

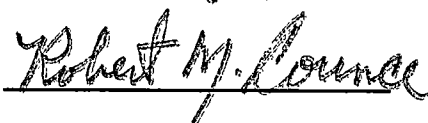
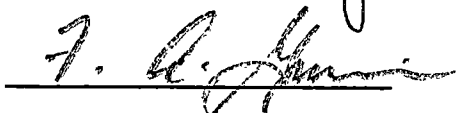
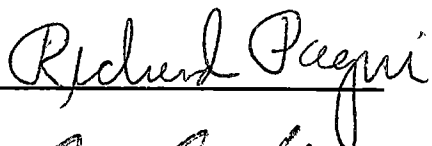
To the Graduate Council:

I am submitting herewith a dissertation written by Sabella Bowers Sauceman entitled "The Effects of Stearic Acid and 2- Undecanone on the Photodecomposition of Pyrene Adsorbed on Coal Fly Ash." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.



E. L. Wehry, Major Professor

We have read this dissertation
and recommend its acceptance:



Accepted for the Council:



Interim Vice Provost and
Dean of the Graduate School

THE EFFECTS OF STEARIC ACID AND
2- UNDECANONE ON THE PHOTODECOMPOSITION OF
PYRENE ADSORBED ON COAL FLY ASH

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Sabella Bowers Sauceman
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DEDICATION

This dissertation is dedicated to my parents,
Bill and Helen Bowers,
without whom this would not have been possible.

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There are many people in the department I wish to thank for their invaluable help during my time here.

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ABSTRACT

Polycyclic aromatic hydrocarbons, known as PAHs, are a class of organic compounds of concern due to their mutagenic and toxic properties. PAHs are prevalent in the earth's atmosphere, either in the gaseous phase or associated with particulate matter, and can undergo photodecomposition in the atmosphere by direct exposure to sunlight, to produce other compounds, which may or may not be more harmful than the parent PAHs.

Coal fly ash is a major type of particulate matter, with which PAHs may be associated in the atmosphere. The ultimate fate of atmospheric particulate matter, due to the health hazards associated with ingestion of respirable size range particles, especially when these particles contain PAHs or their phototransformation products, is of substantial interest.

Recent work has shown that the presence of other organic compounds adsorbed on particulate matter, as well as the chemical and physical properties of the particulate matter, may play a substantial role in the photochemistry of adsorbed PAHs. The current study is an attempt to determine what effects the presence of coadsorbed stearic acid and 2- undecanone have on the photochemistry of pyrene adsorbed on coal fly ash.

Pyrene adsorbed on coal fly ash, in the presence and absence of stearic acid or 2- undecanone, was illuminated with a xenon lamp to simulate exposure to sunlight. Both pyrene and stearic acid or 2- undecanone were deposited from the vapor phase onto coal fly ash to achieve varying coverages of each on the fly ash in order to investigate the effect of coverage. The importance of order of deposition on the fly ash was also explored, using stearic acid as the coadsorbate. The amount of pyrene prior to and following

illumination was quantified after extraction of pyrene in organic solvent by ultraviolet-visible absorption spectrophotometry.

Results showed that the presence of both stearic acid and 2- undecanone increased the extent of photodecomposition of pyrene adsorbed on coal fly ash. Varying the coverage of the coadsorbate had little effect on the extent of photodecomposition of pyrene. Changing the order of deposition of pyrene and stearic acid had no apparent effect on the photodegradation of pyrene adsorbed on coal fly ash.

From the results it was concluded that the chemical properties of the coadsorbates, stearic acid and 2- undecanone, may play a role in the increased photodecomposition of pyrene adsorbed on coal fly ash by acting as an electron acceptor for production of the pyrene cation radical intermediate to the formation of photoproducts, or they may subsequently react with the pyrene cation radical intermediate to produce the pyrene photoproducts.

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CHAPTER I: BACKGROUND TO THE RESEARCH

Introduction

Pollution of the environment has been an ever growing problem over the last century. As technology has improved and industry has grown, so have the problems associated with pollution. As the worldwide population soars, urban areas continue to grow larger, and industry pushes outward toward the surrounding rural areas, looking for room to expand. More and more businesses develop each year, most with waste generation issues. While pollution was once mainly considered a problem in large cities, the enormous growth of industry has left nothing untouched by pollution.

Pollution comes in many forms, from gaseous emissions produced by various sources which pollute the air, to chemicals which pollute the water sources and the land, to solid waste, which must be stored. Landfills overflow with solid waste, drinking water is unsafe in some places, while smog encircles many urban areas. The problems caused by hazardous chemicals dumped into water streams, buried underground, buried offshore, and sprayed over crops have gained national attention.

In an effort to control pollution, governments began adopting regulations, with which companies had to comply. These regulations have been ever-changing, along with the growth of industry. They continue to become more and more stringent in regard to pollution. Companies must strive to comply with the regulations or face stiff financial penalties and disapproval of the public.

There has been a growing concern by society over pollution of the environment.

Efforts have ranged from those made by individuals to those made by corporations to cut down on waste and reduce pollution. In recent years, the focus by scientists has been given to global warming, as well as atmospheric depletion of the ozone layer, and production and release of the compounds "NO_x" and "SO_x" [1,2,3]. All three of these events involve atmospheric emissions, which affect everything around us. Figure 1.1 shows a diagram of the pollution system.

Atmospheric Properties

The atmosphere is key to the fate of airborne pollutants, whether gaseous or particulate. The complex physical and chemical processes of the atmosphere control the life cycle of atmospheric contaminants, while human activities mainly control the concentrations of contaminants released to the atmosphere. Over the last century human mortality can be directly related to the marked rise of airborne contaminants [4].

The earth's atmosphere is divided into two general layers, the upper and lower regions. The lower region consists of the troposphere and the stratosphere. The total altitude of the two regions is approximately 50 km [4,5]. The troposphere extends from the earth's surface to ~15 km [4,5]. In the troposphere, temperature decreases with height, and there is rapid vertical mixing. The troposphere is an area of constant mixing and contains virtually all of the earth's water vapor [4,5]. The presence of water vapor, along with the vertical mixing of the troposphere, and the variation of temperature and pressure in this region cause the formation of clouds. In the stratosphere, which extends from the troposphere to ~50 km, temperature increases with height and vertical mixing is

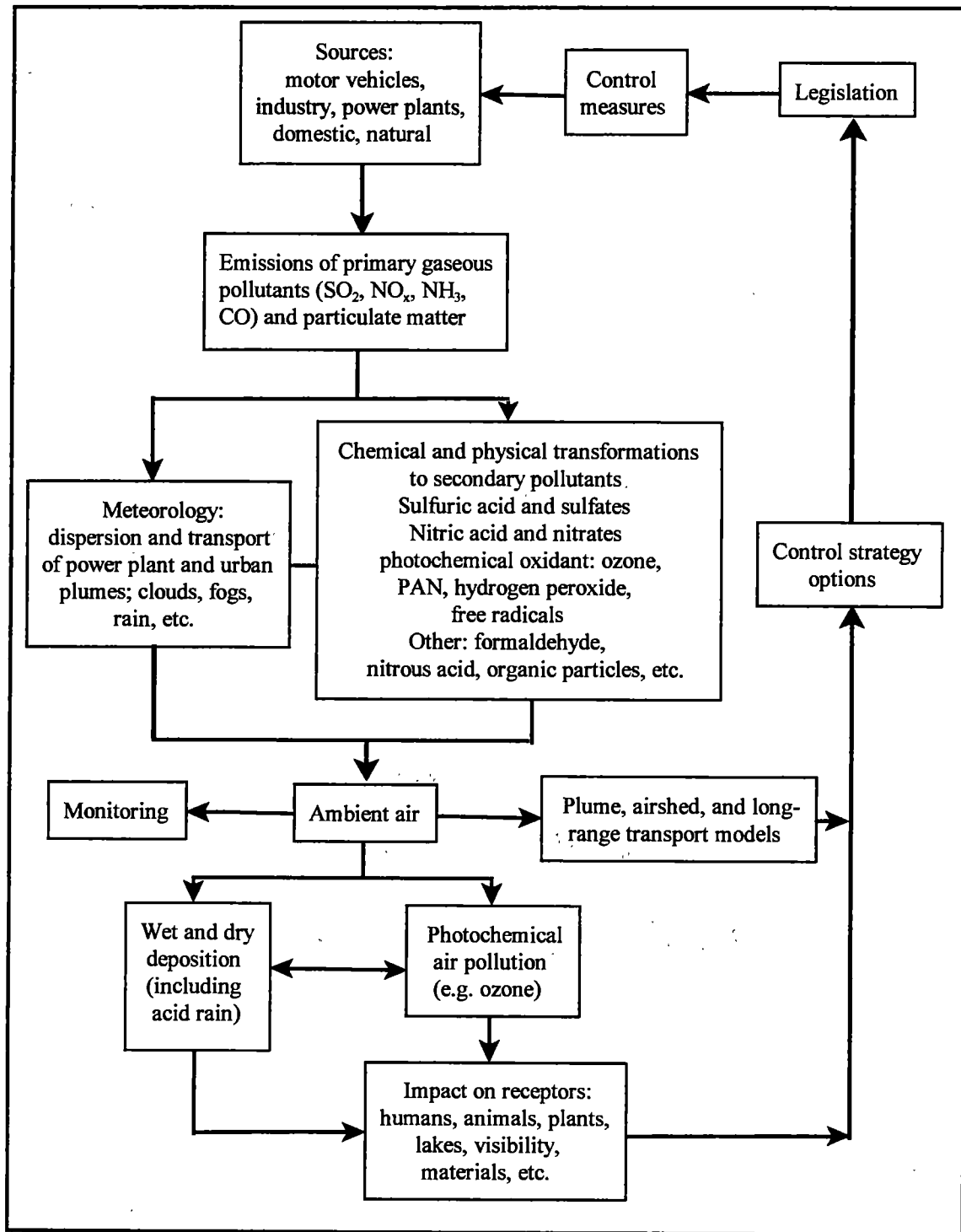


Figure 1.1 The Air Pollution System.

Source: *Atmospheric Chemistry : Fundamentals and Experimental Techniques*,
Finlayson- Pitts, B. J.; Pitts, J. N., Jr., Eds.; John Wiley and Sons: New York, 1986, p.13.

very slow. While mixing in the troposphere takes only hours, mixing in the stratosphere can take years [5,6]. The increase of temperature in the stratosphere is due to the presence of the ozone layer, which absorbs solar UV radiation. Transport of species between the stratosphere and the troposphere is key in atmospheric chemistry.

Atmospheric Pollutants

Background

Atmospheric pollutants are considered to be those substances present in concentrations well above their ambient levels, sufficient to cause an effect on the environment. Two main classes of pollutants exist: 1) particles, often called aerosols, which are solid or liquid particles deriving from natural sources, such as scatter of dust or sea spray; biogenic emissions; volcanoes; and wildfires [7,8,9]; or human activities, such as pesticide and fertilizer use [10,11]; and anthropogenic sources, such as power plants; wood burning or grilling; and mobile sources [7,12,13,14,15]; and 2) chemical species, both gaseous and particle associated, also deriving from the natural sources listed above, including vegetation [16], as well as anthropogenic sources. Various aerosol pollutants and their sources are shown in Table 1.1, along with estimated emissions. In the 1980's total global aerosol emissions were estimated to range from 2500 to 24000 x 10⁶ metric tons, depending on the sampling method and location [7]. The large uncertainty indicates the inefficiency and difficulty of estimating aerosol emissions. Chemical pollutants found in the atmosphere number in the hundreds [17]. Table 1.2 shows some of the common chemical pollutant species derived from natural and anthropogenic sources, respectively.

Table 1.1
Global Emission Estimates for Major Aerosol Types in the 1980s.

Source	Estimated Flux (Tg/ yr)			Particle Size Category ^a
	Low	High	Best	
NATURAL				
Primary				
Soil Dust	1000	3000	1500	Mainly Coarse
Sea Salt	1000	10000	1300	Coarse
Volcanic Dust	4	10000	30	Coarse
Biological Debris	26	80	50	Coarse
Secondary				
Sulfates from Biogenic Gases	80	150	130	Fine
Sulfates from Volcanic SO ₂	5	60	20	Fine
Organic Matter from Biogenic VOC	40	200	60	Fine
Nitrates from NO ₂	15	50	30	Fine and Coarse
Total Natural	2200	23,500	3100	
ANTHROPOGENIC				
Primary				
Industrial Dust, etc. (except soot)	40	130	100	Fine and Coarse
Soot	5	20	10	Mainly Fine
Secondary Sulfates from SO ₂	170	250	190	Fine
Biomass Burning	60	150	90	Fine
Nitrates from NO ₂	25	65	50	Mainly Coarse
Organics from Anthropogenic VOC	5	25	10	Fine
Total Anthropogenic	300	650	450	
TOTAL	2500	24,000	3600	

^a Coarse and fine size categories refer to mean particle diameter above and below 1 μm , respectively.

Note: Sulfates and nitrates are assumed to occur as ammonium salts.

Flux unit: Tg/ yr (dry mass), Tg = 1×10^{12} g.

Source: *Atmospheric Chemistry and Physics*, Seinfeld, J. H.; Pandis, S. N., Eds.; John Wiley and Sons: New York, 1986, p.102.

Table 1.2
Some Natural and Anthropogenic Sources of Toxic Airborne Pollutants.

Sources	Examples
NATURAL	
Crustal Rock and Soils	Heavy Metals - Cadmium, Manganese, Mercury
Vegetation	Selenium, Zinc
Swamps	Hydrogen Sulfide, Volatile Organic Compounds
Volcanoes	Heavy Metals
Fires (forest, brush, grass)	PAH, Heavy Metals
ANTHROPOGENIC	
Industrial Processes, Manufacturing, and Commercial Operations	Various Organic, Inorganic, and Organometallic Substances
Transportation (land, sea, air)	Hydrocarbons and other Organic Compounds, Sulfur and Nitrogen Compounds, and PAH
Waste Treatment and Disposal	Organic, Inorganic, and Organometallic Substances
Combustion Processes (waste, fossil fuel, biomass)	Heavy Metals, Trace Elements, PAH, Poly- chlorinated Dibenzodioxins, Polychlorinated Dibenzofurans
Pesticide Manufacture and Use	Chlorinated Hydrocarbons

Source: Schroeder, W.H.; Lane, D.A. *Environ. Sci. Technol.*, 1988, 22, 240.

The removal of airborne species from the atmosphere, both aerosol and chemical, varies depending on the physical state and chemical properties of the species [18].

Characteristics

Aerosols can be directly emitted or formed from gaseous molecules. There are many types of aerosols, as shown in Table 1.3. Once emitted, particles can change their size and/ or composition by condensation of vapor species, by evaporation, coagulation with other particles, chemical reaction, or conversion to fog or cloud droplets [5,7,19,20,21]. Particle size is initially determined by the means of generation. Larger particles, called coarse particles, are usually formed by natural sources, while smaller, or "fine" particles, are usually formed by combustion processes. In terms of size, coarse particles are those with a diameter $\geq 2.5 \mu\text{m}$, and fine particles are those with a diameter $< 2.5 \mu\text{m}$. There are also many other differences in the two types of particles. They are transformed by different means, removed from the atmosphere by different means, require different techniques for removal, have different chemical composition, optical properties, and, most important, have different deposition patterns in the respiratory tract [7]. While the coarse particles are large enough for the cilia in the upper respiratory tract to propel the particles upward and out of the body through the nose or mouth, the fine particles, due to their small size, tend to become trapped in the alveolar region of the lungs, where gas exchange takes place, and there are no cilia to facilitate transport out of the respiratory tract [5]. An overall comparison of the two particle types can be seen in Table 1.4.

Coarse particles settle out of the atmosphere in a relatively short time, due to their large sedimentation velocities [7,11], remaining anywhere from hours to days, depending on

Table 1.3
Types of Atmospheric Aerosols.

Name	Description
Aerosols	Tiny particles dispersed in gases
Dusts	Suspensions of solid particles produced by mechanical disintegration of material such as crushing, grinding, and blasting. $D_p > 1 \mu\text{m}$.
Fog	A loose term applied to visible aerosols in which the dispersed phase is liquid. Usually, a dispersion of water or ice, close to the ground.
Fume	The solid particles generated by condensation from the vapor state, generally after volatilization from melted substances, and often accompanied by a chemical reaction such as oxidation. Often the material involved is noxious. $D_p > 1 \mu\text{m}$.
Hazes	An aerosol that impedes vision and may consist of a combination of water droplets, pollutants, and dust. $D_p > 1 \mu\text{m}$.
Mists	Liquid, usually water in the form of particles suspended in the atmosphere at or near the surface of the Earth; small water droplets floating or falling, approaching the form of rain, and sometimes distinguished from fog as being more transparent or as having particles perceptibly moving downward. $D_p > 1 \mu\text{m}$.
Particle	An aerosol particle may consist of a single continuous unit of solid or liquid containing many molecules held together by intermolecular forces and primarily larger than molecular dimensions ($> 0.001 \mu\text{m}$). A particle may also be considered to consist of two or more such unit structures held together by interparticle adhesive forces such that it behaves as a single unit in suspension or upon deposit.
Smog	A term derived from smoke and fog, applied to extensive contamination by aerosols. Now sometimes used loosely for any contamination of the air.
Smoke	Small gas-borne particles resulting from incomplete combustion, consisting predominantly of carbon and other combustible material and present in sufficient quantity to be observable independently of the presence of other solids. $D_p \geq 0.01 \mu\text{m}$.
Soot	Agglomerations of particles of carbon impregnated with "tar," formed in the incomplete combustion of carbonaceous material.

Source: *Atmospheric Chemistry and Physics*, Seinfeld, J. H.; Pandis, S. N., Eds.; John Wiley and Sons: New York, 1986, p.97.

Table 1.4
Comparison of Ambient Fine and Coarse Particles.

	Fine Particles	Coarse Particles
Formation	Chemical Reactions Nucleation Condensation Coagulation Cloud/ Fog Processing	Mechanical Disruption Suspension of Dusts
Composition	Sulfate Nitrate Ammonium Hydrogen Ion Elemental Carbon (EC) Organic Compounds Water Metals (Pb,Cd,V,Ni, Cu,Zn,Mn,Fe,etc.)	Resuspended Dust Coal and Oil Fly Ash Crustal Element(Si,Al,Ti,Fe) Oxides CaCO ₃ , NaCl Pollen, Mold, Spores Plant, Animal Debris Tire Wear Debris
Solubility	Largely Soluble, Hygroscopic	Largely Insoluble & Nonhygroscopic
Sources	Combustion (coal,oil, gasoline, diesel, wood) Gas-to-Particle Conversion of NO _x , SO ₃ , & VOCs Smelters, Mills, etc.	Resuspension of Industrial Dust and Soil Suspension of soil (farming, mining, unpaved roads) Biological sources Construction/ Demolition Ocean spray
Atmospheric Lifetime	Days to Weeks	Minutes to Days
Travel	100s to 1000s of km	≤ 10s of km

Source: *Atmospheric Chemistry and Physics*, Seinfeld, J. H.; Pandis, S. N., Eds.; John Wiley and Sons: New York, 1986, p.443.

climate conditions [7,11,22]. Fine particles can be divided into two categories, nuclei mode, diameters 0.005- 0.1 μm , and accumulation mode, diameters 0.1- 2.5 μm . Accumulation size particles account for most of the mass of atmospheric particulate matter [7,11]. Nuclei particles are generally lost by coagulation with larger particles in the atmosphere, immediately upon their formation and/ or release [7]. Particles in the accumulation mode are so named because of their inefficient removal from the atmosphere, which causes them to have longer atmospheric residence times than the other two particle sizes [7]. Atmospheric residence times as large as years have been demonstrated for this class of particles [7,10,23].

Chemical composition of atmospheric particles is varied. Table 1.5 shows typical elements found in atmospheric particles. Particles arising from natural sources (mainly coarse) contain mainly crustal elements, such as Si, Al, Ca, and Fe [23]. Fine particles, generated from combustion, may contain traces of dozens of elements, many of which are present in the oxide form [23].

Fates of Atmospheric Pollutants

Transformations

All but the inert chemical substances, whether gaseous or particle associated, once released into the atmosphere, may be altered in one of two ways. First, the species may undergo photochemical reaction, or second, it may react with another species to produce a new species. Once a species undergoes reaction, it may change the physical state or chemical form of the original species, possibly causing a change in the chemical properties

Table 1.5
Concentrations (ng/ m³) and Size Distribution
of Various Elements Found in Atmospheric Particles.

Element	Mode ^a	Remote	Concentration (ng/ m ³)	
			Rural	Urban
Fe	F and C	0.6-4,200	55-14,500	130-13,800
Pb	F	0.01-65	2-1,700	30-90,000
Zn	F	0.03-450	10-400	15-8,000
Cd	F	0.01-1	0.4-1,000	0.2-7,000
As	F	0.01-2	1-28	2-2,500
V	F and C	0.01-15	3-100	1-1,500
Cu	F and C	0.03-15	3-100	4-500
Mn	F and C	0.01-15	4-100	4-500
Hg	--	0.01-1	0.05-160	1-500
Ni	F and C	0.01-60	1-80	1-300
Sb	F	0-1	0.5-7	0.5-150
Cr	F and C	0.01-10	1-50	2-150
Co	F and C	0-1	0.1-10	0.2-100
Se	F and C	0.01-0.2	0.01-30	0.2-30

^aF= fine mode; C= coarse mode.

Source: *Atmospheric Chemistry and Physics*, Seinfeld, J. H.; Pandis, S. N., Eds.; John Wiley and Sons: New York, 1986, p.442.

(i.e., toxicity, mutagenicity, etc.). Generally, photochemical transformation of a species increases the polarity (i.e., water solubility) of the species [16,20]. The increased water solubility can cause the occurrence of new processes, which may not have taken place with the original species. Thus, the fate of atmospheric chemical species can be quite complicated.

Removal

Removal of gaseous chemical pollutant species from the atmosphere involves condensation of the species onto a particle, followed by particle removal, described below. Evaporation of the pollutant species from a particle, followed by transformation, with subsequent condensation onto a particle again is very common [7,16]. Thus, gaseous species can remain in the atmosphere for long periods (i.e., years), undergoing successive condensation and evaporation processes, before eventual removal by aerosol deposition [7,16].

Removal of pollutant aerosols from the atmosphere can occur by either of two processes, wet or dry deposition. "Wet deposition" is defined as all processes by which species are transported to the earth's surface in aqueous form, such as rain, sleet, hail, snow, fog, and cloud droplet formation [7]. Dry deposition, direct transfer to the Earth's surface without the aid of precipitation, includes the mechanisms diffusion, impaction, and sedimentation [7,11,16]. For particles close to the surface of the earth, dry deposition and settling are thought to be the main methods of particle removal. At 100 m above the earth's surface and beyond, wet deposition is thought to be the main method of particle removal from the atmosphere [7]. A schematic diagram of principal modes, sources,

particle formation, and removal is shown in Figure 1.2.

In summary, pollutants in the atmosphere, whether gaseous or particulate, can suffer many fates, depending on atmospheric conditions. Figure 1.3 shows schematically the fate of airborne pollutants. Eventually, human exposure to these pollutants through water, food, or respiration is almost a certainty.

Polycyclic Aromatic Hydrocarbons

As early as 1775, it was proposed that the high rate of cancer in London's chimney sweeps was attributable to carcinogenic chemicals in soot [8]. In the late 19th century, workers in the shale oil, coal tar, and paraffin refinery industries were also found to have unusually high incidences of skin cancer [8]. Today we know that combustion of fossil fuels may produce a class of compounds known as polycyclic aromatic hydrocarbons, often abbreviated "PAHs," and that many of these PAHs have been found to be carcinogenic and/ or mutagenic [24-27]. PAHs were among the first classes of compounds identified as carcinogenic [8,9].

PAHs are compounds composed of two or more aromatic rings that can be joined together in a variety of geometries. They contain only carbon and hydrogen. A few examples are shown in Table 1.6. More than 100 PAHs have been identified in urban air [9,12,27,28]. The smaller compounds (2- 3 rings) are present predominantly in the gaseous phase, while the larger compounds (5- 7 rings) are found exclusively associated with particles. The intermediate compounds (4 rings) are found in both the gaseous and particulate phases. The majority of PAHs in the atmosphere, 70- 90 % by mass, are in the

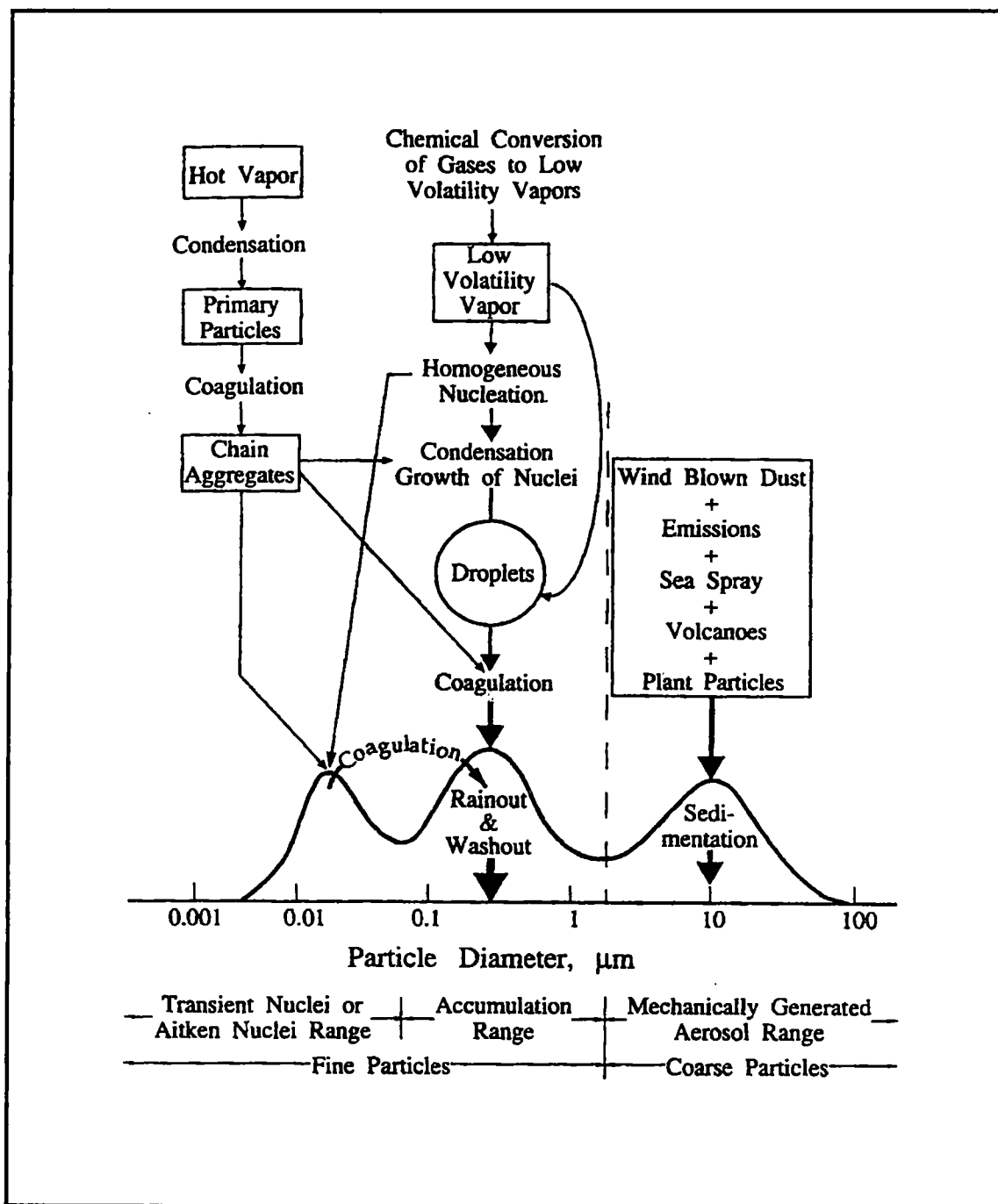


Figure 1.2 Schematic Diagram of Principal Modes, Sources, and Particle Formation and Removal Mechanisms of Atmospheric Particles.

