker extract of fly ash from the electrostatic precipitator collected at the Four Corners Power Station on December 12, 1979; and (b) the sonicated extract of fly ash from the electrostatic precipitator collected at the Four Corners Power Station on December 12, 1979.

Table 17. Concentrations in ppb of different classes of organic compounds identified in extracts of fly ash collected at the Four Corners Power Station on December 12, 1979, and extracted after 1-1/2 y of storage.

Class	Wet scrubber fly ash	Electrostatic precipitator fly ash
Aromatic compounds		
One ring	1750	2429
Two ring	10	520
Three ring	60	210
Four ring	trace	40
Nonaromatic compounds		
<170 molecular weight	330	2070
>170 molecular weight	1810	680
TOTAL	3960	5949

Table 18. Elements and ions present in scrubber water collected at the Four Corners Power Station on December 12, 1979, compared with Morgan Lake intake water and Chaco River destination water reported by Wangen and Wienke (1976). All concentrations in μg/L.

Element or ion[a]	Scrubber water	Morgan Lake intake water	Chaco River destination water
Al	53	500	--
As	110	<10	--
B	50,000	2,300	5,000
Cd	3.9	<4	5
Co	6.4	<1,000	<1
Cu	5.6	30	10
Fe	16	50	40
Li	580	ND[b]	500
Mn	12	20	50
Mo	1,100	10	40
Ni	19	20	10
P	520	--	--
Pb	68	2	0.5
Se	120	1	5
Si	11,000	2,000	5,000
Sr	2,700	ND	2,000
Ti	9	--	--
V	290	<200	ND
Ca	640,000	100,000	350,000
K	12,000	9,000	20,000
Mg	39,000	50,000	100,000
Na	290,000	200,000	300,000
F^-	7,200	3,000	6,000
Cl^-	170,000	100,000	120,000
NO_3^-	13,000	--	--
SO_4^{-2}	2,500,000	685,000	1,400,000

[a] The ions NO_2^{-3}, PO_4^{-3}, and Br^- were not detected.

[b] Not detected.

Table 19. Element concentration in the acid-soluble fraction of extracts of particulate material (μg/g ash weight) collected at the Four Corners Power Station on December 12, 1979.

	Collection site or description of particulate material						
Element	ESP[a] fly ash	Scrubber fly ash	Ash pond	Levee	Duck pond	Morgan Lake	Control[b]
Al	2,800[c]	2,900	3,300	3,000	2,700	740	1,500
As	<74	<74	<74	<74	<74	<74	<74
Cd	<6	<6	<6	<6	<6	<6	<6
Co	<13	<13	<13	<13	<13	<13	<13
Cu	21	34	29	<7	9	11	<7
Fe	1,200	1,500	1,600	2,000	1,300	620	900
Li	3	3	3	<1	3	<1	<1
Mn	120	130	130	49	100	94	50
Mo	<20	<20	30	<20	<20	<20	<20
Ni	<24	<24	<24	<24	<24	<24	<24
P	340	310	500	430	240	210	240
Pb	<48	<48	<48	<48	<48	<48	<48
Se	<125	<125	<125	<125	<125	<125	<125
Si	3,400	2,700	3,500	1,700	1,400	370	950
Sr	62	100	120	58	<13	15	38
Ti	170	190	240	11	26	<2	17
V	18	19	21	<9	14	<9	<9
Zn	36	38	12	25	12	18	2
Ca	14,000	39,000	36,000	19,000	13,000	3,600	6,600
K	2,300	2,300	2,300	1,700	630	470	<300
Mg	320	650	1,900	4,700	1,900	300	750
Na	320	260	710	600	570	22	270

[a] Electrostatic precipitator.

[b] Sediment from ground surface 1/2 mi upwind of plant.

[c] Relative standard deviation <10% for all values except <14% for that of zinc.

DISCUSSION

Information on the organic compounds in solid and liquid wastes from coal combustion is limited. Our investigations have established the identities and quantities of some of the organic compounds in wastes from the Four Corners Coal-Fired Power Station. A large number of compounds were identified but concentrations were generally low.

Griest and Guerin (1979) studied fly ash from a power plant burning eastern Kentucky coal. Benzene extracts of 0- to 3.3-μm ESP hopper ash and of stack ash were analyzed by capillary column GC MS. The major extractable organic material from the two sources was dominated by normal paraffins and similar in composition. The normal paraffins found in both ashes ranged from $C_{17}H_{36}$ to $C_{36}H_{74}$. In the ESP hopper ash, the hydrocarbons appeared to be centered in concentration about $C_{22}H_{46}$, whereas in the stack ash they were more evenly distributed. Bennett et al. (1979) also found a series of high molecular-weight paraffins in stack gas from above an ESP in a 700-MW coal-fired plant that burned Appalachian coal. Our analyses of fly ash from various sources also revealed large concentrations of paraffins (Tables 12 and 16).

Little information is available in the literature on the concentration of PAHs in emissions from coal-fired power plants. Among the factors that affect concentrations are the type of burner, the size of the power plant, load factor, type of fly-ash collection equipment, and the type of coal (Griest and Guerin, 1979). The emission of BaP from plants fired mechanically or manually may range from 0.2×10^{-4} to 3520×10^{-4} lb/ton of coal (Natusch, 1978). Hangebrauck et al. (1974) reported that large, pulverized coal-burning heat sources had the lowest PAH emissions of typical coal-fired utilities (19 μg BaP per million BTU gross output). Extrapolation of this figure to the Four Corners Plant yields 0.26 g/h or 6.24 g/d of BaP. If recovery of BaP by the scrubber system is efficient, then some small amount of this and other PAHs should be present in the waste water and particulate material at the plant.

Griest and Guerin (1979) determined the concentration of PAHs in 0- to 3.3-μm ESP ash and compared it to that found in the similar size fraction of stack ash from above the ESP. They found only pyrene (23 ± 6.4 ng/g) and fluoranthrene (19 ± 0.69 ng/g) present in the ESP ash whereas the stack ash contained BaP (0.69 ng/g) and benzo(a)anthrance (3.5 ng/g) as well as pyrene (1.4 ng/g) and fluoranthrene (5.1 ng/g). Because of the limited quantities of stack ash available, the quantities of PAHs in the extracts were small and some were not significantly different in concentration from those found in the blank.

Our analyses of fly ash showed low concentrations of PAHs with two, three, and four rings and no PAHs with five or more rings. These results, however, may not reflect the actual concentrations of these PAHs in the fly ash. Low recoveries may occur because the conditions under which they were extracted were not optimum or because they were lost or decomposed in the processes used to separate and quantify them.

Studies on effects of extraction procedures or recoveries were performed by Rohrbach and Reed (1976) on marine sediments and by Griest and Guerin (1979) on fly ash. Rohrbach and Reed recovered the highest concentrations of organics using a toluene-methanol Soxhlet procedure. These results contrasted with those of Griest and Guerin who compared the effectiveness of a Soxhlet, refluxing baths, and an ultrasonic microtip apparatus. They found the Soxhlet procedure to be relatively ineffective--no more than 18% of the PAHs were removed. They also tested the extraction efficiency of several solvents and concluded that in a Soxhlet apparatus, benzene was superior to methylene chloride, tetrahydrofuran, methanol, or acetone.

Our studies on the effectiveness of extraction procedures using ^{14}C-naphthalene- and ^{14}C-BaP-labeled fly ash indicated that rotary shaking was as or more effective in removing naphthalene than using a Soxhlet or ultrasonic generator (Appendix A). The BaP was removed more effectively with a sonifier fitted with a microtip. These results confirmed those of Rohrbach and Reed (1976) who reported that rotary shaking was almost as effective as using a Soxhlet for extracting marine sediments and those of Griest and Guerin (1979) who found the sonifier better than a Soxhlet for removing PAHs from ESP fly ash.

The recovery of the radiolabeled BaP increased with increases in the quantities of the compound added with the spike. These data indicate that preferential binding sites on the particles decrease when an excess of the compound is available. Griest and Guerin (1979) suggested that pi-bonding of the electrons in the larger PAHs causes the difficulty in extraction. Because recoveries of some PAHs are still low even when the best current methods are used, there is a need to investigate better extraction techniques or to establish that the compounds are not mobilized after disposal.