Source: *Atmospheric Chemistry: Fundamentals and Experimental Techniques*, Finlayson-Pitts, B. J.; Pitts, J. N., Jr., Eds.; John Wiley and Sons: New York, 1986, p.737.

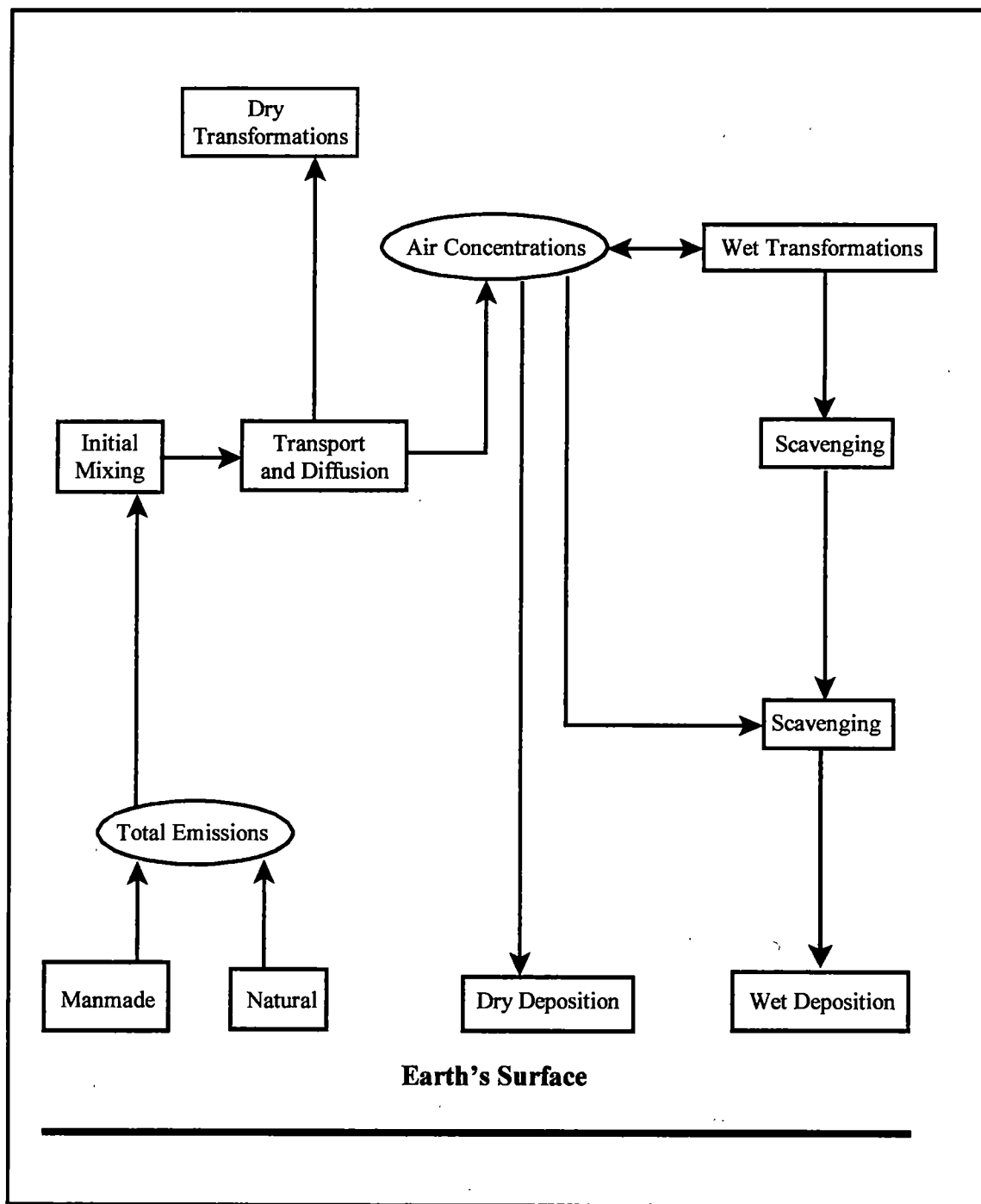
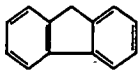
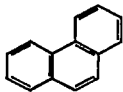
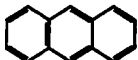
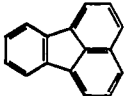
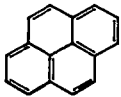
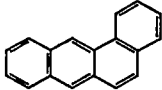
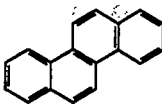


Figure 1.3 Schematic Representation of Fate of Airborne Pollutants.

Source: Schroeder, W.H.; Lane, D.A. *Environ. Sci. Technol.*, 1988, 22, 241.

Table 1.6
Structures and Physical Properties of Representative PAHs.

EPA No.	Nomenclature	Structure	MP(° C)	BP(° C)
55	Naphthalene		80	218
80	Fluorene		116	294
81	Phenanthrene		100	340
78	Anthracene		218	340
39	Fluoranthene		110	375
84	Pyrene		156	399
72	Benz(a)anthracene		158	400
76	Chrysene		255	448
73	Benzo(a)pyrene		177	495

Source: Smith, D.J.T.; Harrison, R.M. *Atmospheric Particles*, Harrison, R.M.; Van Grieken, R., Eds.; John Wiley and Sons, Inc.: New York, 1998, p.255.

particulate phase [29-31]. PAHs preferentially associate with particles of the respirable size range (0.5- 5 μm) [8,9,27,32,33], which are known for their long atmospheric residence times, allowing PAH transport over great distances. The PAHs are found mainly on the surfaces of these particles, facilitating their uptake in the respiratory tract [34-36], and increasing their risk.

PAHs are formed by incomplete combustion of organic (i.e., C and H containing) material, such as coal, wood, gasoline, and diesel fuel [8,9,31,37]. Their formation involves two sequential mechanisms, pyrolysis and pyrosynthesis [27,31,37]. PAH products are strongly dependent on the operating or flame conditions, as well as the source of the organic combustion material [8,9].

There are several sources of PAH generation. Some PAHs are emitted from natural processes, such as natural forest fires, volcanic eruptions, and decomposition of vegetation [9,38], which usually accounts for a small fraction of the total atmospheric PAHs [9,38]; however, most PAHs are generated by anthropogenic sources. These sources can be divided into two categories: stationary and mobile. Stationary sources include residential heating, open burning, industrial processes, power generation, and incineration [9,27]. These sources account for up to 80 % of total annual PAH emissions in the U.S. [9,27]. Mobile sources, which include trains, ships, cars, trucks, and aircraft, are major contributors in urban areas [9,27]. Some PAH emission sources and estimated emissions (tons/ yr) are shown in Table 1.7. It can be seen that residential heating, open burning, and mobile sources are the main contributors to PAH emissions, with power plants only releasing ~5 % of the total PAHs [9,37]. In the early 1980's total PAH emissions in the

Table 1.7
Estimated Atmospheric Emissions of Total PAH by Source Type (t/ yr).

Estimated Atmosphere Emissions of Total PAH by Source Type (t/y):				
Source Type	Total PAH Emissions			
	U.S.A.: (a)	(b) Sweden: (c)	Norway: (d)	
Residential Heating				
Coal & Wood Burning	3939	450	96	48
Oil & Gas Burning	17	930	36	15
Sub Total	3956 (36%)	1380 (16%)	132 (26%)	63 (21%)
Industrial Process				
Coke Manufacturing	632	2490	277	43
Asphalt Production	5	4	-	-
Carbon Black	3	3	-	-
Aluminum Plants	-	1000	35	160
Others	2	-	-	-
Sub Total	640 (6%)	3497 (41%)	312 (62%)	203 (69%)
Incineration				
Municipal	-	-	-	-
Commercial	56	50	2	1
Sub Total	56 (1%)	50 (1%)	2 (1%)	1 (0%)
Open Burning				
Coal Refuse Fires	29	100	-	-
Agricultural Fires	1190	400	1	2
Forest Fires	1478	600	1	5
Others	1328	-	-	-
Sub Total	4025 (36%)	1100 (13%)	2 (1%)	7 (2%)
Power Generation				
Power Plants	13	1	-	-
Industrial Boilers	75	400	7	1
Sub Total	88 (1%)	401 (5%)	7(1%)	1 (0%)
Mobile Sources				
Gasoline Engines	2161	2100	33	13
Diesel Engines	105	70	14	7
Sub Total	2266 (21%)	2170 (25%)	47 (9%)	20 (7%)
Total	11031	8598	502	294

(a): Peters, J.A.; Deangelis, D.G.; Hughes, T.W. *Chemical Analysis and Biological Fate: Polynuclear Aromatic Hydrocarbons*, Cooke, M.; Dennis, A.J., Eds.; Batelle Press: Columbus, OH, 1981, pp.571- 582.

(b)- (d): Ramdahl, T.; Alfheim, I.; Bjorseth, A.; *Mobile Source Emissions Including Polycyclic Organic Species*, Rondia, D.; Cooke, M.; Haroz, R.K., Eds.; Reidel: Dordrecht, The Netherlands, 1983, pp.278- 298.

Source: Baek, S.O.; Field, R.A.; Goldstone, M.E.; Kirk, P.W.; Lester, J.N. *Water Air Soil Pollut.*, 1991, 60, p.281.

U.S. alone were estimated to range from 8.6×10^3 tons/ yr to 1.1×10^4 tons/ yr [9].

Current worldwide total ambient atmospheric concentrations of PAHs range from 0.17 ng/ m³ to >100 ng/ m³ [9,27], depending on the sampling location. Table 1.8 shows a comparison of several studies of European PAH concentrations in ambient air [27]. PAHs are now considered to be one of the most widely distributed types of organic pollutants in the environment [28]. PAHs have been detected in Antarctica, the Arctic, and other remote marine areas of the world [9,27].

Charcoal grilling of meat [6,15,39] and cigarette smoking [39,40] have gained recent attention for being identified as releasing large quantities of PAHs. The quality of indoor air can be greatly influenced by cigarette smoking and wood burning (i.e., fireplaces and stoves), increasing the chances of exposure to PAHs. In less industrialized countries, wood burning, as used for cooking, is a serious contributor to total PAH emissions [13,27]; therefore, contact with PAHs in rural areas can be quite significant. In addition, ambient air concentrations of PAHs in less industrialized countries have been found to be similar to those of the U.S. in the late 1960's and early 1970's, before environmental regulations were imposed [27].

As noted in some entries in Table 1.8, PAHs are also subject to seasonal fluctuations, with concentrations being higher in the winter. Changes in emission patterns of vehicular and stationary sources [9,27], as well as seasonal changes, such as shorter daylight hours and reduced atmospheric temperature [9,27], contribute to the observed seasonal changes.

Gaseous PAHs may undergo different atmospheric transformations, once released, than the particle associated PAHs. Gaseous PAHs may react with other gaseous atmospheric

Table 1.8
Comparison of Total PAH Concentrations Obtained
at Urban Centres throughout Europe (ng/ m³).

PAH EPA No.	Compound	Brown et al.(1996) London, UK	Harrison et al.(1996) Birmingham UK	Jaklin et al.(1988) Linz, Austria	Thrane et al.(1987) Norway
84	Pyrene	18.98	3.33/38.0	10/23	71-234/68-491
72	Benz(a)anthracene	3.83	0.34/5.59	2.5/6.7	13-44/19-158
76	Chrysene	6.61	0.61/6.49	5.3/11	33-101/26-265
73	Benzo(a)pyrene	1.83	0.25/0.81	2.5/5.3	5-24/6-61

Note: / = summer/ winter concentrations.

Source: Smith, D.J.T.; Harrison, R.M. *Atmospheric Particles*, Harrison, R.M.; Van Grieken, R., Eds.; John Wiley and Sons, Inc.: New York, 1998, p.274.

species to form new species [9,16,27], or become associated with an aerosol [9,16,27]. It has been reported that gaseous PAHs react mainly with hydroxyl radicals, N_2O_5 , and NO_2 in the atmosphere, or other gaseous PAHs, if they do not immediately condense onto an aerosol upon release into the atmosphere, which is their more likely fate [4,16,18-20]. Particulate PAHs typically react with the airborne species mentioned above, as well as O_3 , O_2 , SO_x , peroxides, acidic and basic compounds [4,18,19,31], or undergo photochemical transformation, depending on atmospheric conditions, prior to removal from the atmosphere. Studies have shown that some particle associated PAHs are transformed into more harmful products than the parent PAHs [16,27,41-44]. The fate of atmospheric PAHs is shown schematically in Figure 1.4.

Coal Fly Ash

While there are numerous types of atmospheric particulate matter, one important type is coal fly ash, a by-product of coal combustion. Coal fly ash is that part of the generated ash that escapes collection devices and enters the atmosphere. Coal ash comprises a significant portion of the particulate matter released into the atmosphere each year. Coal-fired power plants, one of the anthropogenic sources of particulate matter, generate as much as 25 % of atmospheric particulate matter released each year [45]. In 1980, an estimated 10^8 metric tons of fly ash were released into the atmosphere [46], with US emissions alone predicted to exceed 5 million tons in 1985 [47].

Coal is derived from decomposing organic material, and its exact composition depends on the nature of the plant material [48], the extent of decomposition [49], and the material

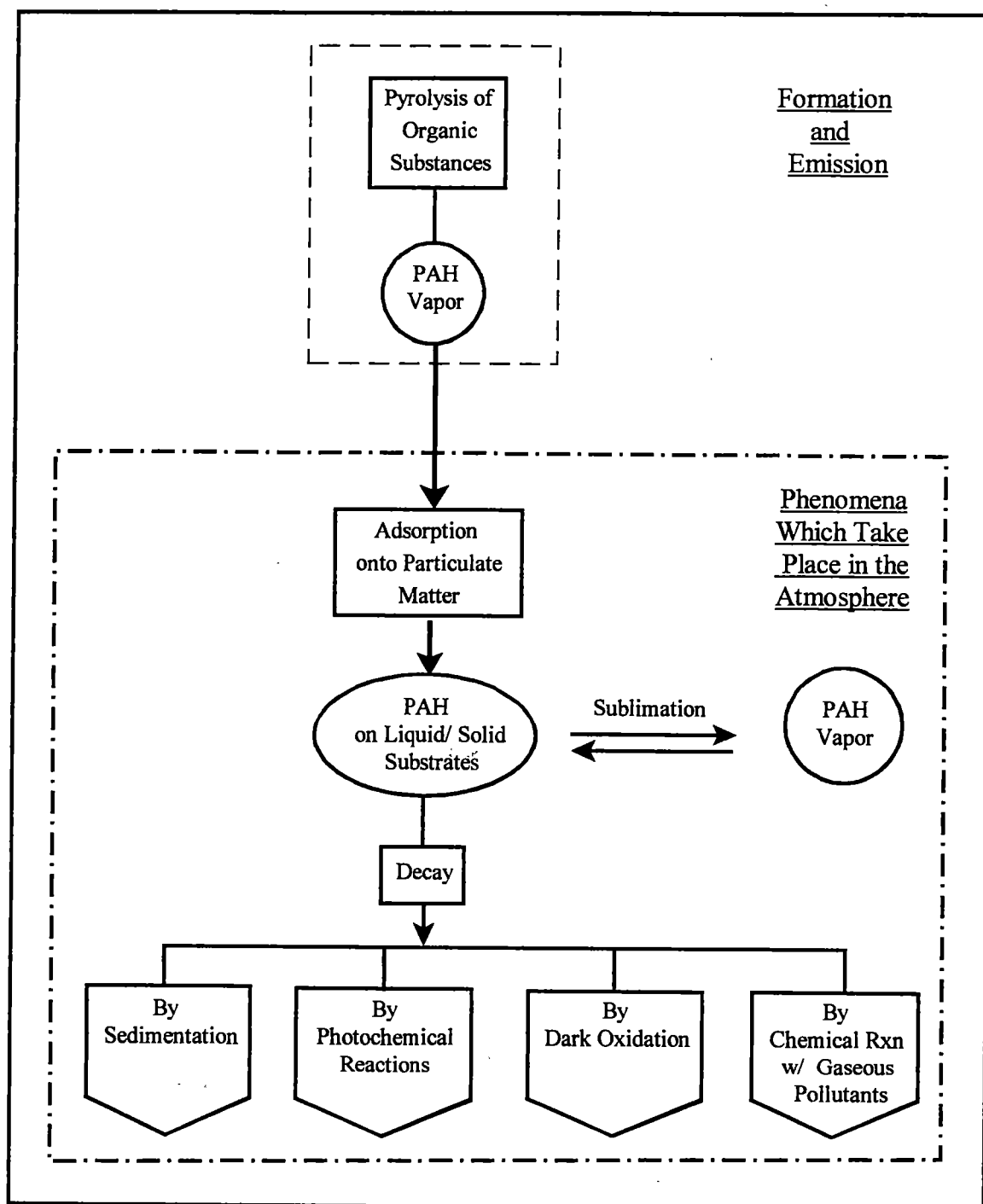


Figure 1.4 Fate of PAHs in the Atmosphere.

Adapted from: Valerio, F.; Bottino, P.; Ugolini, D.; Cimberle, M.R.; Tozzi, G.; Frigerio, A. *Sci. Tot. Environ.*, 1984, 40, 170.

on which decomposition takes place [50]. Coal is made up of mainly C, H, O, N, and S, but can also contain dozens of trace elements [49]. Coal ash particles themselves are quite physically and chemically varied. The properties of ash particles are dependent on the coal composition, the type of combustion process, and the conditions of the combustion process.

Coal ash particles are distributed in all three particulate size ranges discussed earlier, coarse, fine accumulation, and fine nuclei [51,52]. Most coal-fired power plants use an electrostatic precipitator or other stack control device to remove ash particles from the exhaust gas. Although electrostatic precipitators are very efficient (90+ %) for removing a variety of particle sizes [51,53,54], for particles in the respirable range, efficiency is reduced to as low as 67 %, depending on operating conditions [53,54]. Thus, the coal ash particles that escape into the atmosphere tend to be concentrated in the smallest size ranges, including the respirable range. The relationship between particulate matter, PAHs, and human exposure is summarized in Figure 1.5.

Physically, fly ash particles are a mixture of shapes, colors, and sizes. Eleven different particle morphologies have been identified for fly ash [55,56]. Figure 1.6 is a diagram of fly ash morphology. In terms of chemical composition, fly ash particles can be divided into three main categories. A mineral magnetic fraction, a mineral non-magnetic fraction, and a carbonaceous fraction comprise the three categories [57-62].

The mineral non-magnetic fraction of particles accounts for up to 95 % of the mass of most bulk coal fly ashes [56]. Physically, these particles are mainly spherical in shape [56], and non-opaque or mixed opacity in clarity [56]. The spherical particles may be solid,

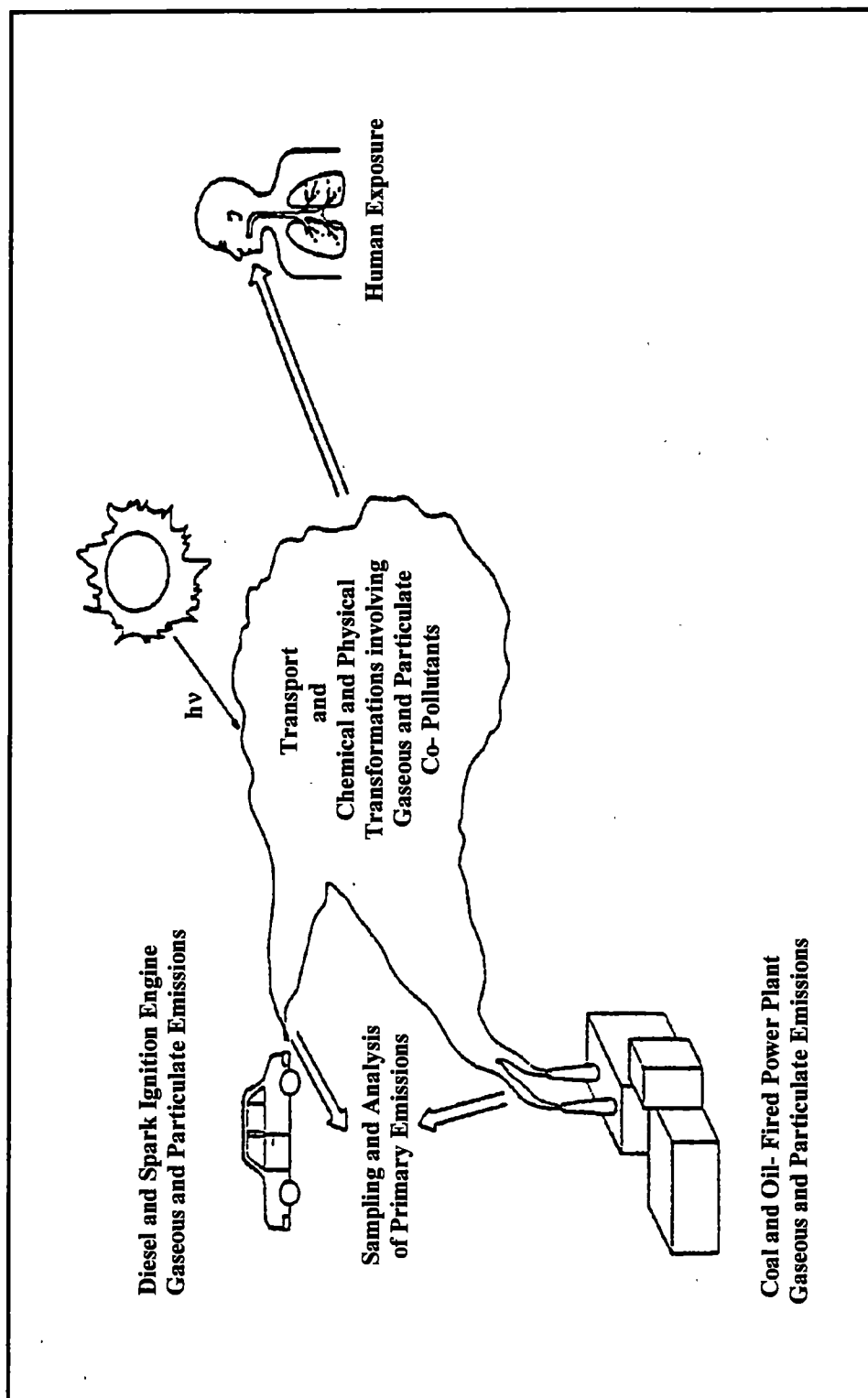


Figure 1.5 Relationship Between Atmospheric Particulate Matter, PAHs, and Human Exposure.
Source: Pitts, J.N., Jr. *Environ. Health Perspec.*, 1993, 47, 117.

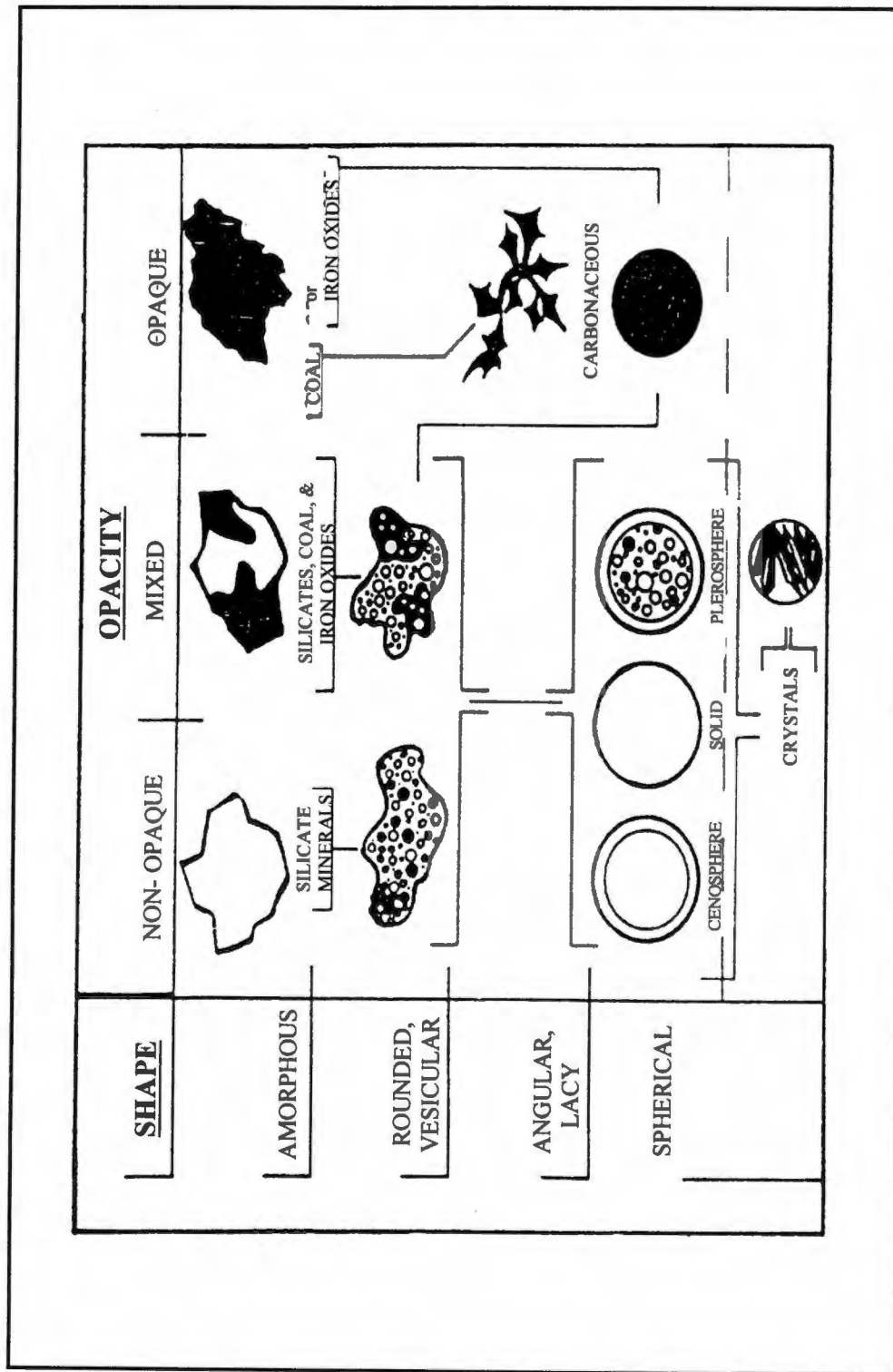


Figure 1.6 Schematic Representation of Fly Ash Morphology.