Low recoveries of PAHs may occur because they are lost or degraded during analysis. When we injected known concentrations of nine PAHs into our gas chromatograph, mass spectrometer, the results indicated that there were large losses of PAHs of more than four rings (Appendix B). It is not known whether the compounds were degraded or adhered to the column.

Some of the compounds listed in the tables are possibly contaminants in the water system at the power plant and not coal derived. Compound concentrations in the extracts are very low and contamination could also have occurred during the extraction

procedure. The phthalates, which are ubiquitous plasticizers, are especially suspect. Some of the compounds could not be identified by GC MS because it can only positively identify those compounds for which known spectra exist.

Different amounts of compounds and of total organic content were found in samples taken at different times and, to some extent, in samples stored for various lengths of time. Operating conditions of the power plant, temperature of the scrubber water, and time before analysis could affect the compounds formed, those released, those captured, those in the water or sediment, and those degraded.

We do not anticipate that fly ash will be classified as a hazardous waste on the basis of concentrations of organic compounds found in the extracts. However, current extraction procedures are ineffective and analytical methods are poorly developed for some of the classes of compounds that may be important. Additional studies to obtain better methods to extract, separate, identify, and quantify organic pyrolysis by-products are required.

Our analysis of acid-soluble extracts of fly-ash waste show many of the elements to be similar in concentration. However, some inorganic constituents in fly-ash waste are high in concentrations, and leachates of these materials may contain concentrations of some constituents in excess of those permitted for discharge.

CONCLUSIONS

Significant amounts of n-alkanes through C_{30} and PAHs up to four rings were found in solid wastes from the coal-fired power plant. No compounds containing more than four rings were identified. Radiolabel studies performed on extraction techniques indicated poor recovery of BaP added to fly ash; therefore, absence of PAHs containing more than four rings in the GC MS analyses may not imply that they are not present in the sediment.

Organic compounds in acidic, basic, and neutral fractions of liquid waste were low in molecular weight and included alkanes, alcohols, ketones, and phthalates. Some of these compounds may have been contamination by-products of the power plant operation process.

Extracts of fly ash from WS and ESP collectors were compared. Higher concentrations of low molecular-weight organic compounds as well as more PAHs were found in ESP fly ash. The WS fly ash contained a series of thunbergenes that are terpene-like compounds.

It should be stressed that these quantities reported are recovered amounts. No postulations or corrections have been applied concerning compounds bound to the ash (see Appendix A). If organic compounds cannot be removed by vigorous extraction with an organic solvent, methylene chloride, it is very unlikely they would be removed by a nonorganic solvent, water.

RECOMMENDATIONS FOR FUTURE RESEARCH

ANALYTICAL PROCEDURES

The efficiencies of extraction procedures need to be investigated further. The multiringed aromatic compounds were poorly recovered compared to the one- and two-ringed compounds (Appendix A). Methods are needed that increase the quantities extracted of PAHs and other compounds with large distribution coefficients (K_ds).

Better methods to separate, identify, and quantify organic constituents in wastes are required. Although GC MS is useful for identifying large numbers of compounds, new techniques to identify compounds of low volatility and high polarity need to be pursued. Separation techniques to be investigated include the further use of column chromatography and the use of high-pressure liquid chromatography (HPLC). The HPLC appears to offer ease of separation with ready identification of the PAHs by fluorescence emissions (Deutscher et al., 1980). Similar separation with thin layer chromatography with in situ fluorimetry is also possible.

The heterocyclic PAHs present can be separated using repeated HPLC runs. Thiophene derivatives, once separated, can be identified by nuclear magnetic resonance. The nitrogen-containing PAH analogs are polar and can be separated by acidic and basic extraction from the neutral PAHs.

PARTITIONING

Data on K_ds of additional representative organic compounds are needed for input to mathematical models. Compounds to be examined include those from different chemical classes and of different molecular size and hydrophobicity (octanol-water partition coefficient). Needed also are the effects of organic carbon content of the solid and liquid phase on K_ds.