Source: Fischer, G.L.; Prentice, B.A.; Silberman, D.; Ondor, J.M.; Biermann, A.H.; Ragaini, R.C.; McFarland, A.R. *Environ. Sci. Technol.*, 1978, 12, 450.

hollow, or solid particles enclosed in larger hollow spheres [56]. Chemically, these particles consist primarily of a glassy aluminosilicate phase or a mullite- quartz crystalline phase, of the general formula $(\text{SiO}_2)_x \cdot (\text{Al}_2\text{O}_3)_y$ [41,56]. The mineral non- magnetic fraction may also contain other elements. Table 1.9 lists those elements identified in the mineral fraction of a sample of coal fly ash taken from an electrostatic precipitator. These species may exist as oxide impurities [47], isomorphic substitutions in the aluminosilicate lattice [57], or solid solutions in the aluminosilicate matrix [58].

The mineral magnetic fraction usually accounts for a very small portion of the mass of a fly ash sample [52,60,62]. Physical properties of this fraction are mixed opacity, and either a rounded vesicular or amorphous shape [56]. The chemical composition of this fraction is either a "magnetic spinel" phase of the general formula $\text{Fe}_x\text{Al}_y\text{O}_4$, or a mixture of iron oxides Fe_2O_3 and Fe_3O_4 dissolved in an aluminosilicate matrix [52,60,62]. Like the non-magnetic fraction, many elements, such as K, Ni, Na, Cr, Mn, Fe, and Al are found in this fraction of particles.

The carbonaceous fraction contains particles with a larger specific surface area than the other two fractions [61,63,64]. Carbonaceous particles are usually dark in color, and exhibit several shapes, including angular, lacy; amorphous; and rounded, vesicular [58]. The internal pore structure of these particles is complex and may allow for organic molecules to be "sequestered" in the pores [61,65]. The composition of carbonaceous particles is mainly elemental carbon, not organic or inorganic carbon [61]. Other elements such as, Al, Se, Fe, Ti, and K are found in trace amounts in these particles [61]. Carbonaceous particles tend to represent a minor (or even negligible) fraction of fly ash

Table 1.9
Elemental Distributions for Mineral Phases of Coal Stack Ash.

Element	Glassy Phase (ppm)	Mullite-Quartz Phase (ppm)
Al	87,000	204,000
Si	393,000	287,000
Fe	19,600	3,400
Na	1,710	256
K	25,000	5,270
Rb	532	12
Mg	10,400	10,500
Sr	798	174
Ba	319	69
Sc	31	7
Ti	10,900	4,630
V	176	127
Cr	169	311
Mn	87	9
Co	25	2
Ni	174	78
Cu	144	17
Zn	209	17

Source: Hulett, J.D., Jr.; Weinberger, A. J.; Northcutt, K.J. *Science*, 1980, 210, 1357.

particles released by power plants that are functioning properly, but may represent a major fraction of ash particles produced by power plants having operational problems. From the descriptions of the main particle fractions above, the inhomogeneity and complexity of most coal fly ash samples is evident. Most ashes, however, can be fractionated according to size, density, and chemical composition [64,66], to further aid in studying their interaction with airborne chemical species. Through research, the influence of different parameters (color, chemical composition, surface area, etc.), which affect the interactions of airborne pollutants, can be ascertained.

Aliphatic Organic Compounds

Other organic compounds are also found to deposit on particulate matter, including fly ash [67-71]. Many of these species are aliphatic organic compounds, which can comprise up to 70 % of the organic matter on particles [71]. Hundreds of aliphatic organic compounds have been identified on particulate matter [71]. These include n- alkanes and n- alkenes, carboxylic acids, aldehydes, and ketones [72-80]. Sources of these compounds are both natural, such as vegetation, and anthropogenic, such as combustion processes, wood burning, and vehicular sources [8,71]. The source determines the type or class of organic compound formed. Table 1.10 shows a listing of several common organic pollutant compounds and their sources. Many of these compounds are present in the atmosphere at levels comparable to or greater than PAHs [71,73,78,80]. For example, in 1982 in California, total measured atmospheric concentrations of n- alkanes and n- alkanoic acids were 53.3 ng/ m³ and 294.3 ng/ m³, while the total gas phase PAH

Table 1.10
Common Organic Pollutants and Their Sources.

Compound Class	Usual Compositional Range	Occurrence
<i>Vascular Plant (also microbiota) Sources --</i>		
<i>n</i> -Alkanes	<i>n</i> -C ₂₃ to <i>n</i> -C ₃₅	Ubiquitous (biogenic)
<i>n</i> -Fatty Acids	<i>n</i> -C ₂₄ to <i>n</i> -C ₃₂	Ubiquitous (biogenic)
<i>n</i> -Fatty Alcohols	<i>n</i> -C ₂₄ to <i>n</i> -C ₃₂	Ubiquitous (biogenic)
Alkanes (<i>n</i> , <i>iso</i> , <i>anteiso</i>)	<i>n</i> -C ₁₇ to <i>n</i> -C ₂₀	Microbial
<i>n</i> -Fatty Acids	<i>n</i> -C ₁₀ to <i>n</i> -C ₂₀	Microbial (ubiquitous)
Alkenoic Acids	<i>n</i> -C _{14:1} to <i>n</i> -C _{18:1}	Microbial (short half life)
<i>iso</i> - & <i>anteiso</i> - Fatty Acids	C ₁₅ -C ₁₉	Bacterial
Diterpenoid Hydrocarbons and Acids	C ₁₉ -C ₂₀	Resinous Plants
ω -Hydroxy Fatty Acids	C ₁₀ -C ₂₄	Higher Plants
α , ω -Dicarboxylic Acids	C ₁₀ -C ₂₄	Various
<i>Petroleum Residue (primary) Sources --</i>		
Isoprenoid Hydrocarbons (pristane, phytane, etc.)	C ₁₀ -C ₂₀	Ubiquitous (fossil fuel, not in gasoline)
Alkylcyclohexanes	C ₁₆ -C ₂₉	Ubiquitous (fossil fuel)
Triterpenoid Hydrocarbons	C ₂₇ -C ₃₅	Ubiquitous (not in gasoline & diesel fuel)
Steranes and Diasteranes	C ₂₇ -C ₂₉	Ubiquitous (not in gasoline & diesel fuel)
<i>Pyrogenic Emissions --</i>		
Polycyclic Aromatic Hydrocarbons (PAH)	C ₁₀ -C ₂₄	Ubiquitous (high Temp)
Ketones and Aldehydes (C _n H _{2n} O)	C ₁₀ -C ₃₂	Ubiquitous (low Temp)
<i>n</i> -Fatty Acids	C ₁₀ -C ₂₀	Vehicular Emissions
Alkylbenzoic Acids	C ₇ -C ₉	Vehicular Emissions
Alkyl-naphthoic Acids	C ₁₁ -C ₁₃	Vehicular Emissions
Oxy-PAH (e.g. quinones, ketones, etc.)	C ₁₀ -C ₁₆	Vehicular Emissions

Source: Simoneit, B.R.T. *Intern. J. Environ. Anal. Chem.*, 1986, 23, 226.

concentration was found to be only 11.04 ng/ m³ [71].

These aliphatic organic compounds may have a direct effect on the fate of particle-bound PAHs, possibly causing more harmful PAH transformation products to be formed [27,41-44]. As noted earlier, some PAHs, while not toxic or directly mutagenic, can be photolyzed in the atmosphere to compounds which are mutagens. Several recent studies (see p.42) have shown that the presence of these organic compounds may play a direct role in atmospheric photodecomposition of particle-bound PAHs [81-84]. Many of these compounds appear to increase the photoreactivity of PAHs [81-84].

When gas phase PAHs encounter particulate matter in the atmosphere, organic compounds may already be present on the surface of the particles, or it is possible that PAHs may sorb onto particles, and subsequently, aliphatic compounds may also sorb onto the same particles. A third scenario is simultaneous deposition of PAHs and aliphatic organic compounds. Whatever the sequence of events, the influence of coadsorbed organic compounds on PAH photoreactivity may be dependent on these conditions. The vapor pressures of the compounds, climate conditions, as well as the locations of the emission sources, probably determine the order of deposition, and in turn any subsequent transformations, either of the PAHs or the coadsorbates.

Interactions of Coal Fly Ash with PAHs: Previous Work

The fate of PAHs, once released, is of importance to the entire environment, as well as humans. These PAHs may react with other atmospheric species, or undergo photochemical transformation while in the atmosphere. Those PAHs that associate

themselves with atmospheric particulate matter will usually suffer a different fate than that of the gaseous PAHs [7,16], as described on p.12.

The principal factors affecting the interaction of PAHs with fly ash particles are the chemical and physical properties of the particle, as well as climate conditions, and concentrations of PAHs [27,64]. As stated earlier, PAHs have been shown preferentially to associate with fine particles, especially those in the accumulation range [27,31,32,33], and are found mainly on the surface of these particles [34-36]. This is due in part to the larger specific surface areas of fine particles compared to coarse particles. Table 1.11 shows the specific surface areas of fly ash particle fractions of various sizes. The adsorption of PAHs onto the surfaces of these fine particles is greatly influenced by the chemical nature of the particles. Thus, both physical and chemical properties play a role in the interaction of PAHs with coal fly ash.

Studies by both Soltys et al. [85] and Griest and Tomkins [86] showed that the extent of adsorption of PAHs from liquid solution onto carbonaceous fractions of coal ash increased with increasing carbon content (bulk weight % C) of the ash. Results are shown in Tables 1.12 and 1.13. In another study by Griest and Tomkins, two bulk coal ashes were separated first by size, then by chemical content into carbonaceous, mineral, and magnetic fractions. The sorptivity (degree of adsorption) of PAHs from liquid solution on these fractions was compared with sorptivity of PAHs on model adsorbents, along with a comparison of the specific surface areas of all adsorbents. The results of this study are shown in Table 1.14. It was determined that the fraction with the highest sorptivity for PAHs was the carbonaceous fraction of both ashes. The mineral and magnetic fractions

Table 1.11
Specific Surface Areas for Size Fractions of a Coal Stack Ash.

Particle Size Fraction (μm)	Specific Surface Area (m^2/g)
< 2.3	1.71
2.3 - 3.3	1.19
3.3 - 6.3	0.99
6.3 - 14	0.60
14 - 21	0.57
21 - 150	0.42

Source: Griest, W.H.; Tomkins, B.A. *Environ. Sci. Technol.*, 1986, 20, 293.

Table 1.12
Sorptivities of Benzo[a]pyrene for Carbonaceous Fractions, Coal Stack Ash.

Ash	% C (bulk ash)	Sorptivity ^a (carbonaceous subfraction)
1	0.32	0.17
2	1.29	0.63
3	8.50	1.23

^aunits = [ng benzo[a]pyrene/ mg ash] / [ng benzo[a]pyrene/ mL solvent].

Source: Soltys, P.A.; Mauney, T.; Natusch, D.F.S.; Schure, M.R. *Environ. Sci. Technol.*, 1986, 20, 177.

Table 1.13
Sorptivities of Benzo[a]pyrene for Three Coal Stack Ashes.

Ash	% Carbon	Sorptivity ^a
1	0.93	7.9
2	2.0	27
3	12.5	1300

^aunits = [ng benzo[a]pyrene/ mg absorbent] / [ng benzo[a]pyrene/ mL solvent].

Source: Griest, W.H.; Tomkins, B.A. *Environ. Sci. Technol.*, 1986, 20, 293.

Table 1.14
Sorptivities of Coal Stack Ash, Ash Fractions, and Model Adsorbents for Benzo[a]pyrene.

Adsorbent	% Carbon	Surface area (m ² / g)	Sorptivity ^a
Ash #1			
bulk (21-150 μ m)	21.08	1.42	1100
mineral fraction	5.24	1.14	110
magnetic fraction	13.0	0.69	340
carbonaceous fraction	35.1	2.40	1200
Ash #2			
bulk (21-150 μ m)	6.52	0.42	190
mineral fraction	7.22	0.26	65
magnetic fraction	0.33	0.41	2.1
carbonaceous fraction	48.1	1.20	6000
Porous glass beads	---	169	11
Amorphous carbon black	ca.100	8.21	9200
Graphite	ca.100	13.2	2700

^aunits = [ng benzo[a]pyrene/ mg ash] / [ng benzo[a]pyrene/ mL solvent].

Source: Griest, W.H.; Tomkins, B.A. *Environ. Sci. Technol.*, 1986, 20, 293.

showed varied results; however, it is apparent for these two fractions that the higher the carbon content, the greater the sorptivity of the ash for PAHs. There was no apparent correlation between specific surface area and sorptivity.

In a related study, Dunstan et al. [62] measured approximate heats of adsorption for pyrene from the gas phase on different fractions of a bulk coal stack ash. Heats of adsorption were measured by injecting pyrene onto a gas chromatographic column packed with an ash fraction, then monitoring the elution of the PAH pyrene as a function of temperature. Again, the carbonaceous fraction showed the greatest retention for PAHs, while the magnetic fraction showed the least retention.

The tendency of PAHs to associate with carbonaceous fractions may be due to 1) the irregular shapes of the carbonaceous particles, which contain complex pore structures [64], and the correspondingly high specific surface areas of these particles and/ or 2) adsorption of the PAH molecules on the particle surface by “chemisorption”, which is a very strong type of adsorption based on chemical properties [87,37]. As stated earlier, carbonaceous particles are composed of elemental carbon, of which graphite, one of the allotropes of carbon, is aromatic in nature. It has been reported that dispersion forces between aromatic PAHs and aromatic particle surfaces can result in strong adsorption [88]. Likely, the affinity of carbonaceous particles for PAHs is a combination of the above factors.

PAHs, once adsorbed on fly ash particles, may undergo transformation before removal from the atmosphere. PAHs may be photolyzed by solar radiation [64,90-92], or photochemical or non- photochemical reaction with other species in the atmosphere, such

as O_x , NO_x and HNO_3 , SO_x , and free radicals, may occur [18,19,42,31,43,90-92]. Solar radiation is emitted in the 290- 700 nm region, while most PAHs absorb in the 290- 450 nm region [93]. Average solar flux is 10^{15} - 10^{17} photons/ $cm^2 \cdot s$ [94,95], and is dependent on climatic conditions.

Photoreactivity of particle- bound PAHs has been studied by several groups using many different particulate adsorbents, including fly ash [90,96,97]. Falk et al. first demonstrated photodecomposition of PAHs under simulated atmospheric conditions [98]. Results showed that benzo[a]pyrene (BaP), a common PAH, adsorbed on filter paper underwent 21 % loss in 24 hr and 22 % loss in 48 hr, while there was only 10 % loss of BaP under similar illumination conditions, when adsorbed on soot. Another study by Tebbens demonstrated that PAHs on soot could be decomposed by exposure to sunlight [99]. Under simulated atmospheric conditions, PAHs have been shown to readily decompose on model surfaces, such as silica and alumina [100-104]. Korfmacher and co- workers observed 40- 50 % loss of BaP adsorbed on alumina, when exposed to a xenon lamp for 80 min, and 95 % loss of anthracene after 3 hr under the same conditions [105,106].

Behymer and Hites measured the photolytic half- lives of several PAHs sorbed on silica gel, alumina, fly ash, and carbon black [96,107]. After deposition of the PAH onto the substrate by evaporation of a suitable solvent containing the dissolved PAH on the substrate, illumination was carried out with a mercury lamp. Results, presented in Table 1.15, showed that photoreactive behavior is primarily dependent on the adsorbent and its physical and chemical properties, rather than the structure of the PAH.

Yokely et al. also studied the photoreactivities of five PAHs adsorbed on eight different

Table 1.15
Half-Lives (in Hours) for the Photolysis of PAH on Different Substrates^a.

PAH	Silica Gel	Alumina	Fly Ash	Carbon Black
Acenaphthylene	0.7	2.2	44	166
Fluorene	110	62	37	> 1000
Phenanthrene	150	45	49	> 1000
Anthracene	2.9	0.5	48	313
Fluoranthene	74	23	44	> 1000
Pyrene	21	31	46	> 1000
Benz[a]anthracene	4.0	2.0	38	651
Chrysene	100	78	38	688
Benzo[e]pyrene	70	110	35	> 1000
Benzo[a]pyrene	4.7	1.4	31	574
Perylene	3.9	1.2	33	865
Benzo[ghi]perylene	7	22	29	> 1000

^a25 mg PAH/ g substrate

Source: Behymer, T.D.; Hites, R.A. *Environ. Sci. Techol.*, 1988, 22, 241.

Table 1.16
Photoreactivity of PAH Sorbed on Eight Coal Stack Ashes^{a, b}.

	TX	AR	WK	NM	ET	IL	EA	KA
% C	0.5	0.3	0.3	1.0	0.5	0.3	1.8	2.8
% Fe	3.4	4.0	16.9	2.5	1.7	16.5	10.9	5.9
Anthracene	++	+	+	+	+	0	0	0
Phenanthrene	+	0	0	+	0	0	0	0
Benz[a]anthracene	++	+	0	0	0	0	0	0
Pyrene	+	+	0	0	0	0	0	0
Benzo[a]pyrene	++	+	+	0	0	0	0	0

Note: 0: little or no reaction (≤ 10 % of PAH consumed); +: moderate reaction (10-50 % of PAH consumed); ++: extensive reaction (≤ 50 % of PAH consumed).

^a24 hr illumination

^b TX= Texas lignite coal ash; AR= Alpha Resources commercial coal ash; WK= Western Kentucky bituminous coal ash; NM= New Mexico subbituminous coal ash; ET= East Tennessee bituminous coal ash; IL= Illinois bituminous coal ash; EA= Eastern Appalachian bituminous coal ash; KA= Kaneb coal ash

Sources: Yokley, R.A.; Garrison, A.A.; Wehry, E.L.; Mamantov, G. *Environ. Sci. Technol.*, 1986, 20, 87.

Wehry, E.L.; Mamantov, G. *Aquatic and Surface Photochemistry*, Helz, G.R.; Zepp, R.G.; Crosby, D.G., Eds.; Lewis Publishers: Ann Arbor, 1994, p.176.

coal stack ash samples. In these studies, the PAHs were deposited onto the ash samples from the vapor phase, rather than from a liquid solvent. The results are given in Table 1.16 and clearly showed that photoreactivity of PAHs varied among fly ash samples. The greatest PAH photoreactivity was exhibited on ashes low in carbon and/ or iron content (denoted "TX" and "AR"). The results strongly indicated the influence of the substrate properties on the photoreactivity of PAHs. The TX and AR ashes were further fractionated according to chemical composition to ascertain which factors most influenced photoreactivity. Results, given in Table 1.17, suggested those ash fractions with high carbon and/ or iron content suppressed PAH photoreactivity, while PAHs sorbed on fractions with high nonmagnetic mineral content exhibited efficient photoreactivity. Fractions high in iron content were also found to suppress PAH photoreactivity [62]. In addition, those ashes dark in color suppressed PAH photoreactivity. Again, the correlation between carbon content and photoreactivity of PAHs was demonstrated by Miller et al. [66]. A bulk ash high in carbon content (22.5 % C) was fractionated and studied. The results are shown in Table 1.18.

It has been proposed that the decreased or suppressed photoreactivity of PAHs as a function of carbon content can be attributed to the irregular surfaces of carbonaceous particles, and the very dark color of the carbonaceous substrate, which therefore may shield PAH molecules from light, causing an "inner filter effect." [108]. Although it is apparent that some fly ashes suppress photoreactivity as compared with model adsorbents, the nature of the surface affects the degree of photoreactivity. Carbon content and specific surface area are most influential; however, other factors likely play a role in

Table 1.17
Photodegradation of Pyrene Adsorbed on KA and TX Ashes and Their Subfractions^a.

Adsorbent	Particle Size(μm)	Initial [Py]($\mu\text{g/g}$)	Final [Py]($\mu\text{g/g}$)	% Change
KA ash (2.8 % C)	<45	96 $\pm$ 5	89 $\pm$ 3	7
KA carbonaceous (36 % C, 2.9 % Fe ₂ O ₃)	75-124	35 $\pm$ 3	34	3
KA magnetic (0.64 % C, 50 % Fe ₂ O ₃)	75-124	26 $\pm$ 3	24 $\pm$ 4	8
KA light mineral (0.25 % C, 4.5 % Fe ₂ O ₃)	75-124	41 $\pm$ 4	32 $\pm$ 3	22
KA heavy mineral (0.87 % C, 6.8 % Fe ₂ O ₃)	75-124	65 $\pm$ 4	44 $\pm$ 8	32
TX ash (0.5 % C)	<45	52 $\pm$ 2	41 $\pm$ 2	21
TX carbonaceous (23 % C, 2.4 % Fe ₂ O ₃)	>124	105 $\pm$ 2	102 $\pm$ 2	3
TX magnetic (0.15 % C, 52 % Fe ₂ O ₃)	75-124	22 $\pm$ 1	19 $\pm$ 2	15
TX heavy mineral (0.65 % C, 3.5 % Fe ₂ O ₃)	75-124	87 $\pm$ 3	65 $\pm$ 3	26

^a24 hr. illumination

Source: Dunstan, T.D.J.; Mauldin, R.F.; Zhong, J.; Hipps, A.; Wehry, E.L.; Mamantov, G. *Environ. Sci. Technol.*, 1989, 23, 305.

Table 1.18
Properties of Subfractions from a High-Carbon Coal Ash Sample.

Fraction No.	Particle Size Range (μm)	Specific Surface Area (m^2/g)	% C ^a	% Fe ^b	Pyrene Photo-decomposition (%) ^c
SM1	<45	2.85	4.4	37.8	3
LC1	<45	14.0	30.4	4.0	3
NM3	75-124	0.68	0.5	5.3	44
HC3	75-124	7.2	66.4	1.6	3
SM3	75-124	0.50	0.4	37.4	42
LC2	45-74	20.0	65.9	1.73	6

^aweight percentage of carbon in fraction.

^bweight percentage of iron in fraction.

^cpercentage of adsorbed pyrene destroyed by 24-hr illumination with xenon lamp.

Source: Wehry, E.L.; Mamantov, G. *Aquatic and Surface Photochemistry*, Helz, G.R.; Zepp, R.G.; Crosby, D.G., Eds.; Lewis Publishers: Ann Arbor, 1994, p.178.

influencing the photoreactivity of PAHs on fly ash particles. Reports by Koester and Hites [97], which involve incinerator ash low in carbon content, and Kamens and co-workers [90], involving diesel and wood soot, support this idea. The study by Koester and Hites showed suppression of dibenzodioxin and dibenzofuran photoreactivity on incinerator ash *low* in carbon content ($<0.5\%$ C), while Kamens and co-workers observed rapid photodecomposition of PAHs sorbed on soot (half-life <1 hr). Clearly, the nature of the substrate plays a significant role in phototransformations of compounds sorbed on particulate matter.

Current work by several groups has focused on the effects of other organic compounds on the photoreactivity of PAHs. Jang and McDow showed that quinones, ketones, benzaldehyde, and furans in solution with PAHs accelerated photodecay of the PAHs when illuminated with a mercury lamp [83]; however, not all members of these classes of compounds accelerated decay, an observation which was not understood. Odum, McDow, and Kamens showed that photodecomposition of benz[a]anthracene (BaA) in solution was enhanced by the presence of methoxyphenols [84], while McDow et al. demonstrated that the presence of coadsorbed hexadecane in solution had little effect on BaA photodecomposition [81]. In any event, the applicability of these studies, in liquid solution, to coadsorbate effects on the photodecomposition of PAHs adsorbed on particulate solids is difficult to assess.

The ability of a coadsorbed organic species to suppress or enhance photoreactivity is believed to depend on several factors. Again, the properties of the adsorbent are most influential, but chemical properties of the coadsorbed organic compounds appear to also

have great influence. A few of these properties are polarity, H atom donating ability, and photosensitizer ability [83,107]. The interaction of PAHs, fly ash particles, and co-adsorbed organic compounds is quite complex. The properties of all three, as well as atmospheric conditions, influence their interaction with each other. There are many areas of research to be explored involving these pollutants and how they effect the environment.

Focus of Research

The health of the human population is directly related to the amount of pollution the world produces. With the rise of so many different types cancer in the world, much attention has been focused on finding a cure or preventive measures. Research has focused on the food we eat, the water we drink, and the air we breathe. Examples were given of several studies which involved the study of other compounds adsorbed on atmospheric particles, and their effects on the photochemistry of PAHs. In the present chapter the background for the current work was discussed, with the relevance of the study highlighted many times throughout the discussion.

In the most recent work by this research group [64], experiments were carried out to determine the feasibility of studying atmospherically relevant organic compounds vapor-deposited on fly ash with PAHs. The ability to vapor- deposit, extract, and quantify organic compounds on a model adsorbent, silica, and coal stack ash fractions was determined. Also explored was the effect in the deposition order of the compounds: 1) PAH followed by organic co- adsorbate versus 2) organic co- adsorbate followed by PAH, and its effect on the photoreactivity of the PAH.

Of the previous two organic co- adsorbates chosen for study, succinic acid was deposited prior to the PAH, pyrene, on silica (a model adsorbent) and several fly ash fractions of a particular ash, while n- decane was deposited after pyrene on the adsorbents. The fly ash from which the fractions was obtained is denoted "KA" in Tables 1.19 and 1.20; it was obtained from a power plant that was malfunctioning at the time and is much higher in carbon content (5.5 % C bulk ash) than most coal fly ashes. The amounts of all compounds deposited on the silica, as well as fly ash, were much higher than those expected to be present in environmental samples; however, a discernible change in the photoreactivity of pyrene in the presence and absence of co- adsorbates was desired. The results of the experiments showed that the photoreactivity of pyrene was slightly increased by the presence of succinic acid on all adsorbents. The presence of n- decane on the adsorbents seemed to have little effect, but could be said to slightly inhibit the photoreactivity of pyrene. A summary of these results is shown in Tables 1.19 and 1.20.

It can be seen from these results that relatively little change was detected in the photoreactivity of pyrene on the fly ash fractions with either co- adsorbate present. The extent of photodecomposition of pyrene adsorbed alone on the ash fractions was small; therefore, no strong conclusions could be drawn in regard to such a slight change in pyrene coverage in the presence of the coadsorbates. It was concluded, in retrospect, that the fly ash chosen for study should have been one for which adsorbed pyrene exhibited significant photoreactivity, in order that changes in apparent photoreactivity caused by co- adsorbates would be sufficiently large to measure with reasonable confidence. Moreover, it was subsequently found that succinic acid itself underwent significant

Table 1.19
Photodegradation of Pyrene in the Absence and Presence of Succinic Acid^a.