CHEMICAL AND BIOLOGICAL TRANSFORMATIONS

A better understanding is needed of kinds and rates of reactions occurring during biological and chemical weathering of organic waste products in the environment. Data are needed on compounds that are resistant to change and on those that are transformed to more toxic or to innocuous compounds. Laboratory studies that simulate probable environmental weathering conditions will identify compounds and processes requiring additional study both in the field and laboratory.

MIGRATION

The movement of compounds through soil columns needs to be assessed under unsaturated as well as saturated flow conditions and under nonequilibrium as well as equilibrium conditions. Data obtained in the laboratory under controlled conditions need to be verified in the field.

BIOTOXICITY AND BIOACCUMULATION

Deleterious effects of chronic, low-level exposure of organic compounds on organisms needs to be evaluated both alone and in combination with trace metals. In addition, information is required on the quantities that accumulate in organisms in man's food chain. Even low concentrations are important for those chemicals that are assumed to have a linear response with dose.

ACKNOWLEDGMENTS

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APPENDIX A. EFFICIENCY OF EXTRACTION PROCEDURES

Samples collected in March 1979 were extracted in a Soxhlet thimble using methanol-toluene (72:28). This resulted in the esterification of acids present and the possible masking of PAH peaks. A study by Rohrbach and Reed (1976) suggested rotary shaking as a second choice to Soxhlet extraction for removal of organics from marine sediment. Griest and Guerin (1979) reported greater extraction efficiency of PAHs from ESP fly ash using sonication as opposed to Soxhlet extraction. We did a similar study comparing a rotary shaker to a sonifier fitted with a microtip using ^{14}C-labeled BaP and naphthalene. The microtip increases the intensity five times and thereby should increase the extraction efficiency.

The C^{14}-labeled naphthalene and BaP were dissolved in acetone and added to 200 g of scrubber fly ash to give a total concentration of approximately 6 ppb. The mixture was subjected to ultrasonic treatment for 2 to 3 min, rotary evaporated, and freeze-dried for 2 to 3 h. The instruments and times used in the experiment are summarized in Table A-1.

In experiment 1, fly ash was extracted twice with methylene chloride and then sequentially with two solvent combinations (Table A-2). In experiments 2 through 8, each sample was repeatedly extracted with one solvent or a combination as shown. Amount recovered was averaged from scintillation counts. Table A-2 shows that methylene chloride is a poor solvent for extracting BaP but good for naphthalene. It also shows ultrasonics to be an order of magnitude more effective than the shakers for extracting BaP when using toluene-methanol (80:20) as a solvent. (The same solvent was used by Griest and Guerin, 1979.) The shaker was more efficient in removing naphthalene in either solvent. Naphthalene also was far easier to recover.

Table A-1. Extraction methods for particulate material.

Method	Equipment	Operation	Time
Sonication	Branson W185-E sonifier cell disruptor with microtip (Danbury, CO)	Spike of 100 W decreasing to 60 W[a]	3 min
Rotary shaker	Eberback model 6150 (Ann Arbor, MI)	220 rev/min	5 h

[a] The microtip should increase the power five times.

Table A-2. The relative efficiency of solvent extraction in percent recovery of compounds added to fly ash.

Experiment	Compound	Method	Solvent	Number of extractions 1	2	3	4	TOTAL
1	^{14}C-labeled	Shaker	Methylene chloride	0.11	0.07	--	--	0.18
	BaP	Shaker	Toluene-methylene chloride (1:1)	--	--	0.5	--	0.5
		Shaker	Toluene-methanol (80:20)	--	--	--	0.39	0.39
TOTAL								1.07
2		Sonifier	Methylene chloride	0.16	0.19	0.14	--	0.49
3		Sonifier	Toluene-methanol (80:20)	1.52	1.33	0.72	--	3.57
4		Sonifier	Toluene-methylene chloride (1:1)	1.1	--	--	--	1.1
5	^{14}C-labeled	Shaker	Methylene chloride	74.2	12.5	4.5	6.2	97.4
6	naphthalene	Shaker	Toluene-methylene chloride (1:1)	81.7	10.3	2.4	1.9	96.3
7		Sonifier	Methylene chloride	46	19.5	--	--	65.5
8		Sonifier	Toluene-methanol (80:20)	38.6	13.4	--	--	52

A combination of these two methods was used in the final extractions of WS and ESP fly ash to optimize both low and high molecular-weight PAH recovery. Samples were first shaker extracted three times with methylene chloride and then sonifier extracted twice with toluene-methanol (80:20).