Adsorbent	% Loss (no coadsorbate)	% Loss (with succinic acid)
Silica Gel	42 ± 12 %	70 ± 6 %
U2 (unfractionated)	2 ± 8 %	11 ± 25 %
F2 (iron fraction)	5 ± 12 %	6 ± 4 %
C2 (carbonaceous fraction)	1 ± 4 %	3 ± 4 %
M2 (mineral fraction)	9 ± 14 %	15 ± 16 %

^a48 hr exposure to filtered lamp output.

Source: Holder, P.S. *Photochemical Transformation of Polycyclic Aromatic Compounds Sorbed on Coal Stack Ash in the Absence and Presence of Coadsorbates*, Ph.D. Dissertation, University of Tennessee, Knoxville, 1993, pp.144-145.

Table 1.20
Photodegradation of Pyrene in the Absence and Presence of *n*-Decane^a.

Adsorbent	% Loss (no coadsorbate)	% Loss (with <i>n</i> -decane)
Silica Gel	68 ± 7 %	37 ± 5 %
U2 (unfractionated)	10 ± 10 %	7 ± 7 %
F2 (iron fraction)	9 ± 8 %	9 ± 3 %
C2 (carbonaceous fraction)	3 ± 6 %	1 ± 3 %
M2 (mineral fraction)	21 ± 12 %	7 ± 5 %

^a24 hr exposure.

Source: Holder, P.S. *Photochemical Transformation of Polycyclic Aromatic Compounds Sorbed on Coal Stack Ash in the Absence and Presence of Coadsorbates*, Ph.D. Dissertation, University of Tennessee, Knoxville, 1993, pp.144-145.

photodecomposition under the conditions used in these experiments, thus casting significant doubt on the results obtained when succinic acid was used as the co- adsorbate.

Several questions were raised by these studies. Was the order of the depositions important and would the same results have been observed if the orders had been reversed (i.e., pyrene followed by succinic acid and n- decane followed by pyrene)? Did the relatively high coverages of the adsorbed compounds bring about the observations or would the presence of the organic compounds, even in much smaller amounts, still produce similar results? One can also ask whether specific classes of organic co- adsorbates are responsible for affecting photoreactivities of PAHs in different ways, or will all organic compounds have similar effects. Finally, one can ask whether the observed results also are dependent on the choice of fly ash or other solid particulate adsorbent.

The current work, described in the subsequent chapters, focused on three of the questions raised above: 1) the nature of the fly ash and the susceptibility of pyrene adsorbed on it to photodecomposition, 2) the relevance of deposition order, and 3) the effect of varying quantities of co- adsorbate. The ash sample used in the current study (derived from the combustion of a Texas lignite; denoted "TX" in Tables 1.16 and 1.17) was chemically unfractionated, low in carbon content (0.64 % C bulk ash), and contained particles in the atmospherically important accumulation mode size range. Additionally, PAHs, including pyrene, vapor- deposited on this ash had been shown in previous work to exhibit efficient photoreactivity [110], so it was reasonable to expect any differences in PAH photoreactivity that might be caused by co- adsorbates to be sufficiently large to be statistically significant.

Pyrene, one of the PAHs shown in previous work to exhibit moderate photoreactivity on different fly ashes [110], was the PAH chosen for these experiments. Pyrene has also been found to be the most abundant PAH emitted by vehicular sources [27,111,112]. In considering compounds for use as co- adsorbates, certain criteria were followed. The compounds must be known to associate with atmospheric particulate matter, and they must be sufficiently volatile for vapor- deposition on the adsorbents. In addition, any compound chosen must be stable toward photochemical and non- photochemical degradation, or must have an ultraviolet absorption spectrum sufficiently different from that of pyrene (by appropriate filtering of source radiation, light that would be absorbed by the co- adsorbate could be eliminated, without also eliminating the wavelengths of light absorbed by pyrene), so that any change in the PAH photoreactivity could be attributed to the co- adsorbate compound and not degradation products. Finally, low toxicity was also an important consideration.

Two different classes of aliphatic organic compounds were investigated as coadsorbates in this study, carboxylic acids and ketones. A representative compound was chosen from each of these classes. Stearic acid, a monocarboxylic acid which derives mainly from vegetation and meat cooking and is commonly detected on atmospheric particulate matter [69,71,75], was selected as a representative carboxylic acid, while 2- undecanone, an alkyl ketone deriving principally from meat cooking [69,71,75], was chosen as a representative ketone. Their structures and physical properties are shown in Table 1.21.

The goals of the current research project were to determine the effects, if any, of the two co- adsorbates individually on the photoreactivity of pyrene adsorbed on coal fly ash.

Table 1.21
Structures and Physical Properties of Coadsorbates Used.

Name	Structure	B.P. (° C)	M.P. (° C)
Stearic Acid	$\text{CH}_3(\text{CH}_2)_{16}\overset{\text{O}}{\parallel}\text{COH}$	183- 184	67- 69
2- Undecanone	$\text{CH}_3\overset{\text{O}}{\parallel}\text{C}(\text{CH}_2)_8\text{CH}_3$	231- 232	11- 13

Source: Aldrich

The order of deposition was investigated, as well as the effects of varying coverages of pyrene and co- adsorbates. In an attempt to more closely mimic atmospheric conditions, coverages of all sorbed compounds were much lower than had previously been used in such experiments.

The power of the lamp source used for the illumination experiments was determined by chemical actinometry in an attempt to compare the photodecomposition results with other studies.

The research described in the subsequent chapters can be divided into three main sections:

- 1) determination of the power (W/ cm^2) of the lamp used for the illumination of the adsorbent samples with sorbed compounds by chemical actinometry
- 2) investigation of the effect of stearic acid on the photochemistry of pyrene when vapor- deposited on a fly ash fraction prior to or following pyrene with varying coverages of both pyrene and stearic acid
- 3) investigation of the effect of 2- undecanone on the photochemistry of pyrene, when vapor- deposited on fly ash prior to or following the deposition of pyrene, all other conditions remaining the same as those used in the stearic acid study, again with varying coverages.

CHAPTER II: EXPERIMENTAL

Introduction

A variety of analytical techniques was required in carrying out the research goals described in the previous chapter. These techniques can be divided into three main categories, according to their purpose. They are grouped as follows:

1. Deposition- The method used for the gas- phase deposition of PAH and coadsorbates onto coal ash particle surfaces.

2. Illumination- A. The method used to illuminate the coal ash sample after deposition of PAH and/ or coadsorbates.

B. The method used to determine the power of the illumination source.

3. Extraction and Quantification- The methods used to extract and quantify the PAH and coadsorbates from the coal ash sample prior to and following illumination of the sample.

These methods, as well as the materials used in the research, are discussed in detail in this chapter.

Materials

Adsorbents

Coal Stack Ash

The coal stack ash used for the experiments was from the electrostatic precipitator of a coal-fired steam plant burning Texas lignite, and was obtained from Oak Ridge National Laboratory [62]. The bulk ash had previously been characterized and was found to have the following elemental composition: Si (25.7 %), Al (7.5 %), C (0.5 %), Fe (3.4 %), Ca (14.5 %), Mg (1.9 %), Na (0.4 %), and K (0.5 %); an aqueous extract of the ash had a pH of 10.8 [110]. The bulk ash specific surface area was determined by nitrogen adsorption to be $2.61 \text{ m}^2/\text{g}$, with a specific average pore volume of 5.0 mL/g [110]. This particular ash was chosen because of its low carbon content. In previous work by this group, PAHs were found to show much greater photoreactivity on coal ashes with lower carbon and iron content, as well as those lighter in color [110]. In view of the objective of the research (studying the influence of coadsorbates on the photochemistry of adsorbed PAHs), it was not deemed appropriate to use an ash on which adsorbed PAHs exhibited little detectable photochemistry.

The bulk ash was previously fractionated by particle size using sieves [62]. The bulk ash was passed in succession through sieves of the following mesh size - 45, 75, 125, and $150 \mu\text{m}$. The ash fractions were then collected and labeled as "U", to denote that no other fractionations (e.g., by chemical composition) were undertaken. The fractions were additionally given a number, from 1 to 5, to indicate the particle diameter. The five fractions were designated U1 ($<45 \mu\text{m}$), U2 ($45\text{-}74 \mu\text{m}$), U3 ($75\text{-}124 \mu\text{m}$), U4 ($125\text{-}149$

μm), and U5 (>150 μm). The fraction used in these studies was U1. This fraction, chosen for the small particle sizes, contains some particles of the respirable size range [113], and therefore is the most relevant for study, according to the significance of this work noted in the opening chapter. This particle size range also has the longest atmospheric lifetime [9,27,111-113], which again demonstrates the greater relevance of this fraction.

Silica

Silica gel 60 with a particle diameter 75- 125 μm, 70- 230 mesh, was used as a “model” adsorbent for the studies. It was obtained from EM Reagents .

Both adsorbents were degassed prior to use by passing a stream of nitrogen (National Welders Supply Co.) through the sample for 24 hours at 200 °C.

Adsorbates

Pyrene- 99+ % purity, supplied by Fisher Scientific, was vacuum sublimed before use. The two coadsorbates used in the studies were stearic acid- 99+ % purity, and 2-undecanone- 99 % purity, both supplied by Aldrich. The two coadsorbates were used as received. Latex gloves were worn when handling pyrene, whether adsorbed or not.

Solvents

The various solvents used for the extraction and quantification methods were all

reagent grade. They were toluene (Mallinckrodt or Fisher), methanol (Mallinckrodt or Fisher), and acetone (Mallinckrodt or Fisher).

All other materials used are described in the experimental section pertaining to the material in question.

Vapor Depositions

The apparatus used to carry out the vapor depositions of the adsorbates was previously described in detail by Mauldin [114], and is shown in schematic form in Figure 2.1. The original apparatus was designed from two (Blue M General Signal) Mechanical Convection Ovens (Model OV- 472A- 3). Modifications to the original apparatus described by Korfmacher [115] and Engelbach [116] were made by Mauldin to allow for easier and more efficient depositions. This entire apparatus was contained in a fume hood to vent possibly harmful vapors.

The adsorbate to be deposited was placed in a specially designed glass diffusion cell (Ace Glass), shown in Figure 2.2, and placed vertically into oven 1. The cell was clamped at both ends to glass joints (Ace Glass) with Teflon O-rings (Viton). The glass joints were connected to the inlet and outlet stainless steel tubing (1/ 16 in o.d.) by Swagelok stainless steel connectors. Stainless steel tubing (1/ 16 in o.d.) connected oven 1 to oven 2 and was heated by a heating tape (Thermolyne).

A second specially designed glass cell (Ace Glass Inc.), called the deposition cell, was contained in oven 2. A diagram of the deposition cell can be seen in Figure 2.3. The

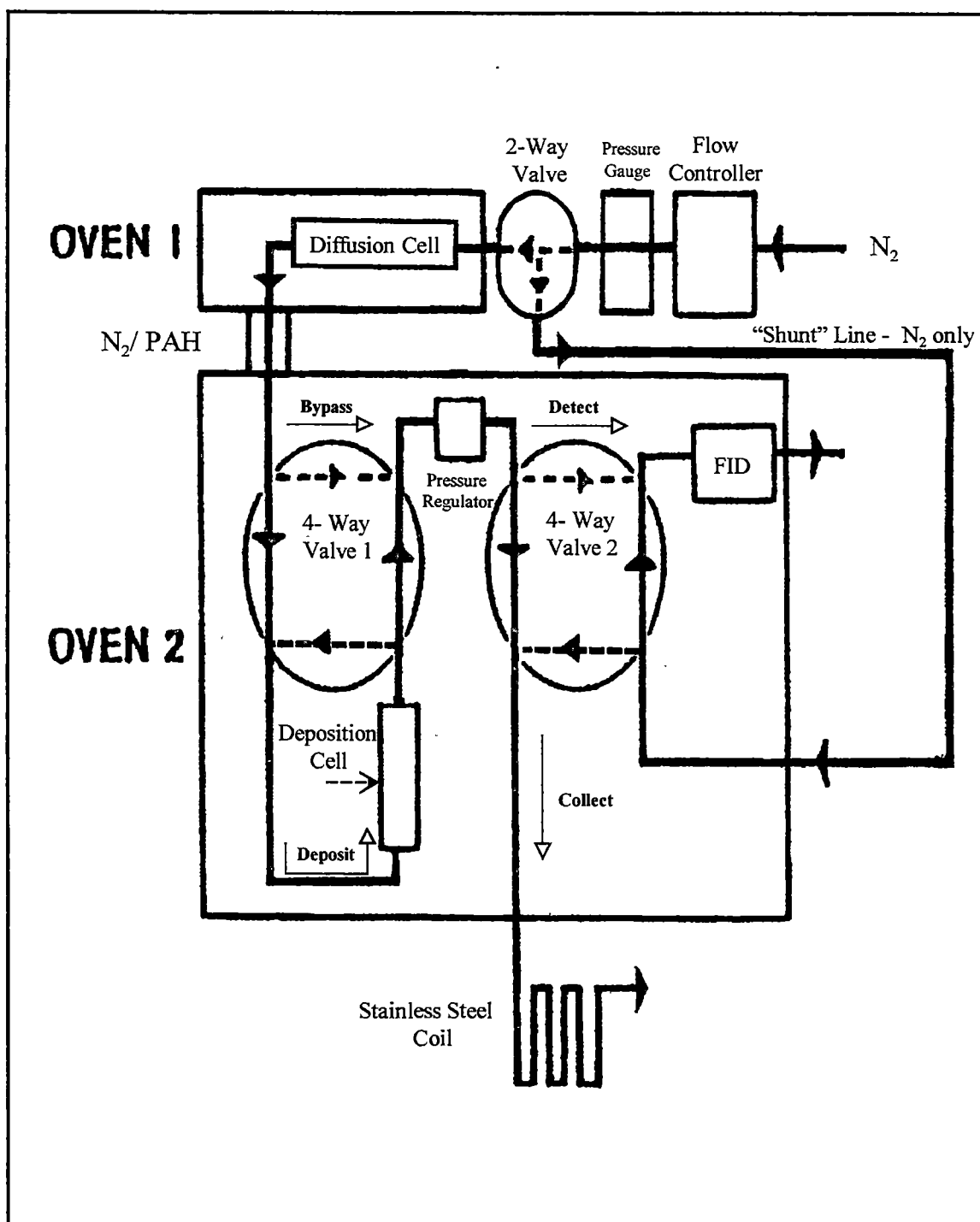


Figure 2.1 Schematic Diagram of Vapor Deposition Apparatus.

Adapted from: Hipps, A.D. *Photochemical Investigations of Surface Adsorbed Polycyclic Aromatic Hydrocarbons*, M.S. Thesis, University of Tennessee, Knoxville, 1989, p.22.

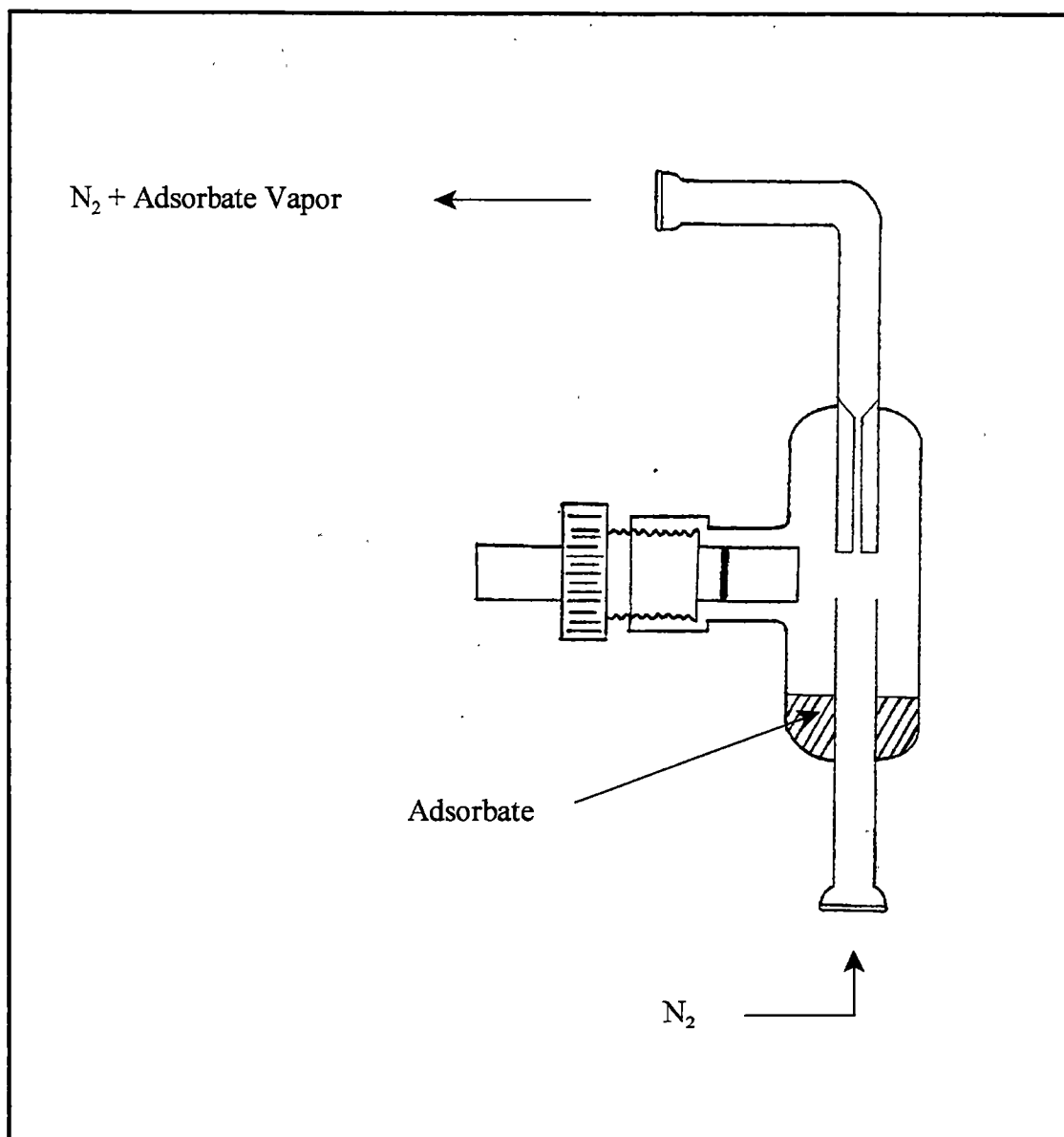


Figure 2.2 Schematic Diagram of Diffusion Cell Used to Generate Adsorbate Vapor.

Adapted from: Yokely, R.A. *The Photochemistry of Polycyclic Aromatic Hydrocarbons Adsorbed on the Surface of Coal Fly Ash*, Ph.D. Dissertation, University of Tennessee, Knoxville, 1985, p.39.

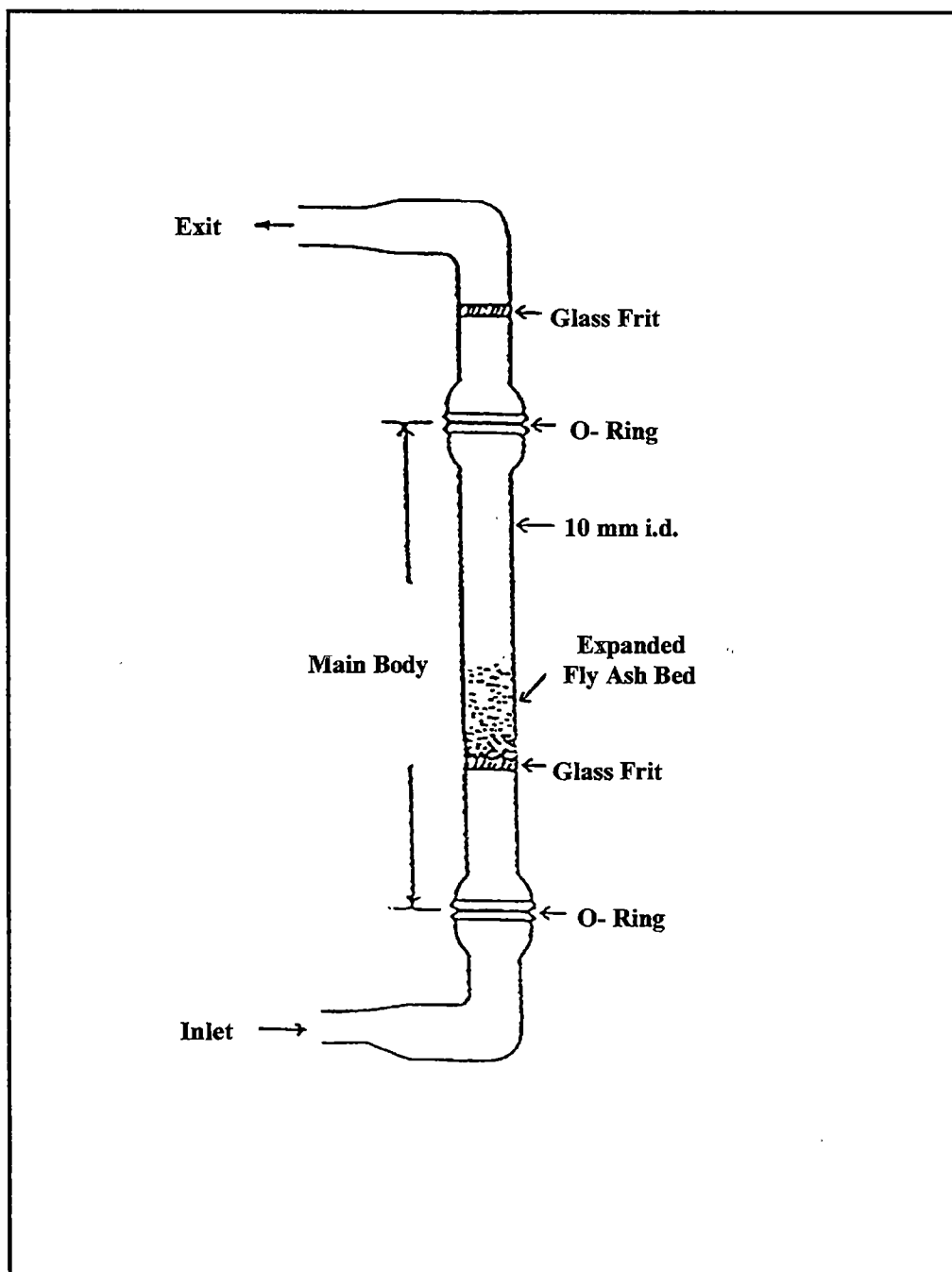


Figure 2.3 Schematic Diagram of Cell for Deposition of Adsorbate Vapor on Adsorbent.

Source: Korfmacher, W.A. *The Decomposition of Organic Matter Adsorbed on Coal Fly Ash*, Ph.D. Dissertation, University of Illinois Urbana- Champaign, 1978, p.46.

deposition cell, which was also placed vertically in the oven, contained a glass frit on the bottom, on which 2-10 g of adsorbent rested. The cell was clamped at both ends to glass joints with Teflon O-rings (Viton). In the top joint there was another glass frit to prevent adsorbent from becoming trapped downstream in the stainless steel tubing. The joints were connected to the inlet and outlet stainless steel tubing (1/ 16 in o.d.) by stainless steel Swagelok connectors. Also, the stainless steel outlet tubing (1/ 16 in o.d.) connected to the deposition cell passed out of oven 2, at which point it was wrapped in a heating tape, and was connected by way of a Swagelok connector to either a cooled stainless steel coil or a Teflon tube, which was placed in a flask of water. The heating tape was necessary to prevent condensation of the adsorbate in the stainless steel tubing and causing a blockage.

The cooled stainless steel coil was used to collect the adsorbate that passed through the apparatus. It was cooled in order to cause condensation of the adsorbate on the walls of the coil, so that all of the adsorbate passing out of the apparatus could be collected, and quantified to determine the concentration of vapor- phase adsorbate in the nitrogen stream flowing through the apparatus. The Teflon tube in a water- filled flask was used to ensure the nitrogen/ adsorbate vapor stream was not vented to the laboratory, when the adsorbate was not being collected for quantification.

A gas chromatographic FID, flame ionization detector (Gow- Mac, model # 12- 800), attached to oven 2 was used to monitor the concentration of vapor- phase adsorbate in the system. Compressed dry grade air with a flow rate ~250 mL/ min and hydrogen with a flow rate ~25 mL/ min (National Welders Supply Co.), both controlled by rotameters, were used as fuel for the FID, with nitrogen (National Welders Supply Co.), flow rate ~

30- 40 mL/ min controlled by a rotameter, as the carrier gas. An electrometer (GowMac # 40- 900) set at 1 mV was used to monitor the FID signal, and a chart recorder (Kipp and Zonen BD 40) recorded the signal. The range of the electrometer was changed according to the adsorbate signal output to provide a "FID plot" that could be used to determine the quantity of adsorbate that deposited on the adsorbent (see p.63 for more detail).

Use of bidirectional valves in the two ovens allowed for several paths for the adsorbate/ carrier stream. The adsorbate- free carrier stream could be directed through the system tubing, through an empty deposition cell, to the heated detector for zeroing. The valves also allowed for direction of the adsorbate/ carrier stream through the entire heated apparatus, to coat the system walls and empty cells with adsorbate before deposition, in order to obtain an accurate adsorbate flow rate, as well as bypassing of the adsorbate stream during temperature equilibration of the adsorbent during a deposition. Finally, the valves allowed for collection of the adsorbate stream for flow rate determination, and repairing of leaks without shutting down the entire system. Figure 2.4 shows the different paths of flow through the ovens that can be obtained and tells the purpose of the path.