APPENDIX B. LIMITATIONS OF GAS CHROMATOGRAPHY, MASS SPECTROMETRY IN DETECTION OF POLYNUCLEAR AROMATIC HYDROCARBONS

Equal amounts of nine standard PAH compounds were directly injected into a GC MS column (Hewlett-Packard 5985B with a 30-m wall-coated, open tubular SE52-2 column with a 0.25-mm i.d. and splitless injection). The peak areas were not in proportion to the amounts injected. (Fig. B-1 shows the same phenomenon for a GC spectrum.) The amounts needed for detection of individual compounds are given in Table B-1.

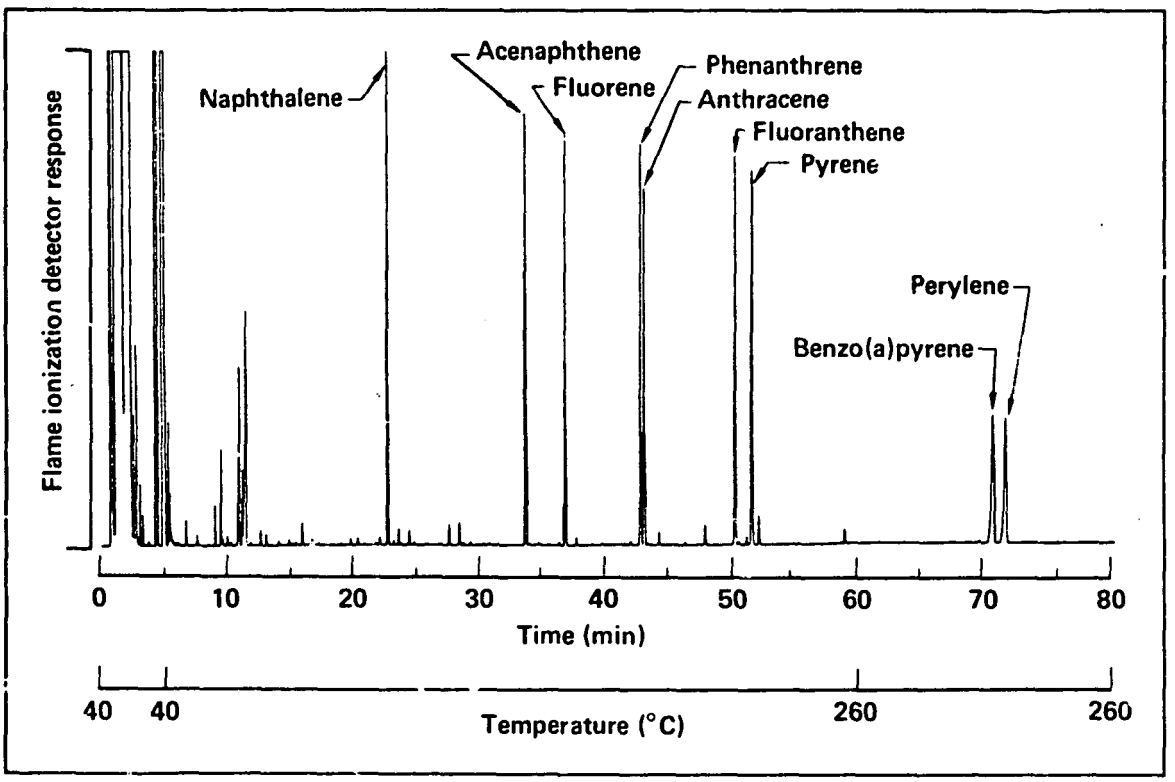

Figure B-1. Gas chromatogram of a polynuclear aromatic hydrocarbon standard solution. The gas chromotograph was fitted with a DB-5 column.

Table B-1. Gas chromatography, mass spectrometry detection limits.