Refer to the diagram of the apparatus (Fig. 2.1) for the following description of the procedure. The temperature of oven 1 largely controlled the rate of flow of the adsorbate, while the temperature of oven 2, and the total time that the adsorbate stream passed through the deposition cell, were used to control the quantity of adsorbate that was adsorbed. Initially, with oven 1 off, an adsorbate- free nitrogen carrier stream was directed through the system tubing, through an empty deposition cell, tracing the

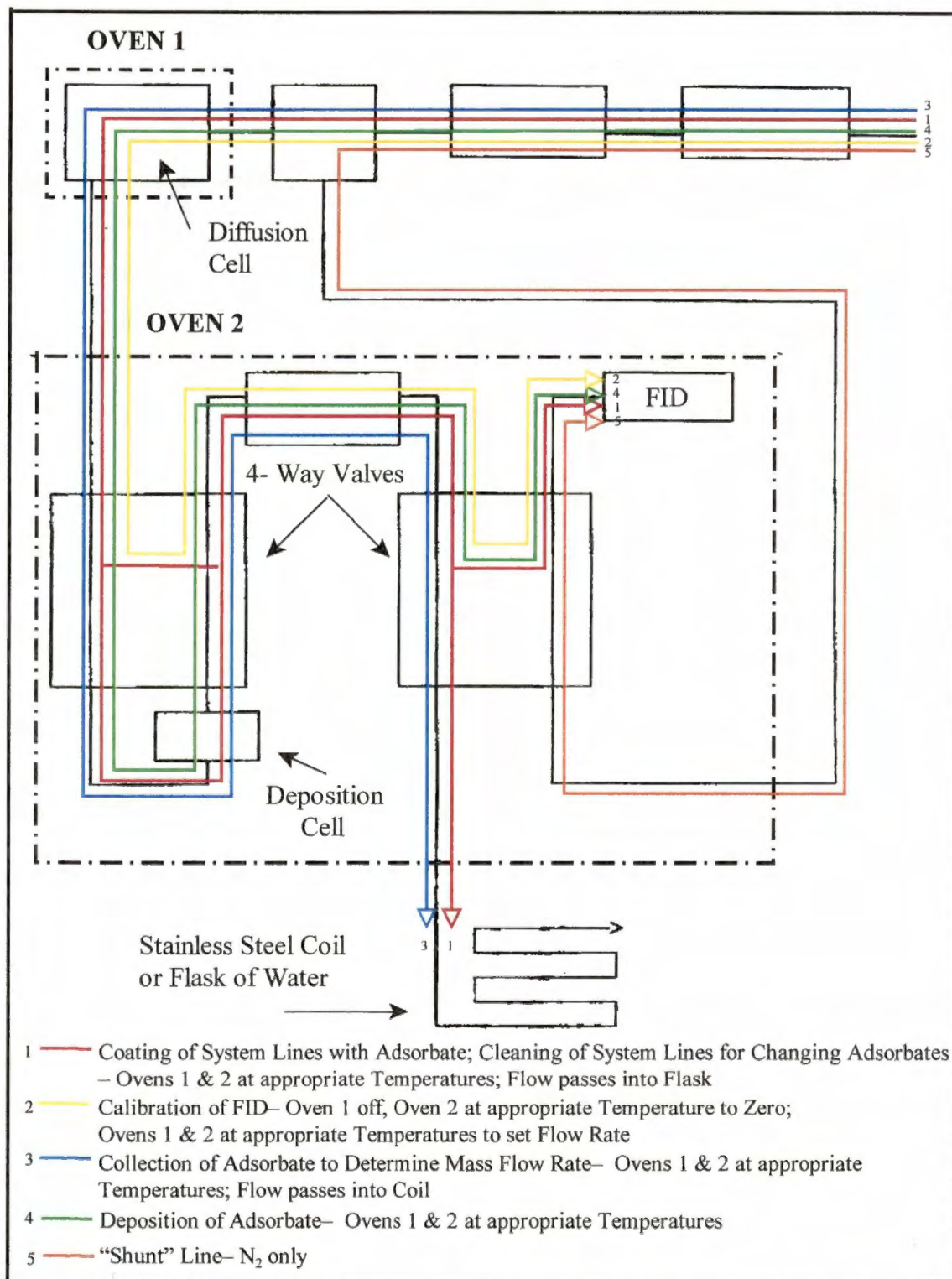


Figure 2.4 Schematic Diagram of Paths through Apparatus Showing the Various Vapor Pathways.

adsorbate path during a deposition, to the heated FID for zeroing.

An appropriate oven 1 temperature was then chosen, depending on the adsorbate, so as to generate a reasonable quantity of vapor in the diffusion cell. A stream of nitrogen (flow rate ~30-40 mL/ min) was passed through the stainless steel tubing and, by way of a two-way valve, was directed into oven 1 and through the diffusion cell containing the vapor. The nitrogen carrier stream containing the adsorbate vapor was then directed into oven 2, which contained the deposition cell. The temperature of oven 2 was kept at least 5° C higher than the temperature of oven 1 to prevent excessive condensation of the adsorbate on the walls of the stainless steel tubing in the system. Use of the first two-way valve in oven 2 allowed the adsorbate/ carrier stream to bypass the deposition cell, while the second two-way valve was used to direct the adsorbate/ carrier stream to the FID for monitoring.

Once the system was equilibrated at the appropriate oven temperatures, the nitrogen/ adsorbate stream was directed through oven 1 and through an empty deposition cell in oven 2 by way of the first two-way valve, for "coating" of the system tubing, and was directed, by way of the second two-way valve, out of oven 2 through the Teflon tubing into a water-filled flask, to ensure no vapor was vented to the laboratory. Prior to deposition of an adsorbate on an adsorbent, it was necessary to coat all of the system tubing with the adsorbate being used for deposition. This was done in order to ensure that, once quantitative measurements were made, all (or virtually all) of the adsorbate that was removed from the vapor stream deposited on the adsorbent, rather than on the tubing. If this had not been done, the inferred quantity of adsorbate that deposited on an

adsorbent would have been erroneously high.

The quantity of adsorbate that was deposited on an adsorbent was determined by measuring the extent to which the concentration of adsorbate in the vapor phase decreased as the adsorbate vapor stream passed through the bed of adsorbent. Accordingly, following the coating of the system tubing with adsorbate, a mass flow rate (MFR) determination was carried out in order to establish the vapor- phase adsorbate concentration in the absence of adsorption by the adsorbent. Again, using an empty deposition cell in oven 2, the nitrogen/ adsorbate stream was directed through oven 1 and through the cell in oven 2, then out of oven 2, using the second two-way valve, to the stainless steel coil, immersed in an ice bath, for collection of the adsorbate vapor over a known period of time (see below for details on how the MFR was quantified). Both the coil connection and the Teflon tubing connection, when used, were maintained at least 5° C higher than the temperature of oven 2 to prevent excessive condensation of the adsorbate on the walls of the connections.

After the MFR of the adsorbate was determined, a deposition was carried out. During a deposition the adsorbate/ carrier stream in oven 2 was directed, using the first two- way valve, through the deposition cell, containing a known amount of adsorbent. For deposition on the model adsorbent, the frit size in the deposition cell was 25- 50 μm , while the frit size was 10- 20 μm for deposition on the U1 ash fraction. The smaller frit size was necessary for deposition on the U1 ash to prevent clogging of the frit by the smaller fly ash particles, and causing a buildup of pressure and reduced adsorbate flow rate. After the adsorbate/ carrier stream was passed through the deposition cell containing the adsorbent,

the stream was directed using the second two-way valve to the FID for monitoring of the adsorbate signal. A pressure regulator in oven 2 was used to control the back pressure in the system generated by the frits and the adsorbent to maintain the flow rate of the adsorbate through the system. The gradually higher temperatures at the various connections in the apparatus (i.e., oven 1- oven 2, oven 2- coil/ teflon tubing) were necessary to prevent condensation of the adsorbate at the connections, which could cause a blockage.

The mass flow rate, MFR, of the adsorbate was determined by a timed collection of adsorbate/ carrier flow into the cooled stainless steel coil, while passing through the empty deposition cell in oven 2. This was done to calibrate the FID for the subsequent determination of the quantity of adsorbate deposited on the adsorbent. The coil was then rinsed with a suitable solvent into a volumetric flask, which was filled to the mark. Toluene and occasionally methanol were used as solvents for pyrene, while acetone was used as solvent for stearic acid and 2- undecanone. The concentration of adsorbate in the flask was then determined by an appropriate analytical method, depending on the adsorbate- UV/ visible spectrophotometry for pyrene, and gas chromatography for stearic acid and 2- undecanone. Once the quantity of adsorbate collected over a given time period was known, the mass flow rate of adsorbate was calculated (quantity of adsorbate/ time) and used to determine the length of time needed for deposition of a given amount of adsorbate on a given quantity of adsorbent. The desired sample coverages were obtained in this manner.

After a deposition was performed for a predetermined amount of time using a given

amount of adsorbent sample, the actual coverage of adsorbate on the adsorbent was determined by a plot of FID signal versus time obtained from the electrometer and chart recorder. A diagram of a FID plot is shown in Figure 2.5. The point labeled M_d on the plot represents the point at which adsorbate/ carrier flow was at the maximum for the selected oven temperatures, while flow was directed through oven 2 to the detector, bypassing the deposition cell. At time t_0 the first two- way valve was switched and adsorbate/ carrier flow was directed through the deposition cell containing the adsorbent. The signal then decreased as time progressed, due to adsorption of the adsorbate by the adsorbent, and approached the 0 point on the vertical axis. This point represented the zero point of the detector, which is the signal obtained with adsorbate- free nitrogen carrier flow passing through oven 2, through an empty deposition cell, to the detector, at the oven 2 temperature to be used for deposition.

At time t_f the deposition was stopped by switching the flow again to bypass the deposition cell. The signal then returned to the M_d level at some time, t_m . If the deposition was not stopped at time t_f , after a very long time period (ca. 24 or more hrs, depending on sample size and flow rate) the adsorbate/ carrier flow signal eventually began to rise and returned to the M_d level, indicating that the adsorbent was “saturated” with adsorbate. For the studies in this work, all depositions were stopped before the saturation point.

The coverage of adsorbate on the sample was then determined by the following equation:

$$\text{Coverage} = (\text{MFR}) \times (t) \times (f)$$

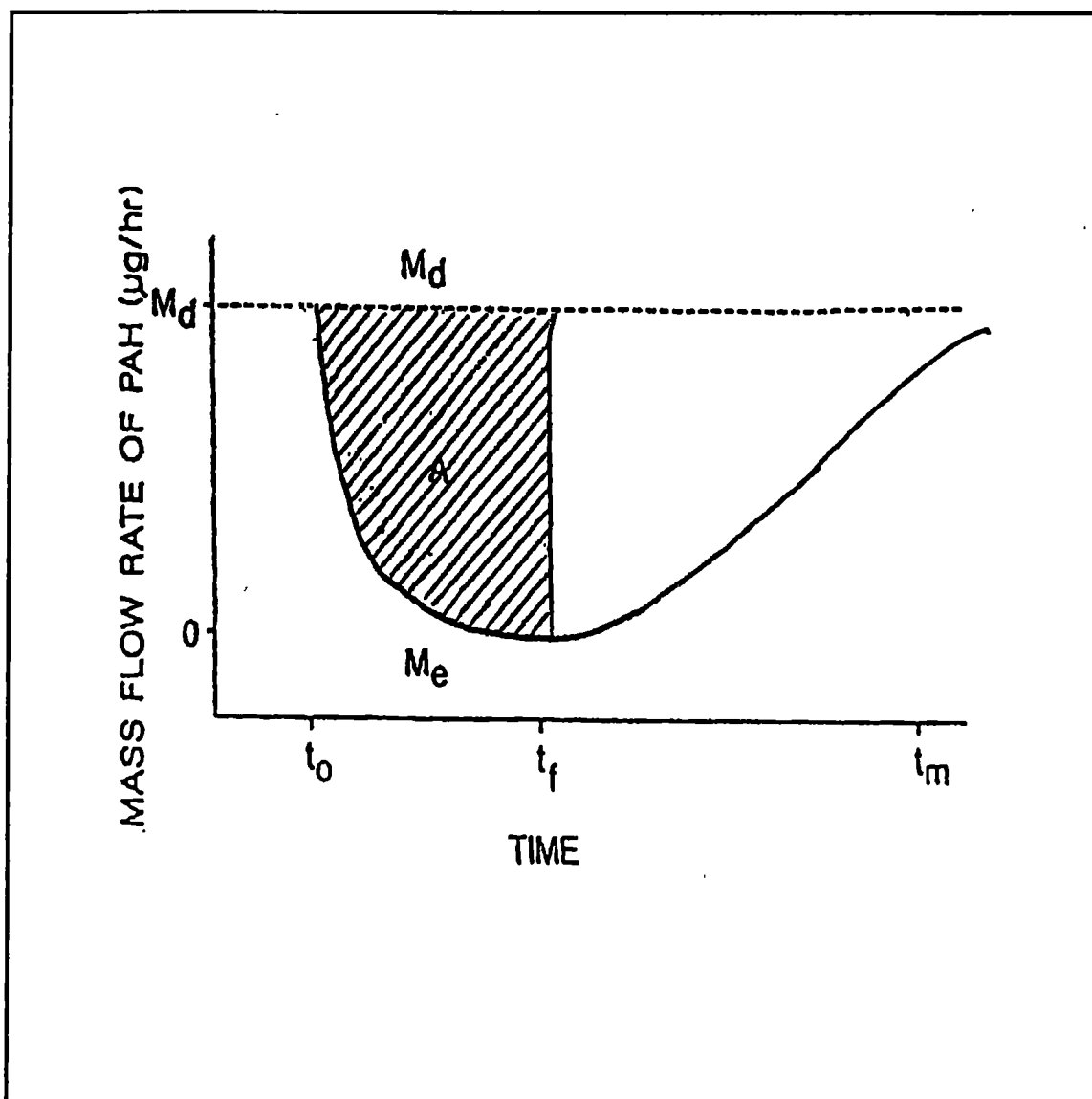


Figure 2.5 Diagram of FID Plot Used to Determine Quantity of Adsorbate Deposited on Adsorbent.

Source: Engelbach, R.J.; Garrison, A.A.; Wehry, E.L.; Mamantov, G. *Anal. Chem.*, 1987, 59, 2542.

where MFR is the mass flow rate, t is the total time of the deposition, and f is the fraction of vapor- phase adsorbate retained by the adsorbent. One determined f from the FID plot by finding the ratio of the area labeled A to the rectangular area bounded by t_o , t_p , M_e and M_d . These areas were determined by the cut and weigh method. The time of the deposition was known and the MFR was calculated from a timed collection of adsorbate, as described on p.62.

In the current work much smaller adsorbate coverages, $\sim 50\text{-}75\ \mu\text{g adsorbate/g}$ adsorbent, were used than had previously been tried by other members of this research group. This was done in an attempt to prepare realistic samples that more nearly mimic atmospheric conditions, wherein coverages of individual adsorbates found on particulate matter can be very small, $\sim 1\text{-}10\ \mu\text{g/g}$ or less, due to the fact that many different adsorbates are typically found on a single adsorbent [71,77].

Temperatures at which depositions were performed had to be chosen carefully when two different adsorbates were to be deposited on a single sample. Two main types of samples were prepared. In the first type, the coverage of the PAH, pyrene, was held constant and the coadsorbate coverage was varied; in the second, the coadsorbate coverage was constant and the pyrene coverage was varied. This was done for both the stearic acid and 2- undecanone coadsorbates. In addition, the order of deposition varied for the two coadsorbates, depending on whether the coadsorbate was more or less volatile than the PAH. One was deposited prior to the PAH, while the other was deposited after the PAH was deposited.

Illuminations

Photodegradation Experiments

Once the vapor- deposited samples were prepared, they were then subjected to conditions meant to simulate those which the particles would encounter in the atmosphere. When not in use, the prepared samples were stored in the dark in a desiccator.

For the illumination experiments a Cermox LX 300 UV xenon lamp (ILC Technology) powered by an illuminator power supply (ILC Technology # PS 300-1) set at 11 A was used. The spectral output of the lamp as a function of wavelength can be seen in Figure 2.6. This spectrum can be compared with the spectrum of sunlight shown in Figure 2.7. The xenon lamp was chosen because its spectral output over the wavelength range in which pyrene adsorbs is similar to that of natural sunlight.

The sample to be illuminated was placed approximately 62 cm from the lamp. The sample was contained in a special quartz cell, with a strategically mounted quartz rod for stirring, at 10° to horizontal, and was attached via a tapered ground glass joint to a Rinco rotary evaporator motor (Valley Electromagnetic Corp.), which rotated the sample at approximately 60 rpm to ensure the entire sample surface was exposed to the incident radiation, while a slight vacuum was applied via a water aspirator to hold the quartz cell onto the glass joint. A detailed diagram of the quartz illumination cell can be seen in Figure 2.8.

The lamp output was filtered by a 22 cm water- filled cell containing quartz windows at either end to allow passage of the ultraviolet radiation, while the water attenuated the near infrared output of the lamp, so that thermal changes in the sample would not be induced.

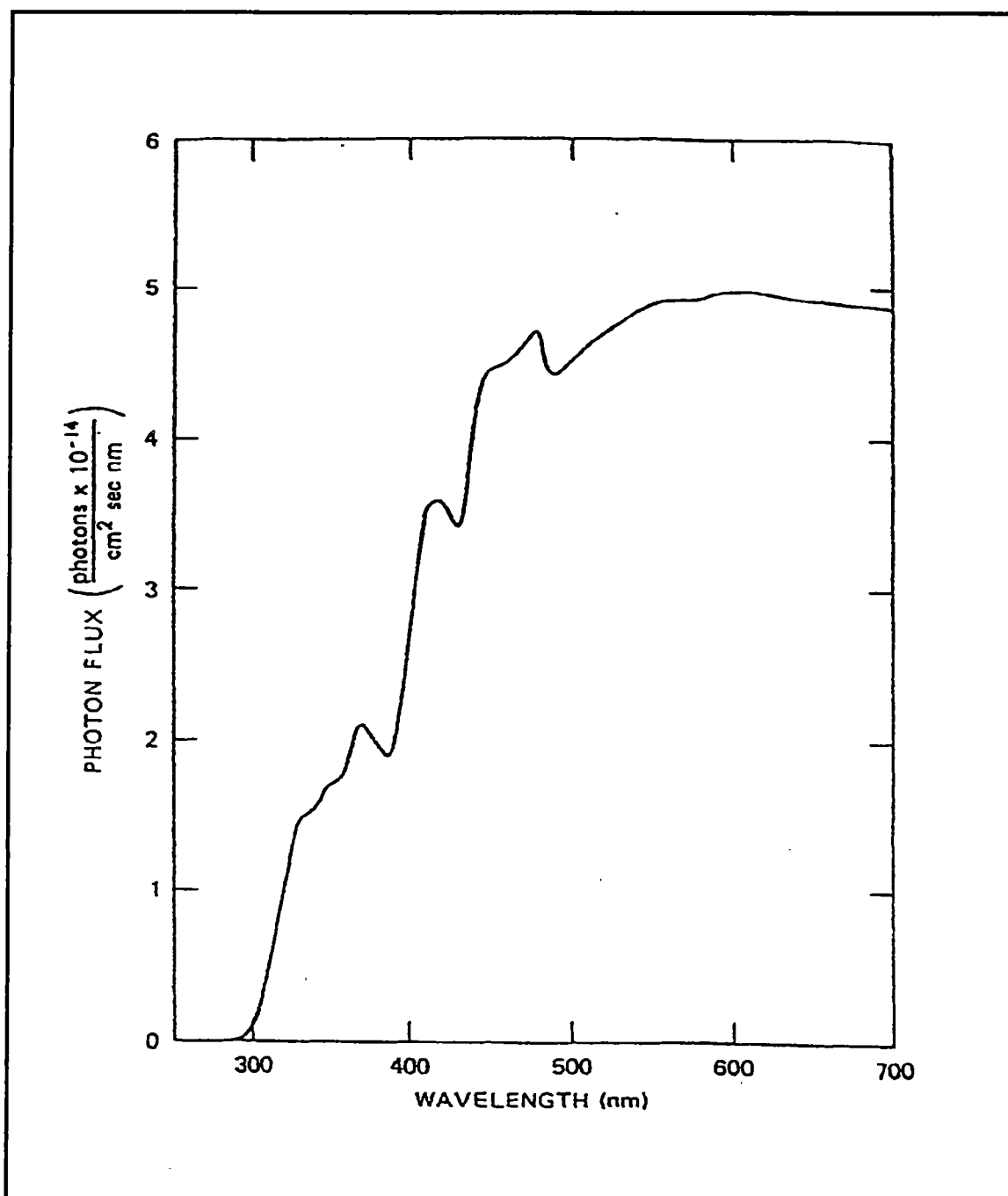


Figure 2.6 Solar Intensity as a Function of Wavelength.

Source: Dulin, D.; Mill, T. *Environ. Sci. Technol.*, 1982, 16, 815.

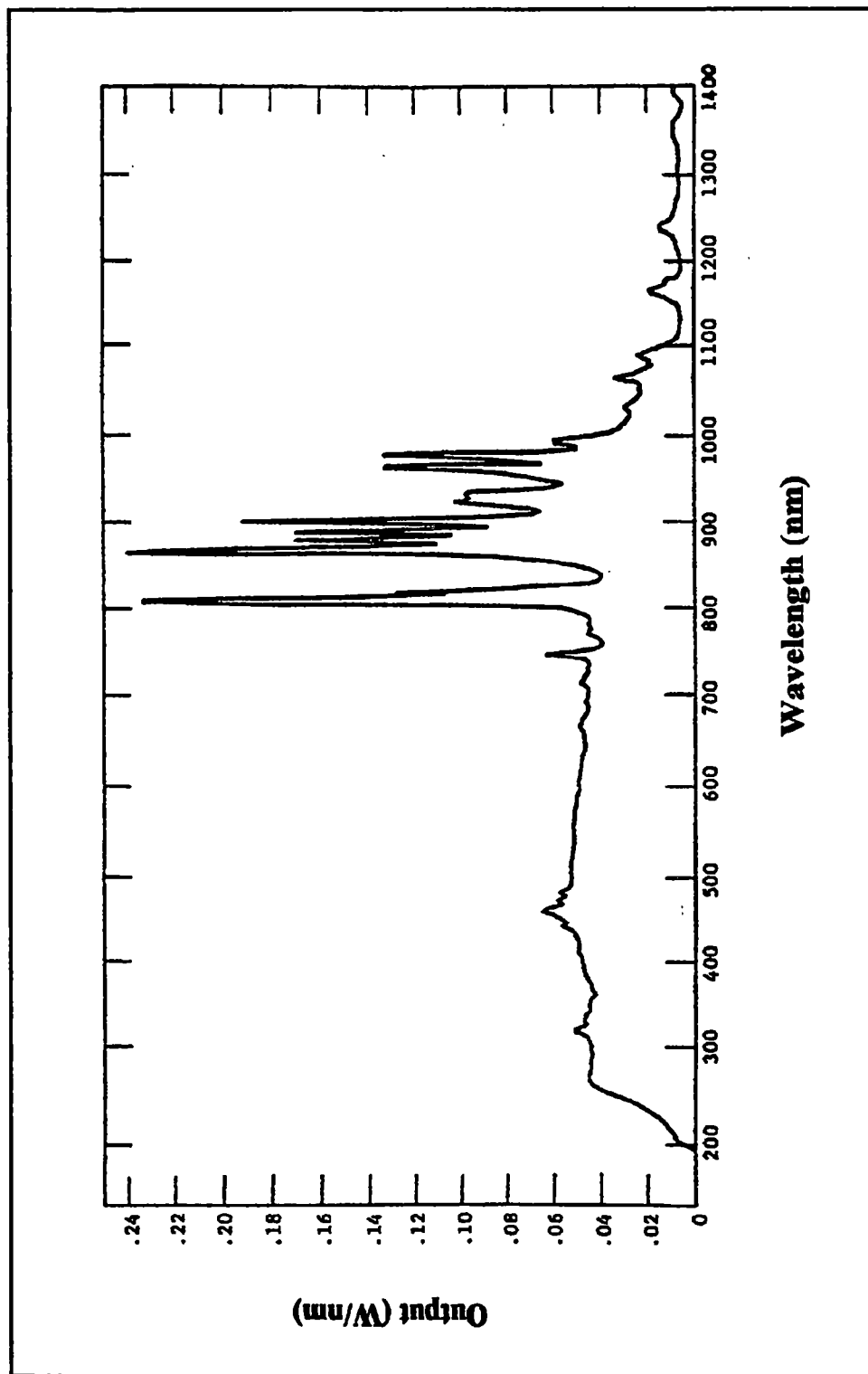


Figure 2.7 Output of Cernax Lamp.

Source: Manufacturer's Literature Supplied by ILC Technology

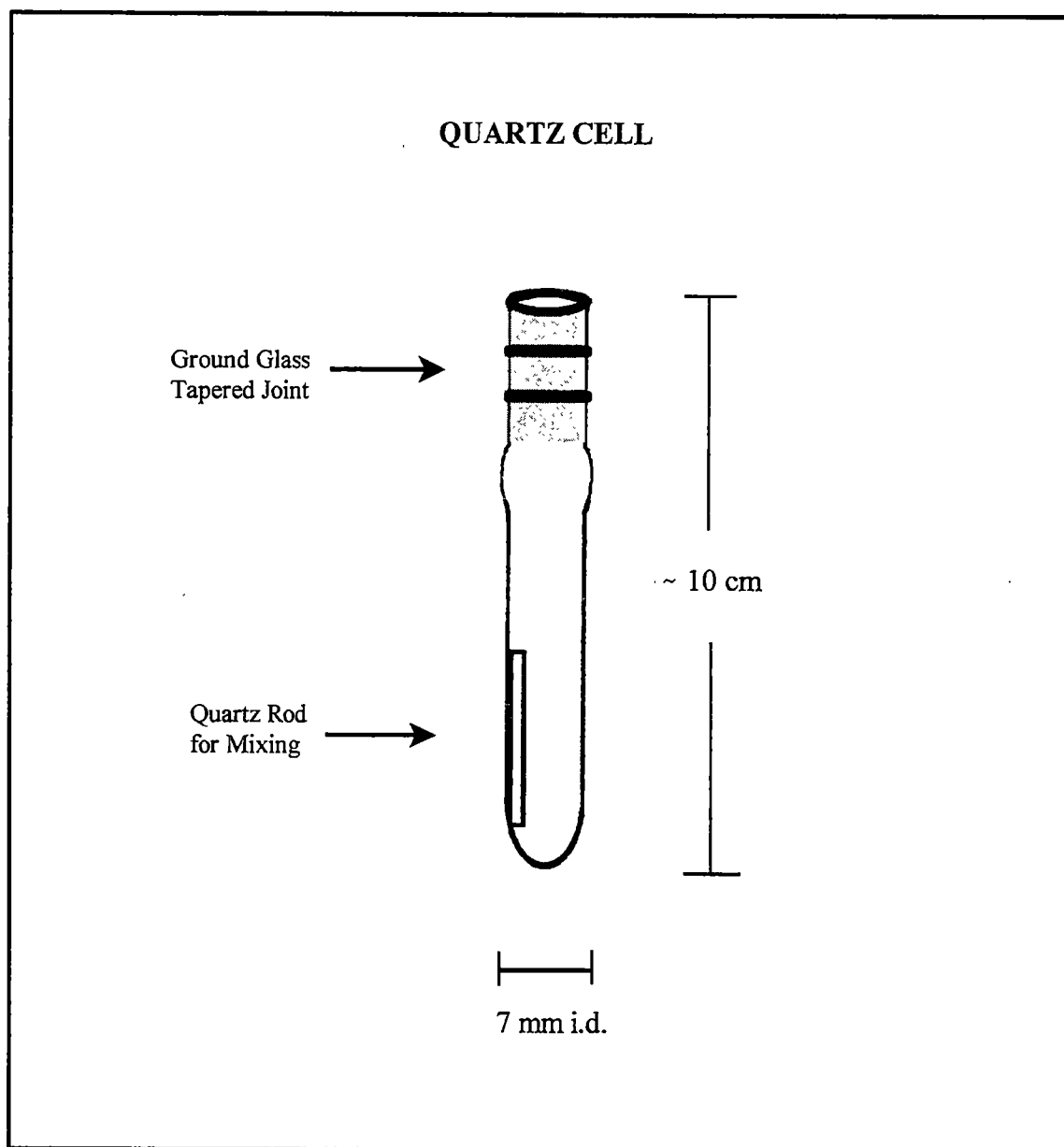


Figure 2.8 Diagram of Illumination Cell.

This cell was placed directly in front of the lamp and can be seen in Figure 2.9. A 280 nm cut-off filter (Melles-Griot # 03FCG117) was placed in alignment with the lamp and sample quartz cell approximately 10 cm in front of the sample quartz cell. This was done to prevent photodecomposition of the coadsorbate adsorbed on the sample, while allowing photodegradation of the pyrene. The transmittance spectrum of the filter can be seen in Figure 2.10. The ozone generated by the xenon lamp was vented to a fume hood through a large hose with an attached fan. The entire illumination apparatus was housed in the dark by way of black drapes in order to eliminate the chance of extraneous light (i.e., room light) affecting the experiments. The entire set-up is shown in Figure 2.11.

To ensure that adsorbates did not desorb from the adsorbent surface during irradiation conditions, experiments were performed in which each of the adsorbates on both silica and fly ash were rotated in the dark for 24 hours and then quantified. The samples were also periodically tested for nonphotochemical reactions. The extent to which an adsorbate underwent photodecomposition was inferred by measuring its disappearance upon illumination of the sample; consequently any extraneous process causing loss of an adsorbate (e.g., desorption or nonphotochemical decomposition) would be construed as resulting from photodecomposition.

Appropriate illumination times were determined by trial and error. They were to be long enough to cause a verifiable decrease in the coverage of the pyrene, while remaining short enough to not cause any detectable decrease in the quantity of the coadsorbate, or to cause the pyrene to be completely consumed by photodecomposition. Optimum illumination times were determined to be 3-6 hrs for a sample size of approximately 0.500

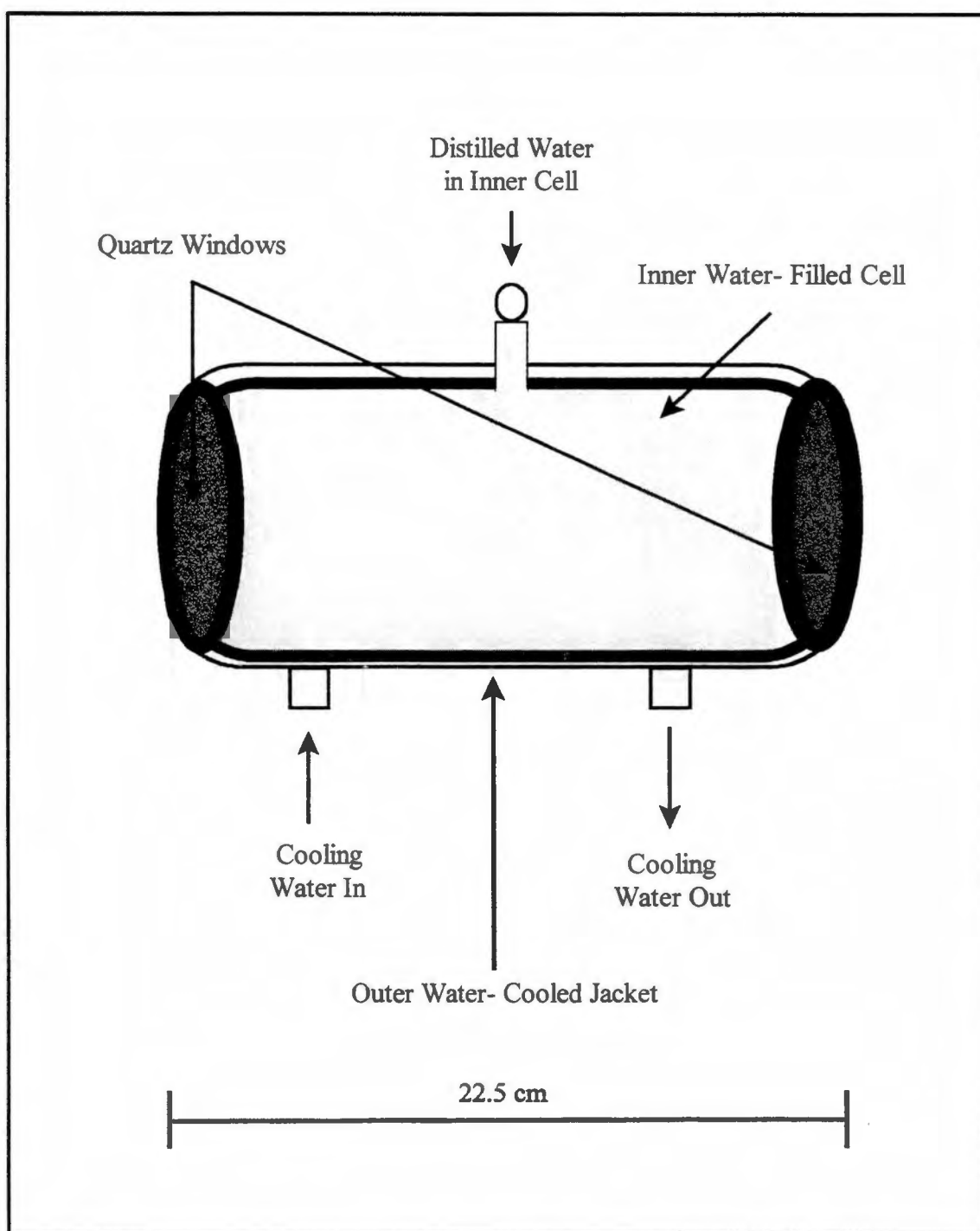


Figure 2.9 Schematic Diagram of Water Filter placed Between Lamp and Sample.

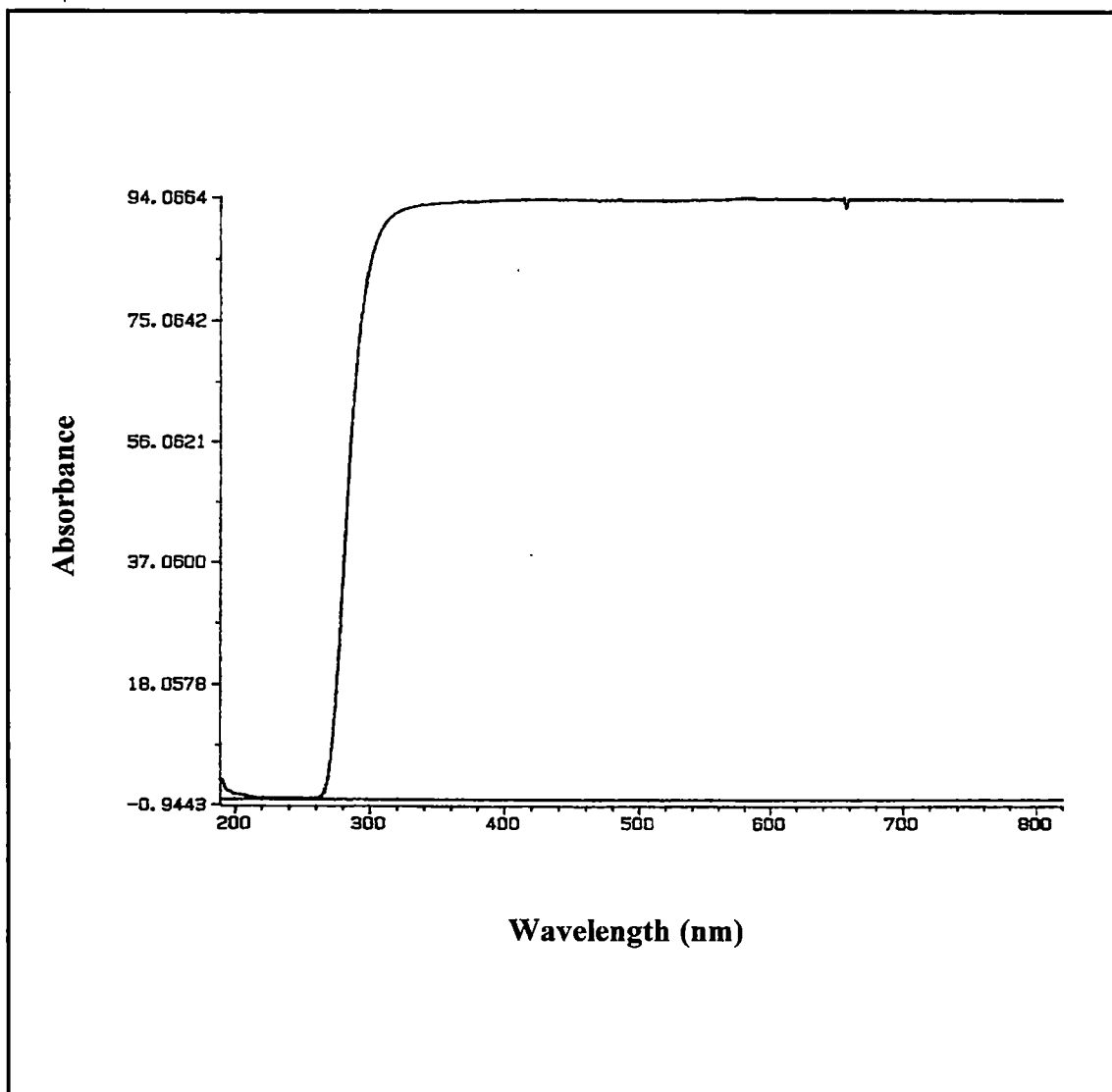


Figure 2.10 Transmittance Spectrum of Cut- Off Filter.

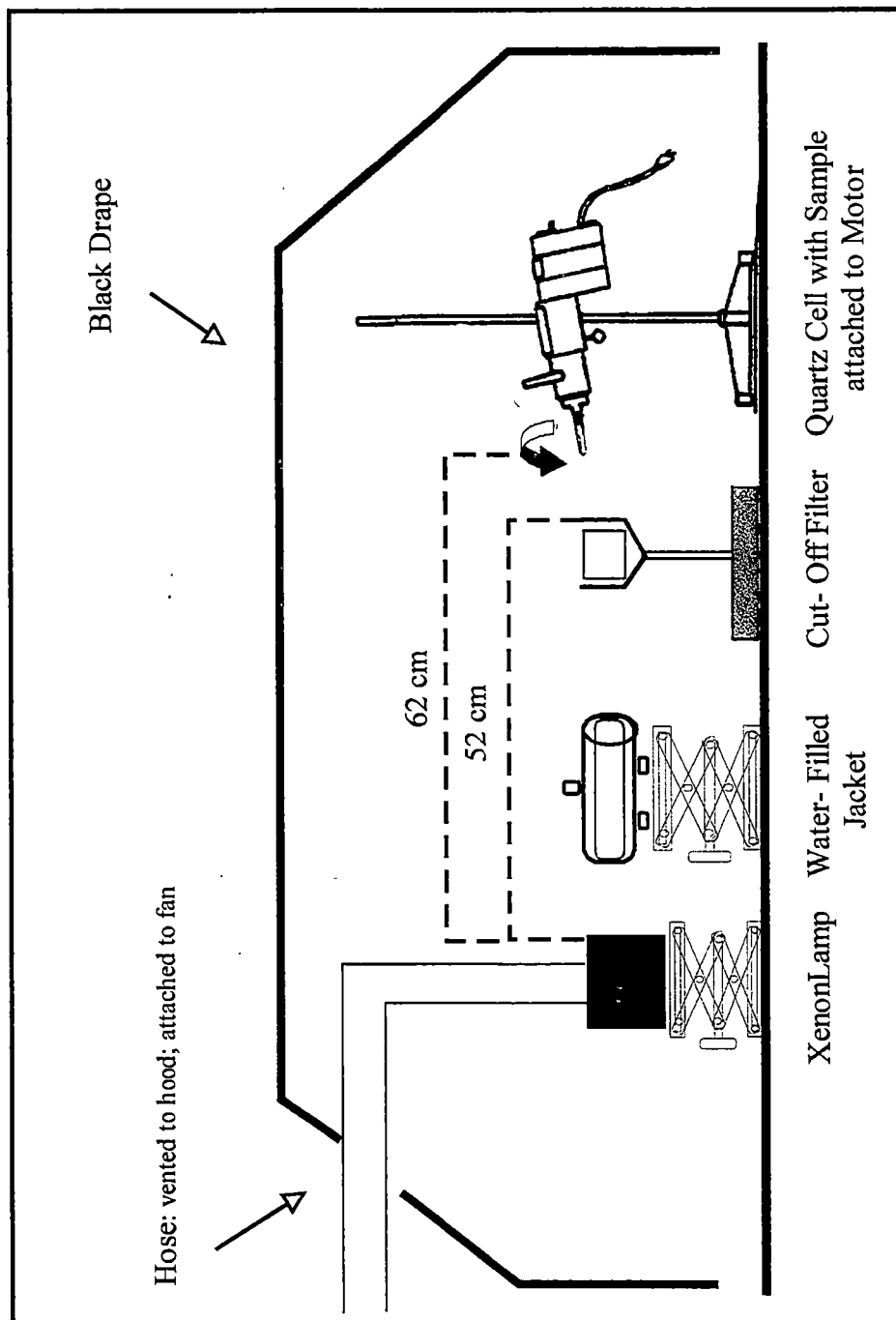


Figure 2.11 Schematic Diagram of Illumination Apparatus.

g adsorbent, depending on the quantities of the adsorbates present. Prior to each illumination, the lamp was allowed to warm up for 10 min to ensure that each illumination was performed under the same lamp conditions. Following the warm-up period, a known amount of sample was placed in the quartz sample cell, illuminated for a predetermined time period, then the sample was placed in a vial and stirred in the dark for an additional 24 hrs prior to quantification. This was done to make sure the sample was as homogenous as possible prior to extraction of the adsorbate (see p.80 for details on extraction procedure).

Xenon Lamp Power Measurement

A new lamp was used for the illumination experiments. The power of the lamp was determined by a chemical actinometry system as described by Hipps [117]. The power of the lamp was needed in order to be able to compare the results of the current illumination experiments to those from previous work.

A chemical actinometer is a photochemical reaction system which can be used to measure the power of an illumination source. A general chemical actinometry system is represented by the following reaction, in which a reactant A absorbs radiation and produces a photochemical product B.

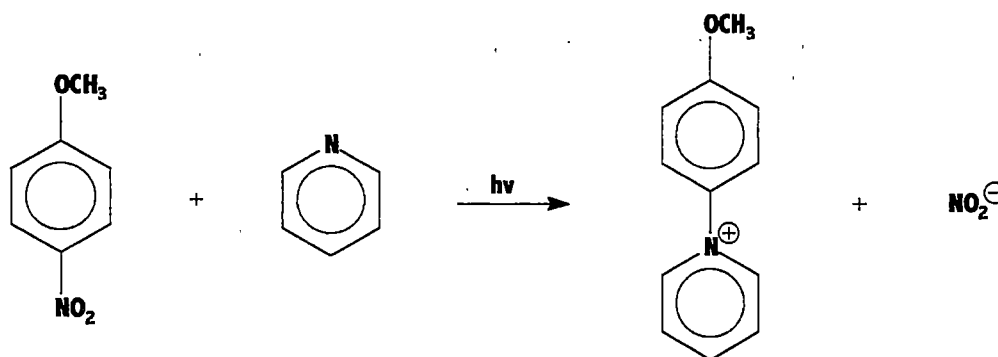


A chemical actinometer must meet several criteria. It must absorb radiation at the wavelength of interest; the product quantum yield must be known; and it must be insensitive to temperature changes, reactant concentration changes, light intensity changes, and wavelength of absorption changes [117]. The actinometer should also be sensitive

enough for measurable reaction to occur, but not for complete destruction of the reactant to occur during the illumination time.

There are several examples of commonly used chemical actinometers in the literature, such as the uranyl oxalate and potassium ferrioxalate actinometers, as well as the more recent polymer film actinometers [118-120]. The common disadvantages of these actinometer systems are complex stoichiometry, difficulty in preparation and analysis, and quantum yields dependent on wavelength [118-120].

The chemical actinometer used for determining the power of the xenon lamp was the p- nitroanisole/ pyridine (PNA/ PYR) actinometer [94]. The reaction is shown below.



The PNA/ PYR actinometer is an aqueous system that absorbs radiation in the 220- 410 nm range. This actinometer system was chosen for the following reasons: suitability for use with polychromatic incident radiation, ease of use, simple stoichiometry, ease of preparation and analysis, absorption in the ultraviolet region, and inexpensive cost [94].

Stock solutions of p- nitroanisole and pyridine were prepared in order to make the actinometer solution. A 1.37×10^{-2} M pyridine, PYR, stock solution was prepared by

dissolving pyridine (Aldrich) in HPLC- grade water (Fisher) and diluting to 1 L, while a 1.31×10^{-3} M p-nitroanisole, PNA, stock solution was prepared by dissolving p-nitroanisole (Aldrich) in 250 mL acetonitrile (Acros) and diluting to 1 L with HPLC-grade water. The actinometer solution used for illumination was prepared by mixing 2.00 mL of each stock solution and diluting to 50 mL with HPLC- grade water.

The same illumination apparatus described previously (p.66) was used for the determination of the lamp power and intensity. Three mL of actinometer solution was transferred to a quartz cuvette (0.90 cm path length) and placed approximately 62 cm from the lamp in the center of the beam of light.. The sample solution was then illuminated for 30, 20, 10, and 5 min at 11 A, after a 10 min lamp warm- up period. The lamp was left on continuously during the timed illuminations. A new 3 mL actinometer solution was used for each illumination. Also, three separate 3 mL actinometer sample solutions were illuminated for 10 min each, following a 30 min lamp warm- up period for each illumination. Analysis of the samples following illumination was by high performance liquid chromatography, using the internal standard method.

Following illumination, the solutions were immediately transferred to a 5 mL flask, which contained 0.5 mL 3.65×10^{-5} M p- nitrotoluene (Acros), PNT, as the internal standard, and was diluted to the mark with 1 % aqueous acetonitrile solution. The PNT was taken from a stock solution prepared by diluting PNT to 100 mL with acetonitrile, then further diluting to 1L with HPLC- grade water. The illuminated actinometer sample solutions, as well as all stock solutions, were kept wrapped in foil while in use, in addition to being stored in the dark when not in use, to prevent any decomposition due to exposure

to room lighting.

For analysis of the actinometer sample solutions, a Hewlett Packard HPLC 1100 with an ODS Hypersil reversed- phase 12.5 cm (4 mm i.d.) C- 18 column and UV-visible detector was used. The detector was set at 310 nm. A flow rate of 1.5 mL/ min with 50:50 water, acetonitrile solvent was used. Three PNA standard solutions, 3.15×10^{-7} M, 3.15×10^{-6} M, and 3.15×10^{-5} M, were prepared for the calibration curve. The PNT concentration in each standard solution was 3.66×10^{-6} M. The three PNA standard solutions were also quantified by HPLC. The calibration curve is shown in Figure 2.12. A chromatogram of an actinometer sample solution injection is shown in Figure 2.13. Peak area of the PNA peak was used to determine the quantity of PNA (mol/ L) remaining after illumination.

The power of the radiation that is adsorbed by A in photons per unit time is determined from the absorbance of the reactant, the quantum yield of the reaction, the time of illumination, and the amount of photochemical product B produced. The stoichiometry of the actinometric reaction is 1:1, PNA to product; therefore, calculation of the number of molecules of PNA prior to and following illumination allowed quantification of the number of product molecules formed. The quantum yield of the reaction was dependent upon the PYR concentration and was found using the following equation [94]:

$$\text{quantum yield} = 0.44 [\text{PYR}] + 0.00028$$

Knowing the quantity of product molecules formed, n_p , the quantum yield of the reaction, ϕ_b , and the fraction of incident light absorbed by the reactant, $1 - 10^{-A}$, the power of the lamp, P_o , was calculated using the equation below.

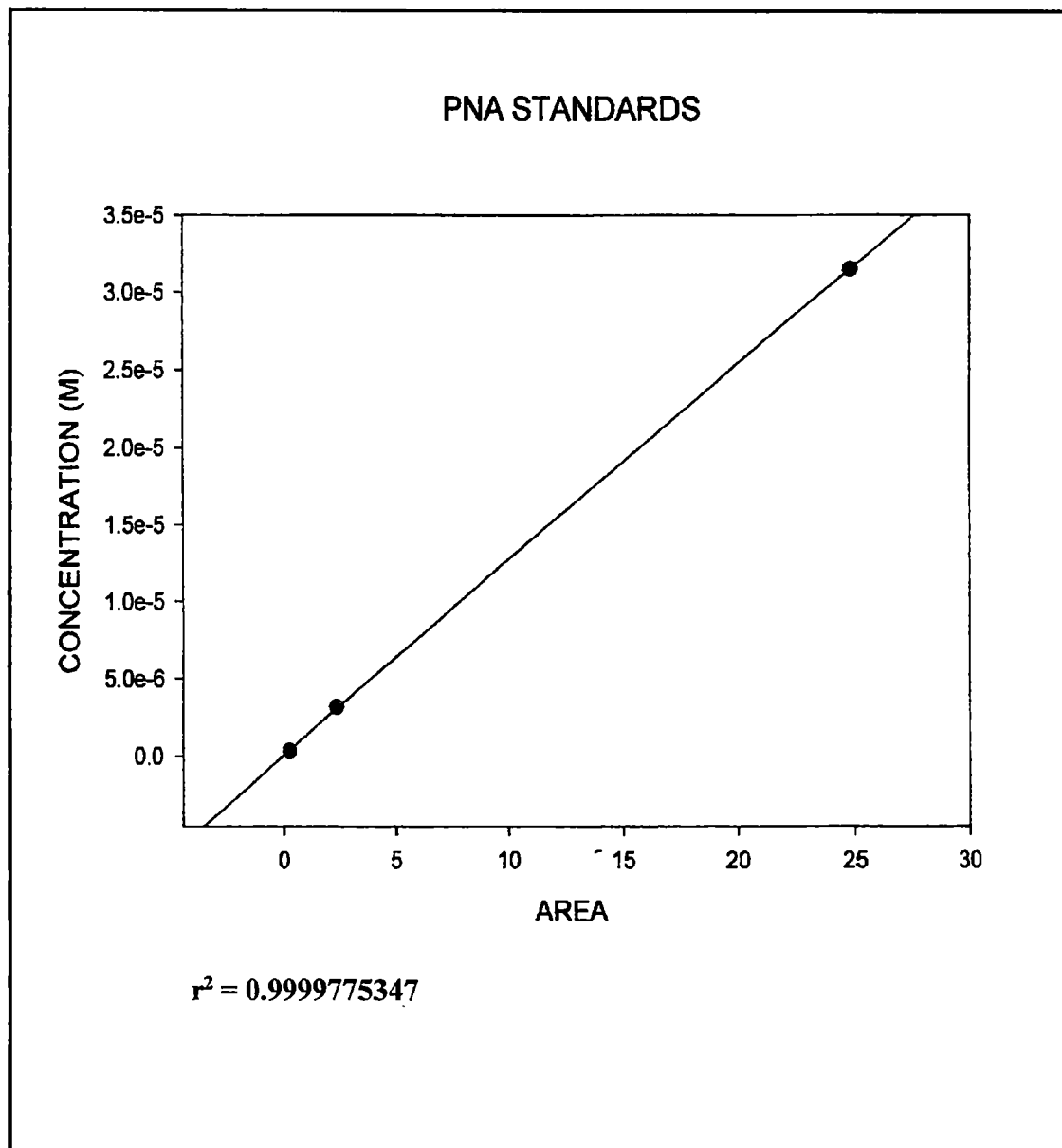


Figure 2.12 Calibration Curve of PNA Standards for Quantification of Actinometry Solution.

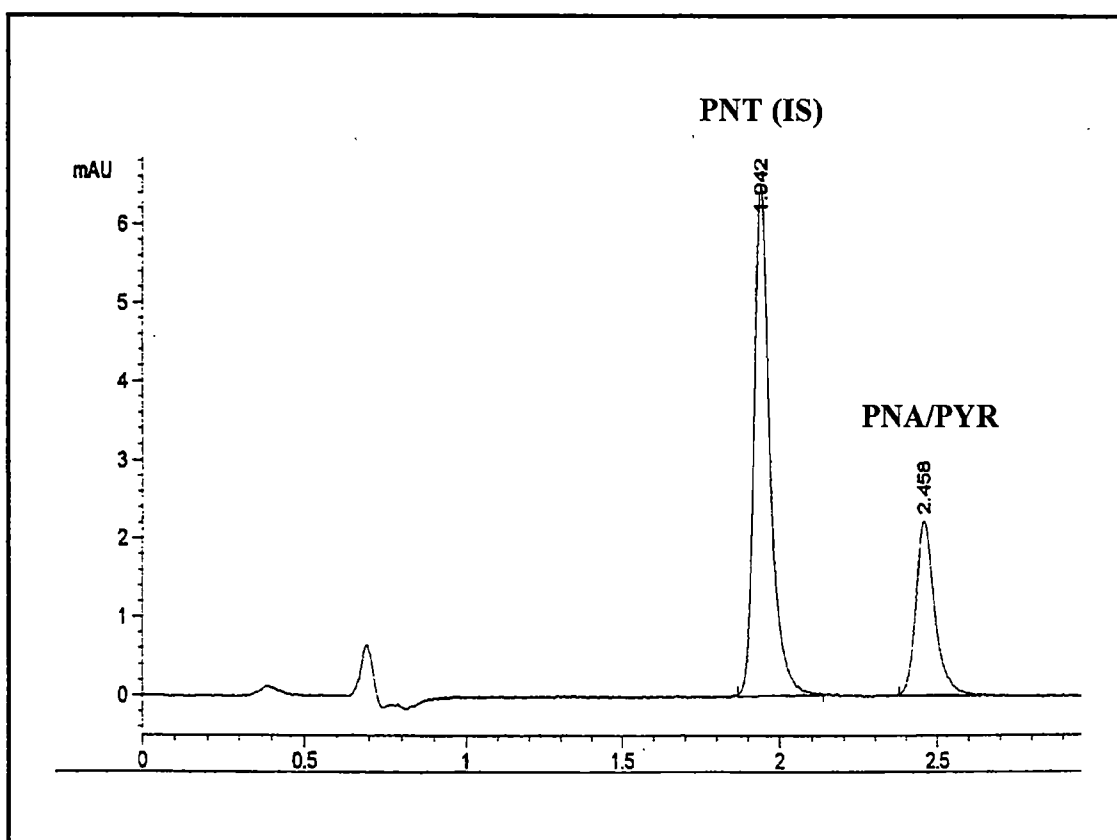


Figure 2.13 Chromatogram of HPLC Injection for Quantification of Actinometry Solution.

$$P_o = n_b / \phi_b t (1 - 10^{-A})$$

The equations used to determine the average absorbance of the actinometer, A, over the range of wavelengths passed by the source/ filter combination, as well as all equations used in the determination of lamp power, are listed and defined in the Appendix. Any assumptions are noted in the Appendix.