Compound	Concentration required (ppm)[a]
Naphthalene	1
Acenapthene	4
Fluorene	6
Phenanthrene	4.5
Anthracene	6.5
Fluoranthrene	6.5
Pyrene	4.5
Benzo(a)pyrene	16
Perylene	20

[a] Concentration in injected solution.

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REFERENCES

Bennett, R. L., K. Knapp, P. W. Jones, J. A. E. Wilkerson, and P. E. Strup (1979), "Measurements of Polynuclear Aromatic Hydrocarbons and Other Hazardous Organic Compounds in Stack Gasses," in Polynuclear Aromatic Hydrocarbons, Third Intern. Symp. Chemistry and Biology, Carcinogenesis and Mutagenesis, P. W. Jones and P. Leber, Eds. (Ann Arbor Science Publishers Inc., Ann Arbor, MI), pp. 419-428.

Deutscher, S. B., J. H. Richardson, and J. M. Ondov (1980), "Time-Resolved Laser Induced Fluorescence with High Performance Liquid Chromatography for the Analysis of Polycyclic Aromatic Hydrocarbons in Fly Ash," Second Symposium on Environmental Analytical Chemistry, Brigham Young University, Provo, UT, June 18-20, 1980.

Giger, W., and M. Blumer (1974), "Polycyclic Aromatic Hydrocarbons in the Environment: Isolation and Characterization by Chromatography, Visible, Ultraviolet, and Mass Spectrometry," Anal. Chem. 46, 1663-1672.

Griest, W. H., and M. R. Guerin (1979), Identification and Quantification of Polynuclear Organic Matter (POM) on Particulates from a Coal-Fired Power Plant, Oak Ridge National Laboratory, Oak Ridge, TN, interim report.

Hangebrauck, R. P., D. J. Von Lehmden, and J. E. Meeker (1974), "Emissions of Polynuclear Hydrocarbons and Other Pollutants from Heat-Generation and Incineration Processes," J. Air Pollut. Control. Assoc. 14, 267-278.

Mulik, J. D., and E. Sawicki (1979), "Ion Chromatography," Environ Sci. Technol. 13, 804-809.

Natusch, D. F. S. (1978), "Potentially Carcinogenic Species Emitted to the Atmosphere by Fossil-Fueled Power Plants," Env. Health Perspect. 22, 79-90.

Ondov, J. M., R. C. Ragaini, and A. H. Biermann (1979a), "Emissions and Particle Size Distribution of Minor and Trace Elements at Two Western Coal-Fired Power Plants Equipped with Cold-Side Electrostatic Precipitators," Environ. Sci. Technol. 13, 946-953.

Ondov, J. M., R. C. Ragaini, and A. H. Biermann (1979b), "Elemental Emissions from a Coal-Fired Power Plant: Comparison of a Venturi Wet Scrubber System with a Cold-Side Electrostatic Precipitator," Environ. Sci. Technol. 13, 598-607.

Peck, E. S., A. L. Langhorst, and D. W. O'Brien (1979), "Analysis of Natural Waters with an Automated Inductively-Coupled Plasma Spectrometer System," Fifth Annual Meeting, Federation of Analytical Chemistry and Spectroscopy Societies, Boston, MA, Oct. 30, 1978 (Analytical Chemistry and Spectroscopy Society, Cleveland, OH), pp. 1-12.

Rohrbach, B. G., and W. E. Reed (1976), Evaluation of Extraction Techniques for Hydrocarbons in Marine Sediments, Institute of Geophysics and Planetary Physics, University of California at Los Angeles, Los Angeles, CA, pub. 1537.

Strickland, J. D. H., and T. R. Parsons (1972), A Practical Handbook for Seawater Analysis, Fisheries Research Board of Canada, Ottawa, Canada.

Wakeham, S. G., and J. W. Farrington (1960), "Hydrocarbons in Contemporary Aquatic Sediments," in Contaminants and Sediments, R. A. Baker, Ed. (Ann Arbor Science Publishers Inc., Ann Arbor, MI), pp. 3-32.

Wangen, L. E., and C. L. Wienke (1976), A Review of Trace Element Studies Related to Coal Combustion in the Four Corner's Area of New Mexico, Los Alamos National Laboratory, Los Alamos, NM, LA-6401-MS.

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