Extraction and Quantification of Adsorbates

Although the quantity of PAH and/ or coadsorbate that was deposited on the adsorbent was determined from the FID plot following deposition, as described on p.63, the quantities of PAH and coadsorbate that could be extracted from the adsorbent following deposition were also determined. This was done to compare the quantities of the two coadsorbates on the adsorbent following illumination to the quantities prior to illumination.

The sample size and solvent used for the extraction procedure depended on the adsorbate to be quantified. For pyrene ~25 mg of adsorbent on which pyrene, in the presence or absence of a coadsorbate, had been deposited was weighed by difference (empty flask- [flask + adsorbent]) in a 25 mL volumetric flask, and the flask was filled to the mark with toluene. Three to four replicate samples of adsorbent were prepared in this manner, then all samples were placed in a Branson 1210 ultrasonicator for sonication in the dark for 1 hr. The samples were sonicated in the dark to prevent any photodecomposition of pyrene by ambient light. Following sonication, the samples were

allowed to settle for 1 hr, if the adsorbent was silica, or 1 day, if the adsorbent was fly ash. After the adsorbent particles settled, the concentration of pyrene in the toluene phase was quantified, as described in the following paragraph. Knowing the volume of toluene used, the mass of pyrene extracted from the adsorbent could be calculated from the measured concentration.

Quantification of pyrene was carried out using ultraviolet/ visible (UV/ Vis) spectrophotometry and a Beer's- law plot. The absorbance of pyrene solutions was measured using a Hewlett- Packard 8452A diode array UV/ Vis spectrophotometer. A Hewlett- Packard 7440A color pro plotter was used to plot the spectra when needed.

Six standard solutions of pyrene ranging in concentration from $7.58 \mu\text{g}/\text{mL}$ to $0.48 \mu\text{g}/\text{mL}$ were prepared for the calibration curve. The appropriate amount of pyrene was dissolved in methanol to prepare the most concentrated standard, while the other five were prepared by diluting the concentrated solution. The absorbance of the standards was measured at 334 nm, and a calibration curve (Beer's- law plot) was prepared.

Once the pyrene was extracted from the adsorbent, the absorbance of each solution at 334 nm was measured. The absorption spectrum of pyrene can be seen in Figure 2.14. From the calibration curve and the measured absorbance, the concentration of extracted pyrene in the solutions, prior to and following illumination, was determined. Using the known sample sizes that were weighed for extraction and the known volume of toluene, the coverage of pyrene on the adsorbent in $\mu\text{g pyrene}/\text{g adsorbent}$ was calculated.

For extraction of stearic acid, ~75 mg of adsorbent containing stearic acid, in the presence or absence of pyrene, was weighed by difference in a 25 mL volumetric flask,

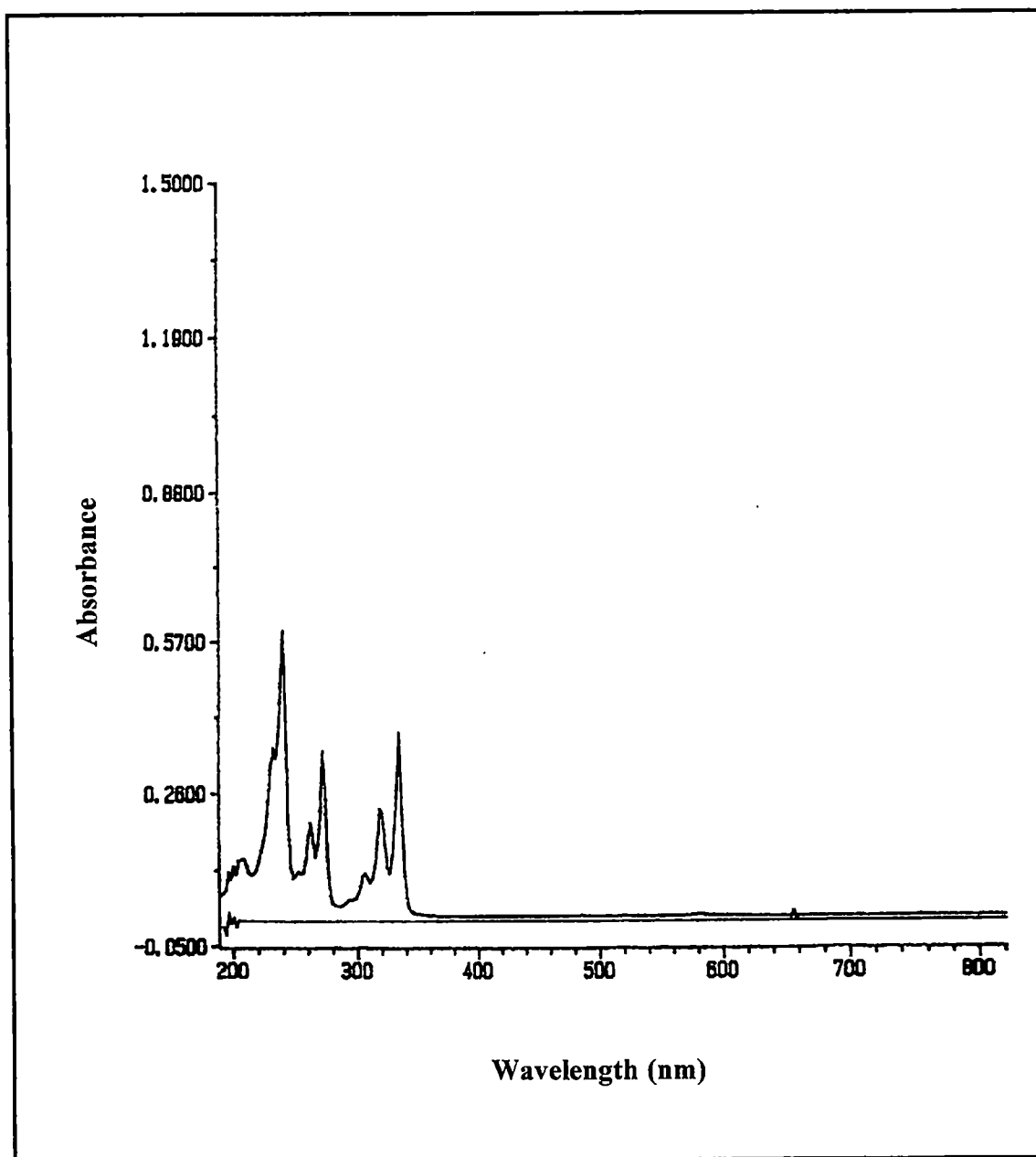
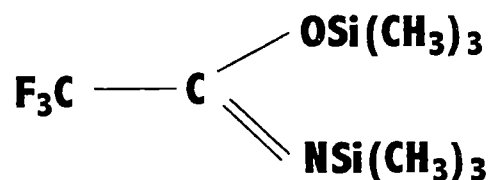


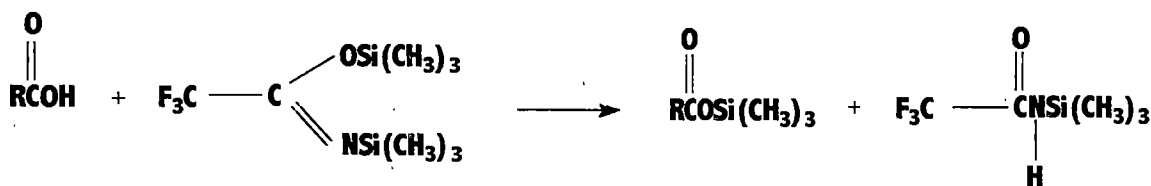
Figure 2.14 Absorption Spectrum of Pyrene in Methanol (10 ppm).

and the flask was filled to the mark with acetone. Again, 3- 4 samples were prepared and sonicated for 1 hr. These samples were not prone to photodecomposition by ambient light; therefore, they were not kept in the dark during sonication. Following sonication, each sample was allowed to settle for 2 hrs, and the solvent containing the extracted stearic acid was then transferred to a round- bottom flask for quantification. Each 25 mL volumetric flask was rinsed with several mL acetone, and the rinses were also transferred to the appropriate round- bottom flask.

The quantification of stearic acid was carried out by gas chromatography (GC), using the internal standard method of analysis. A silylating reagent was used to derivatize stearic acid and succinic acid into more volatile compounds, prior to injection into the GC. The reagent N,O- bis(trimethylsilyl)trifluoroacetamide (Pierce), hereafter abbreviated “BSTFA”, whose structure is shown below, was used to silylate stearic and succinic acid.



Silylation of organic compounds is often used to increase the volatility of slightly volatile compounds to a level sufficient for GC analysis [121]. Silylation also may improve peak shape and column performance [121]. Silyl derivatives are quite thermally stable and are the most commonly used derivatizing agents for GC analyses [122]. A general silylation reaction of a carboxylic acid with BSTFA is shown below.



Following extraction of stearic acid and transfer of the extract to round- bottom flasks, 0.5 mL of succinic acid internal standard solution was added to each flask. The acetone was then evaporated using a rotary evaporator (Wheaton Heidolph). To the white residue that remained, 0.15 mL BSTFA was added, and the flask was sealed and heated for 20 min at 70° C. After the flask was cool, the silylated solution was injected into the GC.

A Hewlett- Packard 5890A gas chromatograph with flame ionization detector and 3392A integrator was used for the analyses. The capillary column was a 10 m J & W DB-5 column (5 % phenyl, 95 % methyl polysiloxane, 0.25 μm film thickness) with 0.25 mm i.d. A temperature program was used for timely analysis of the samples. Initial temperature was 100° C with a 3 min hold, then increasing to a final temperature of 250° C at a rate of 15° C/ min, with a 15 min hold at the final temperature. The injector port temperature was held at 200° C, while the detector was held at 250° C.

Succinic acid, prepared by dissolving succinic acid in acetone, was used as the internal standard. Prior to the analysis of samples, three solutions containing mole ratios of 1:1 succinic to stearic acid, 1:2 succinic to stearic acid, and 2:1 succinic to stearic acid were prepared for a molar response factor determination. The succinic acid internal standard solution prepared for the analyses, and a stearic acid standard prepared for the molar

response factor determination were used. The three mole ratio solutions were injected into the GC, and the ratios of the molar response factors for stearic acid and succinic acid were calculated. Each time a fresh solution of internal standard was prepared, the molar response factor was recalculated. The average molar response ratio was used with the peak areas from the integration report to calculate the quantity of extracted stearic acid in the sample solutions, prior to and following illumination. From the known weight of the extracted samples, the coverage of stearic acid on the adsorbent was determined and reported as μg stearic acid/ g adsorbent. A chromatogram of a stearic acid sample is shown in Figure 2.15.

For extraction of 2- undecanone , ~85 mg of adsorbent containing 2- undecanone, in the presence or absence of pyrene, was weighed by difference in a 2 mL volumetric flask, and the flask was filled to the mark with acetone. Three samples were prepared and sonicated for 1 hr. These samples were also not prone to photodecomposition by ambient light, and thus were not sonicated in the dark. The solvent containing the extracted 2- undecanone was transferred to a 5 mL volumetric flask for quantification. Each 2 mL flask was rinsed with acetone and the rinses were transferred to the appropriate 5 mL flask.

Quantification of 2- undecanone was also by gas chromatography, using the internal standard method. The same GC and column type used in the stearic acid analyses were used; however, a new 10 m portion of column was installed prior to analysis of the 2- undecanone samples. Temperature programming was used for the quantification of 2- undecanone. The initial temperature was 75° C with a 2 min hold, increasing at 20° C/ min

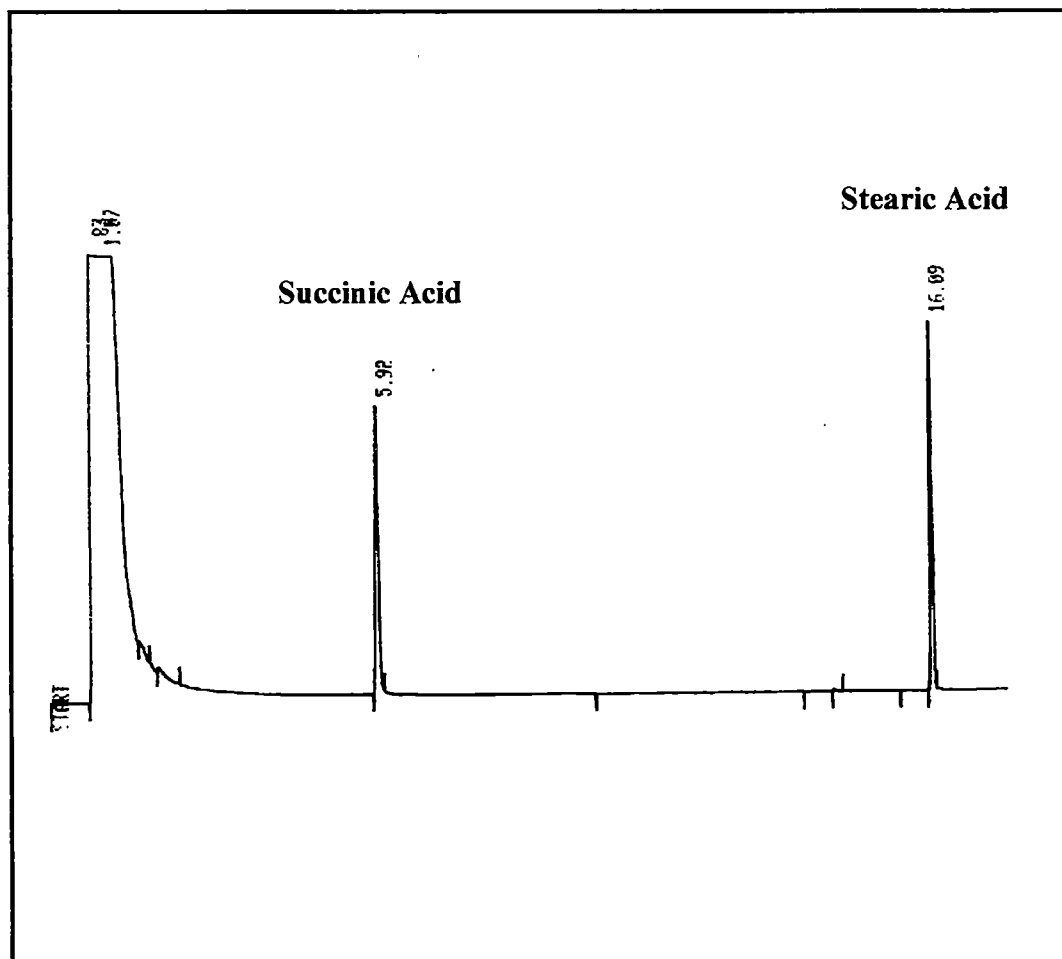


Figure 2.15 Chromatogram of Stearic Acid Injection for GC Analysis.

to 110° C, followed by another increase at 5° C/ min to the final temperature of 135° C, with a 1 min hold at the final temperature. Injector and detector ports were held at the same temperatures as those for the stearic acid analyses.

The internal standard used was diphenylmethane, solutions of which were prepared in acetone. The molar response factor ratio for 2- undecanone to the diphenylmethane internal standard was determined in the same manner as described for the stearic acid quantification. Diphenylmethane and 2- undecanone were sufficiently volatile for GC analysis to need no derivatization.

Once the 2- undecanone was extracted from the adsorbent and the extract was transferred to 5 mL flasks, 0.50 mL diphenylmethane internal standard was added. Each flask was then filled to the mark with acetone. The solutions were then ready for injection into the GC. A chromatogram of a typical sample can be seen in Figure 2.16. Using the molar response factor and the peak areas from the integrated report, the quantity of 2- undecanone extracted from the adsorbent, prior to and following illumination, was calculated. From the known sample sizes used for extraction, the coverage of 2- undecanone on the adsorbent was determined and reported as μg 2- undecanone/ g adsorbent.

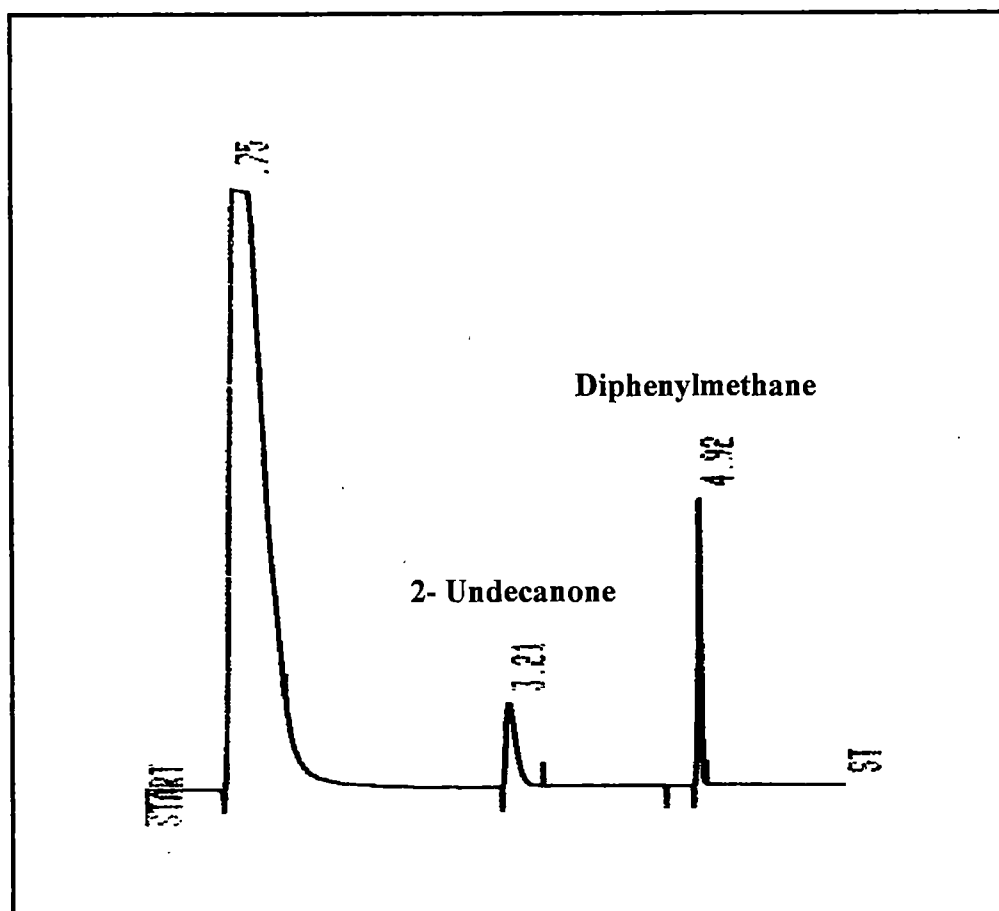


Figure 2.16 Chromatogram of 2- Undecanone Injection for GC Analysis.

CHAPTER III: RESULTS AND DISCUSSION

Introduction

The goal of the current work, as stated in the opening chapter, was to determine the effects, if any, of two different coadsorbates on the photoreactivity of pyrene adsorbed on coal fly ash. The order of deposition (i.e., pyrene followed by coadsorbate or vice versa) was investigated, as well as varying the coverages of both pyrene and the coadsorbates.

In choosing the coadsorbates for study, certain criteria, listed below, had to be satisfied.

1. The coadsorbates should be known to associate with atmospheric particles.
2. They should be of low toxicity.
3. They must be sufficiently volatile, so that they can be deposited from the vapor phase onto the adsorbent, and must not thermally desorb from the adsorbent during depositions or illuminations.
4. They should be stable against photochemical and non- photochemical degradation.

As stated in Chapter 1, it was wondered whether the order of deposition of compounds on particulate matter had an effect on the photochemistry of pyrene; therefore, in determining the choice of coadsorbates for study, it was decided to select one compound which was more volatile than pyrene, and one which was less volatile than pyrene. The reasoning behind this decision was that, in the atmosphere, the less volatile compound more likely would be found already associated with atmospheric particles when pyrene encountered the particles, while the more volatile compound likely would encounter

particles already containing adsorbed pyrene.

Selection of Coadsorbates

The organic compounds commonly found on atmospheric particulate matter were first studied to determine suitable classes of compounds for study. Previously in this research group, an alkyl carboxylic acid and an n-alkane were chosen for investigation as coadsorbates (refer to p.43). The carboxylic acids were again chosen for study, as this class of organic compounds is the most abundant class found associated with atmospheric aerosols [69,71,75], the main sources of these acids being predominantly plant matter and to a lesser extent meat grilling [69,71,75]. In addition, the carboxylic acid chosen previously (succinic acid) was, in hindsight, an unsuitable choice for study, and therefore did not provide any solid conclusions as to the effects of a member of this class of compounds on the photochemistry of pyrene, when coadsorbed with this compound. The particular carboxylic acid chosen for this work was stearic acid, based on the physical properties of the acid, shown in Table 1.21, p.48. Also, stearic acid does not absorb appreciably in the UV- visible regions, exhibiting an absorption maximum at ~204 nm, and would not be expected to photodegrade under the illumination conditions used in these studies. The absorption spectrum of stearic acid can be seen in Figure 3.1. Stearic acid was the compound deposited on the adsorbent prior to the deposition of pyrene on the adsorbent (i.e., a compound less volatile than pyrene).

The other coadsorbate was chosen from the ketones. This class of organic compounds is also found on atmospheric particulate matter, although to a lesser extent than the

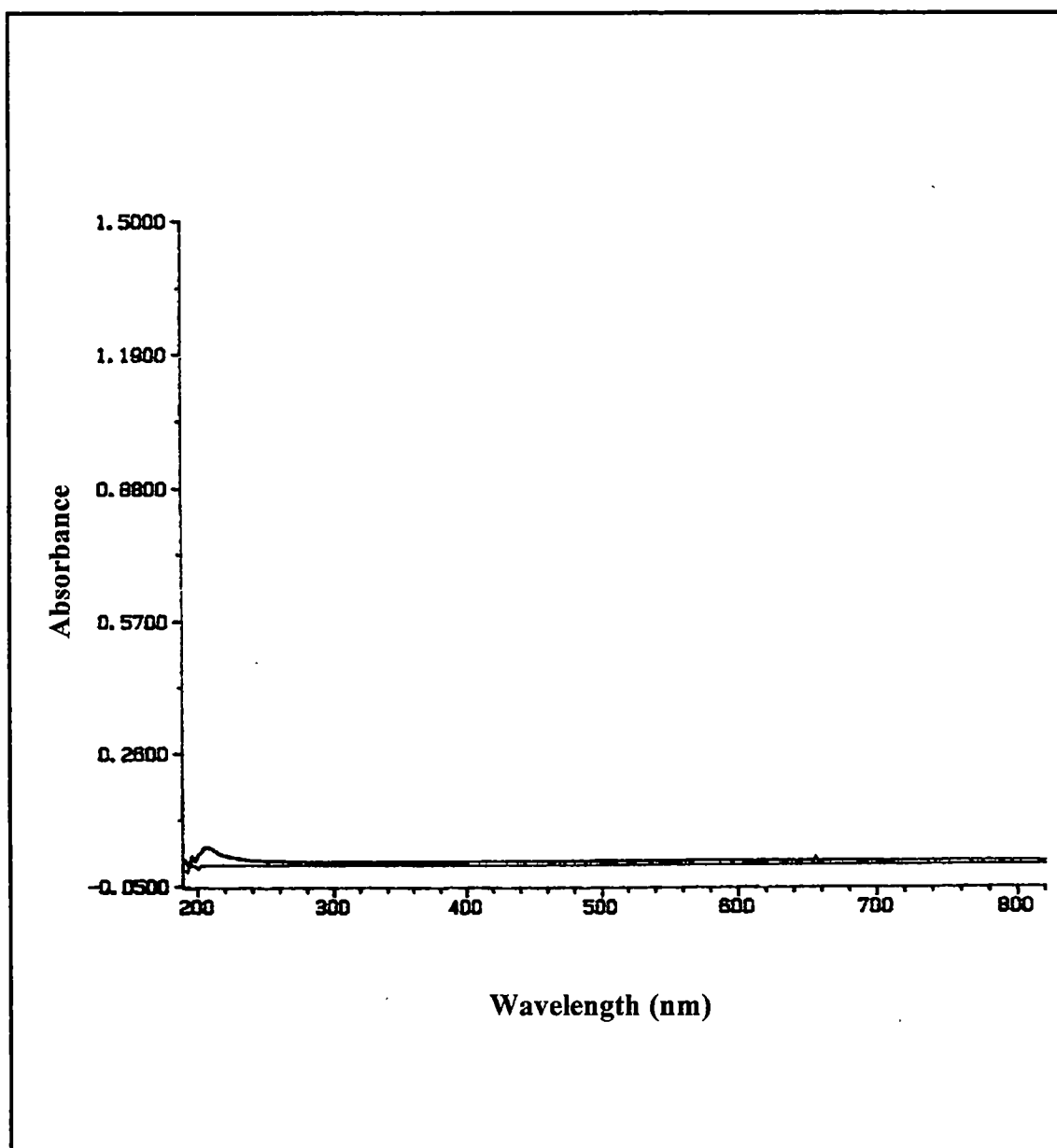


Figure 3.1 Absorption Spectrum of Stearic Acid in Methanol (10 ppm).

carboxylic acids, but comprises a major class of organic compounds derived from outdoor meat grilling and cooking [69,71,75]. The ketone 2-undecanone was chosen from the literature as a representative ketone for study as a coadsorbate, based on its physical properties, given in Table 1.21, p.48. Finally, many ketones also do not absorb considerably in the wavelength range used in the illumination experiments in this work. Ketones exhibit an absorption maximum at ~280 nm. The absorption spectrum of 2-undecanone can be seen in Figure 3.2. The compound 2-undecanone was deposited on the adsorbent following the deposition of pyrene on the adsorbent, as a compound significantly more volatile than pyrene.

Preliminary Experiments

After choosing the coadsorbates it was necessary to perform a series of initial experiments to ensure that stearic acid and 2-undecanone could indeed be utilized as coadsorbates in this study. The background experiments were as follows:

1. Vapor deposition/ Extraction
2. Sorptivity/ Desorptivity
3. Non- photochemical stability
4. Photochemical stability

First, it had to be demonstrated that the coadsorbates could be vapor deposited on the adsorbents over a reasonable range of oven 1 temperatures (oven 1: max. temp. ~200° C, min. temp. ~40° C); also, it was necessary to show that, once deposited, the coadsorbates could be extracted from the adsorbent for subsequent analysis. Thus, a reasonable mass

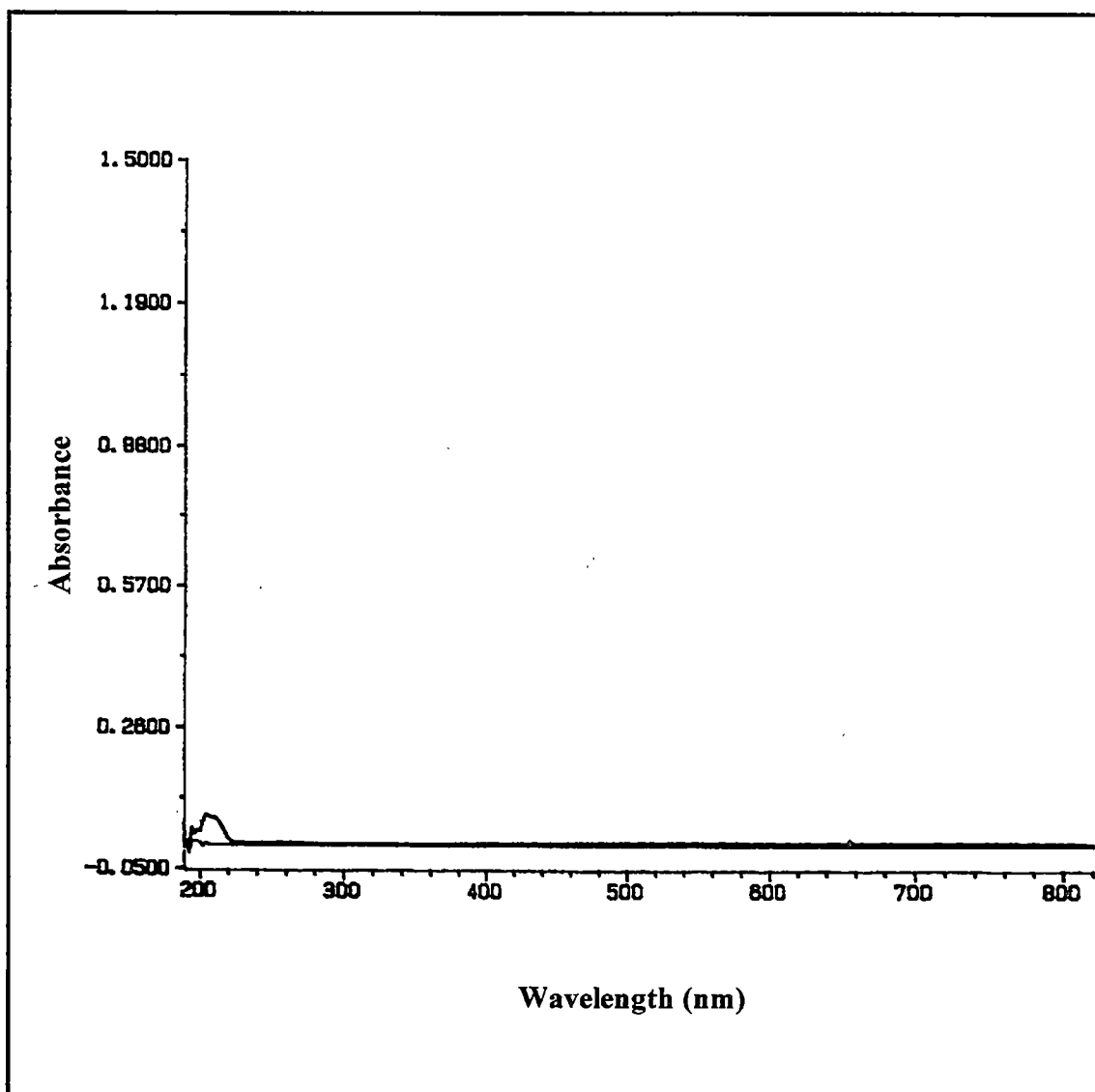


Figure 3.2 Absorption Spectrum of 2- Undecanone in Methanol (10 ppm).

flow rate of adsorbate had to be generated within the temperature limits of oven 1. If mass flow rates of the coadsorbates were excessively high, a low coverage ($\sim 50 \mu\text{g/g}$) could not readily be achieved, while too low a flow rate could lead to excessively long deposition times.

In addition, it had to be demonstrated that the coadsorbates did not appreciably desorb from the adsorbents at oven temperatures used during the vapor deposition of pyrene, when deposited prior to pyrene, or cause the desorption of pyrene from the adsorbents at oven temperatures necessary for their own vapor deposition on the adsorbents, when deposited following pyrene. Silica gel was used as the adsorbent for these initial vapor deposition and sorptivity/ desorptivity experiments, since the ability of an adsorbate to desorb from the surface of an adsorbent was greater for silica gel than fly ash.

Table 3.1 shows the temperatures of ovens 1 and 2 used for vapor deposition of stearic acid and 2- undecanone on silica gel, and the coverage of the silica gel sample in μg coadsorbate/ g silica gel after a timed deposition. From these results it can be seen that a sufficient coverage of both stearic acid and 2- undecanone on silica gel can be achieved in a reasonable amount of time. It must be noted that, to keep the mass flow rate of 2- undecanone at a level that could be effectively used, it was decided to operate oven 1 at room temperature during subsequent depositions. The results of Table 3.1 demonstrate the ability to vapor deposit and extract with acetone and analyze both stearic acid and 2- undecanone. Second and third solvent extractions of stearic acid and 2- undecanone revealed no additional adsorbate in the extract for either stearic acid or 2- undecanone; thus, all adsorbate that could be extracted was removed in one extraction. The vapor

Table 3.1 Vapor Deposition Experiments for Stearic Acid and 2-Undecanone.

Adsorbate	Oven 1	Oven 2	Time	Sample Weight ^a	Coverage ^b
Stearic Acid	145°C	155°C	3.47 hr	1.7198 g	817 ± 62 µg/ g
Stearic Acid	145°C	155°C	1.32 hr	1.6892 g	308 ± 36 µg/ g
Stearic Acid	126°C	132°C	1.03 hr	2.4344 g	53.2 ± 3.6 µg/ g
Stearic Acid	124°C	135°C	2.46 hr	2.1763 g	98.6 ± 7.2 µg/ g
2-Undecanone	58°C	132°C	2.83 hr	2.0804 g	1768 ± 158 µg/ g
2-Undecanone	35°C	132°C	21.00 hr	1.9380 g	3070 ± 307 µg/ g
2-Undecanone	36°C	132°C	3.00 hr	2.1212 g	567 ± 11 µg/ g
2-Undecanone	Off	132°C	3.50 hr	2.1314 g	920 ± 46 µg/ g

^a units= g silica gel^b units= µg adsorbate/ g silica gel

deposition experiments were followed by sorptivity/ desorptivity experiments under various oven conditions for both coadsorbates. To determine whether stearic acid would desorb during the vapor deposition of pyrene, stearic acid was vapor deposited onto two different samples of silica gel at two sets of oven temperatures, one "high" (oven 1 145° C, oven 2 155° C) and one "low" (oven 1 126° C, oven 2 132° C). The coverages of both samples were then determined by solvent extraction, followed by GC analysis. A portion of the "high- temperature" sample was then placed in oven 2 and exposed to pyrene/ N₂ flow at oven temperatures typically used to vapor deposit pyrene (90° C- 110° C), for varying time periods. The coverage of stearic acid was again determined following this exposure. This same procedure was carried out with the "low- temperature" sample. The results of this experiment are shown in Table 3.2. From the data it can be seen that very little, if any, stearic acid was desorbed from the silica gel; therefore, it was concluded that stearic acid could be vapor deposited prior to pyrene on the adsorbent, without being desorbed from the adsorbent at the oven temperatures typically used for pyrene vapor deposition.

Although stearic acid was to be used as the coadsorbate deposited prior to pyrene, it was also desired to ascertain whether pyrene could be vapor deposited on silica gel prior to stearic acid without being desorbed at the oven temperatures used for stearic acid vapor deposition, or displaced by stearic acid during deposition. Therefore, pyrene was vapor deposited on three different samples of silica gel at two different sets of oven temperatures. Two depositions were performed at oven 1 90° C, oven 2 100° C, while the other deposition was performed at oven 1 110° C, oven 2 160° C. The pyrene coverages

Table 3.2 Effect of Exposure to Pyrene Stream on Stearic Acid Coverages on Silica Gel.

Stearic Acid Deposition Temperatures ^a	Initial Coverage, Stearic Acid ^b		Pyrene Deposition Temperatures ^a		Pyrene Deposition Time ^c	Final Coverage, Stearic Acid ^b
	Oven 1	Oven 2	Oven 1	Oven 2		
145	155	817 ± 62	90	100	2.03	850 ± 56
145	155	817 ± 62	90	100	5.00	782 ± 41
126	132	118 ± 7.5	100	110	1.75	125 ± 5.4
126	132	118 ± 7.5	100	110	4.00	111 ± 8.3

^a °C

^b µg stearic acid/ g silica gel

^c hr

of the samples were determined following deposition. A portion of these silica gel samples was then exposed to N₂ flow only at the oven temperatures typically used for stearic acid vapor deposition (oven 1 145° C, oven 2 155° C), as well as the lowest oven temperatures that could be used to generate a reasonable mass flow rate of stearic acid for vapor deposition (oven 1 125° C, oven 2 132° C). The coverage of pyrene on the three silica gel samples was determined following this exposure. The results of this experiment, involving the desorption of pyrene from silica gel at oven temperatures used for stearic acid vapor deposition, are shown in Table 3.3.

It is apparent that, at the usual oven temperatures used for stearic acid deposition, (oven 1 145° C, oven 2 155° C), pyrene was almost completely desorbed during a deposition of 4.0 hr or longer. It appears from the results that, as the oven temperatures for stearic acid vapor deposition are lowered, the resulting desorption of pyrene decreases. The difference in the quantity of pyrene desorbed from the silica gel for the second and third samples in this table can be attributed to the difference in the oven 2 temperatures used for the pyrene vapor deposition. In the second sample the oven 2 temperature was 100° C, while for the third sample the oven 2 temperature was 160° C. A higher oven 2 temperature presumably results in the pyrene molecules being adsorbed at more energetic adsorption sites on the adsorbent, and thus more tightly retained by the adsorbent [105,106]. By vapor depositing pyrene at a higher oven 2 temperature and subsequently lowering the oven temperatures (1 and 2) used for stearic acid vapor deposition, pyrene desorption could be kept to a minimum.

Two silica gel samples with pyrene vapor deposited at a "high" (161° C) and "low"

Table 3.3 Effect of Exposure to Nitrogen Stream at Stearic Acid Deposition Temperatures on Pyrene Coverages on Silica Gel.

Pyrene Deposition Temperatures ^a	Initial Coverage, Pyrene ^b		Stearic Acid Deposition Temperatures ^a		Flow	Time ^c	Final Coverage, Pyrene ^b	% Loss Pyrene
	Oven 1	Oven 2	Oven 1	Oven 2				
90	100	284 ± 2.2	145	155	N ₂	4.08	64.9 ± 0.52	77.1 %
89	100	133 ± 5.9	125	132	N ₂	4.08	108 ± 2.8	19.1 %
110	160	104 ± 2.6	125	132	N ₂	4.08	94.5 ± 1.1	8.2 %

^a °C

^b µg pyrene/ g silica gel

^c hr

(131° C) oven 2 temperature (both higher than that normally used to vapor deposit pyrene, (~100° C) were exposed to stearic acid/ N₂ flow for a period of time at the lowest oven temperatures (oven 1 125° C, oven 2 132° C) that would generate a reasonable stearic acid flow rate, to determine whether stearic acid would displace pyrene from the silica gel. These results are shown in Table 3.4. It appears that, at either oven 2 temperature used for pyrene deposition, the desorption/ displacement of pyrene was quite small at the lower stearic acid oven temperatures used in this experiment; therefore, it was concluded that stearic acid could be vapor deposited either prior to pyrene or following pyrene on the adsorbent without significant loss of either coadsorbate, using proper oven temperatures, sample sizes, and deposition times.

Desorption experiments involving 2- undecanone vapor deposited on silica gel under varying oven conditions were also performed. Pyrene was vapor deposited onto three samples of silica gel, since 2- undecanone is more volatile than pyrene, and would likely encounter atmospheric particles already containing adsorbed pyrene. The samples were then exposed to 2- undecanone/ N₂ flow for various periods of time at the lowest oven temperatures that would generate a reasonable mass flow rate of 2- undecanone. The oven 2 temperature used during the pyrene vapor deposition was "high" (145° C) in order to minimize the desorption of pyrene from the silica gel when exposed to 2- undecanone/ N₂ flow at the oven temperatures needed to deposit 2- undecanone. The results of this experiment are shown in Table 3.5.

From the results it seems that little pyrene was desorbed from the silica gel during the exposure to 2- undecanone/ N₂ flow at the oven temperatures used to vapor deposit from

Table 3.4 Effect of Exposure to Stearic Acid Stream on Pyrene Coverages on Silica Gel.

Pyrene Deposition Temperatures ^a	Initial Coverage, Pyrene ^b		Stearic Acid Deposition Temperatures ^a		Flow	Stearic Acid Deposition Time ^c	Final Coverage, Pyrene ^b	% Loss Pyrene
	Oven 1	Oven 2	Oven 1	Oven 2				
112	161	164 ± 3.3	125	132	St.A./N ₂	0.50	159 ± 5.0	2.3 %
111	131	192 ± 2.9	126	132	St.A./N ₂	1.00	184 ± 4.3	4.3 %

^a °C

^b µg pyrene/ g silica gel

^c hr

Table 3.5 Effect of Exposure to 2-Undecanone Stream on Pyrene Coverages on Silica Gel.

Pyrene Deposition Temperatures ^a		Initial Coverage, Pyrene ^b	2- Undecanone Deposition Temperatures ^a		Flow	2- Undecanone Deposition Time ^c	Final Coverage, Pyrene ^b	% Loss Pyrene
Oven 1	Oven 2		Oven 1	Oven 2				
121	145	265 ± 42	off	100	2-U/N ₂	4.20	252 ± 95	4.9 %
121	145	200 ± 24	off	100	2-U/N ₂	2.15	193 ± 4	3.5 %
121	145	67.2 ± 14.0	off	100	2-U/N ₂	4.67	61.9 ± 3.2	7.9 %

^a °C

^b µg pyrene/ g silica gel

^c hr

2-undecanone. It was concluded from these results that pyrene could be successfully vapor deposited on the adsorbent prior to 2- undecanone without substantial loss of pyrene from the adsorbent during the vapor deposition of 2- undecanone.

Finally, the ability to vapor deposit 2- undecanone prior to pyrene was investigated to ascertain whether it was possible. Two separate portions of a sample of silica gel containing vapor deposited 2- undecanone were each exposed for several hours to pyrene/ N_2 flow, one at "high" oven temperatures for pyrene deposition (oven 1 121° C, oven 2 145° C), which generate a higher pyrene mass flow rate, and thus a relatively short deposition time (ca. 6 hr), and the other at the typical oven temperatures used for pyrene vapor deposition (oven 1 90° C, oven 2 100° C), which would necessitate a longer deposition time (ca. 15 hr). The results of these experiments are shown in Table 3.6.

It appears from these two experiments that, at the higher pyrene deposition oven temperatures, which would require shorter deposition times, a considerable quantity of 2-undecanone was lost. Likewise, at the lower oven deposition temperatures, any gain accomplished by use of the lower oven temperatures was offset by the longer deposition times that would be required at the lower oven temperatures. Both sets of oven temperatures used for pyrene deposition produced substantial loss of 2- undecanone from the silica gel. Therefore, no further attempt was made to vapor deposit 2- undecanone prior to the vapor deposition of pyrene, as there do not appear to be any realistic conditions under which such depositions could be expected to be feasible.

After it was determined that the coadsorbates could be vapor deposited and extracted adequately for study, it was necessary to ensure that the coadsorbates did not desorb from

Table 3.6 Effect of Exposure to Pyrene Stream on 2-Undecanone Coverages on Silica Gel.

2- Undecanone Deposition Temperatures ^a	Initial Coverage, 2- Undecanone ^b		Pyrene Deposition Temperatures ^a		Flow	Pyrene Deposition Time ^c	Final Coverage, 2- Undecanone ^b	% Loss 2-Undecanone
	Oven 1	Oven 2	Oven 1	Oven 2				
off	100	209 ± 9	121	145	Py/ N ₂	6.00	65.7 ± 7.6	68.6 %
off	100	209 ± 9	90	100	Py/ N ₂	12.00	88.6 ± 7.8	57.7 %

^a °C

^b µg 2- undecanone/ g silica gel

^c hr

the surface under the conditions used for the illumination experiments. To determine this, samples of silica gel with vapor deposited stearic acid and 2- undecanone were rotated in the dark for 24 hr at room temperature in the illumination apparatus shown on p.73 (see also Figure 2.11); but the xenon lamp illumination source was not turned on. The results of this experiment are shown in Table 3.7. It appears from the results that there is likely no appreciable loss of either coadsorbate from the silica gel after rotation in the dark for 24 hr, and there was not expected to be any loss of the coadsorbates from the silica gel without exposure to the xenon lamp (light) or a thermal source (heat). Pyrene had been shown in previous work by this group to be stable against desorption during illumination experiments [64]. The temperature of silica gel rises only $\sim 3^{\circ}\text{C}$ over a 24 hr period during rotation in the illumination cell in the center of the light beam [64]; thus, thermal degradation of either coadsorbate would not be expected to occur during illumination experiments in the presence of the light. The results of this desorption experiment confirmed the stability of stearic acid and 2- undecanone adsorbed on silica gel toward desorption (i.e., volatilization) in the dark.

Following this experiment, non- photochemical stability experiments were performed with the coadsorbates. Due to the possibility of samples being used over a period of weeks following preparation, it was necessary to determine the non- photochemical stability of the coadsorbates over time to ensure that the samples did not substantially degrade once deposited. The time frame over which the samples could be used, once prepared, was determined by monitoring the coverage of silica gel samples containing vapor deposited stearic acid and 2- undecanone over several weeks. All samples, when

Table 3.7 Effect of 24 Hour "Dark" Rotation on the Coverage of Stearic Acid and 2-Undecanone Adsorbed on Silica Gel.

Coadsorbate	Initial Coverage ^a	Final Coverage ^a	% Loss
Stearic Acid	2049 ± 164	1989 ± 334	2.9 %
Stearic Acid	236 ± 11.6	240 ± 10.7	1.7 %
2- Undecanone	3070 ± 307	2934 ± 411	4.4 %
2- Undecanone	210 ± 8.9	209 ± 11.7	0.5 %

^a µg adsorbate/ g silica gel

not in use, were stored in the dark in a desiccator. Several samples of silica gel with vapor deposited stearic acid and 2- undecanone had been prepared for the various preliminary experiments already described; therefore, these same samples were monitored for non-photochemical degradation over time. Table 3.8 shows the results of these non-photochemical degradation experiments. From the results it appears that no appreciable desorption of stearic acid occurs over a period of as long as ~4- 5 weeks on silica gel when stored in the dark in a desiccator, while no appreciable desorption of 2- undecanone occurs over periods as long as ~4 weeks under the same conditions. The time frame necessary to prepare a sample with vapor- deposited pyrene and a vapor- deposited coadsorbate, followed by illumination and analysis, was approximately 2- 3 weeks, depending on the sample size and coverage level necessary for the sample, as well as the illumination time period. Thus, these results verify that the samples, once prepared, could be used over the time period needed to complete the necessary photochemical experiments. The initial and final coverages of a sample were both determined following an illumination, just in case non- photochemical degradation had taken place after vapor deposition.

The final preliminary experiment was to determine the photochemical stability of stearic acid and 2- undecanone under the illumination conditions necessary to cause appreciable (~25 %) photodegradation of pyrene. It was important to ensure that the two coadsorbates did not photodegrade during the illumination experiments, which would lead to an inability to determine whether the coadsorbate or the degradation product(s) were responsible for the observed photochemical effect, if any, on adsorbed pyrene. To

Table 3.8 Non- Photochemical Degradation of Stearic Acid and 2-Undecanone Adsorbed on Silica Gel.

Adsorbate	Time Elapsed ^a	Coverage ^b	% Loss
Stearic Acid	0	822 ± 162	-----
Stearic Acid	1	858 ± 148	- 4.4 %
Stearic Acid	2	854 ± 158	- 3.9 %
Stearic Acid	3	831 ± 169	- 1.1 %
Stearic Acid	4	801 ± 118	- 2.6 %
Stearic Acid	5	804 ± 32	2.2%
2- Undecanone	0	850 ± 45	-----
2- Undecanone	1	850 ± 15	-----
2- Undecanone	2	843 ± 48	0.8 %
2- Undecanone	3	843 ± 16	0.8 %
2- Undecanone	4	819 ± 22	3.7 %
2- Undecanone	5	779 ± 42	8.4 %

^a wk

^b µg adsorbate/ g silica gel

determine whether either coadsorbate would photodegrade during illumination experiments, several samples of silica gel and coal fly ash with vapor deposited stearic acid and 2- undecanone were illuminated for varying periods of time in the presence and absence of a 280 nm cut- off filter. The filter was used to eliminate any wavelengths at or below 280 nm emitted by the xenon lamp that would be absorbed by either stearic acid or 2- undecanone, both of which weakly absorb in the ~200- 280 nm range. Following illumination of a sample, the coverage of the coadsorbate on the sample was redetermined to measure any loss of the coadsorbate during the illumination period. It was assumed that any loss upon exposure to the lamp was due to photodegradation, since previous experiments revealed no loss of either coadsorbate during rotation in the illumination apparatus in the dark (i.e., volatilization).

The results of these photochemical stability experiments can be seen in Table 3.9. Stearic acid adsorbed on silica gel appears to degrade significantly without the use of the cut- off filter to eliminate the wavelengths between 190 and 280 nm. As expected, the degradation of stearic acid increases with increasing illumination time. However, with the use of the filter, placed in front of the sample in the illumination apparatus (see p.73), there appears to be negligible degradation of stearic acid, either when adsorbed on silica gel or coal fly ash during a 6 hr illumination period. Illumination experiments were not planned to exceed 6 hr, since this amount of time provided adequate degradation of pyrene (~25 %).

The extent of degradation of 2- undecanone was greater than that of stearic acid during a 24 hr illumination period. As seen in Table 3.9, use of the cut- off filter did not

Table 3.9 Photochemical Stability of Stearic Acid and 2-Undecanone adsorbed on Silica Gel and Texas Ash in the Presence and Absence of a 280 nm Cut-off Filter.

Coadsorbate	Adsorbent	Filter Used	Initial Coverage ^a	Time Illuminated ^b	Final Coverage ^a	% Loss
Stearic Acid	Silica Gel	No	237 ± 9	24.0	156 ± 16	34.2
Stearic Acid	Silica Gel	No	237 ± 9	2.8	176 ± 10	25.7
Stearic Acid	Silica Gel	Yes	237 ± 9	2.0	236 ± 13	0.4
Stearic Acid	Fly Ash	Yes	254 ± 13	3.0	250 ± 6.5	1.5
Stearic Acid	Fly Ash	Yes	121 ± 8.2	6.0	122 ± 8.4	- 0.8
2-Undecanone	Silica Gel	No	3316 ± 457	24.0	1151 ± 70	65.3
2- Undecanone	Silica Gel	Yes	210 ± 9	24.0	169 ± 11	19.2
2- Undecanone	Silica Gel	Yes	210 ± 9	6.0	203 ± 3	3.3
2- Undecanone	Fly Ash	Yes	186 ± 11	3.0	195 ± 15	- 4.8
2- Undecanone	Fly Ash	Yes	69.3 ± 10.5	3.0	68.1 ± 16.8	1.7

^a µg adsorbate/ g adsorbent

^b hr

completely eliminate the degradation of 2- undecanone during a 24 hr illumination period, but did substantially decrease the degradation from 65 % to 20 %. Since illuminations were not expected to exceed 6 hr, it was only necessary to ensure that 2- undecanone did not degrade appreciably during a 6 hr illumination period. Repeated illuminations of 2- undecanone for 3 hr, as well as 6 hr, caused no appreciable degradation of 2- undecanone on silica gel or coal fly ash, as shown in Table 3.9.

Effect of Stearic Acid on Pyrene Photodecomposition

After completion of the preliminary experiments, the effects of stearic acid and 2- undecanone on the photochemistry of pyrene when coadsorbed on coal fly ash were investigated.

For stearic acid on fly ash, two different sets of experimental samples were prepared containing coadsorbed pyrene and stearic acid of varying coverages. One set of samples contained stearic acid vapor deposited initially on the fly ash, followed by vapor deposition of pyrene, which would be the most likely order of deposition onto particles in the atmosphere, given the relative volatilities of the compounds. A second set of samples contained pyrene vapor deposited first on the fly ash, followed by vapor deposition of stearic acid. In the first set of experiments, one sample was prepared by vapor depositing stearic acid on fly ash to produce a "low" coverage of stearic acid ($\sim 50\text{--}75\text{ }\mu\text{g}$ stearic acid/ g fly ash), followed by vapor deposition of pyrene onto the sample to produce a "low" coverage of pyrene ($\sim 50\text{--}75\text{ }\mu\text{g}$ pyrene/ g fly ash). A second sample contained a similar quantity of stearic acid, but a much larger coverage of pyrene ($\sim 200\text{ }\mu\text{g}$ pyrene/ g

fly ash).

Two more samples were prepared by vapor depositing stearic acid on fly ash to produce a "high" coverage of stearic acid ($\sim 200 \mu\text{g}$ stearic acid/ g fly ash), again followed by vapor deposition of pyrene onto one of the two samples to provide a "low" coverage of pyrene ($\sim 50\text{-}75 \mu\text{g}$ pyrene/ g fly ash), and vapor deposition of pyrene onto the other sample to provide a "high" coverage of pyrene ($\sim 200 \mu\text{g}$ pyrene/ g fly ash).

In addition to these four samples, pyrene alone was vapor deposited onto two separate samples of fly ash to create a sample having a "low" coverage of pyrene ($\sim 50\text{-}75 \mu\text{g}$ pyrene/ g fly ash), and a sample having a "high" coverage of pyrene ($\sim 200 \mu\text{g}$ pyrene/ g fly ash). These two samples containing pyrene alone were control samples.

Separate portions of all six samples were each illuminated for a 3 hr period and a 6 hr period. The coverage of both pyrene and stearic acid adsorbed on fly ash was determined prior to and following illumination with the xenon lamp. The decomposition of pyrene in the presence and absence of stearic acid (control sample) was compared, as well as the effect of coverage levels. The results of the two illumination experiments, 3 hr and 6 hr, are shown in Tables 3.10 and 3.11, respectively.

From the results of Table 3.10 it can be seen that the presence of stearic acid increases the extent of photodecomposition of the "low" coverage pyrene samples compared with the photodecomposition of "low" coverage pyrene without stearic acid. The photodecomposition of pyrene on the samples with "high" coverage pyrene was not significantly altered by the presence of stearic acid in a 3 hr illumination. In Table 3.11 it appears that the presence of stearic acid increases the photodecomposition of both the

Table 3.10 Illumination of "Low" and "High" Coverage Pyrene for 3 Hours on Coal Fly Ash in the Absence and Presence of Coadsorbed Stearic Acid^a.

Initial Coverage, ^b Pyrene	Final Coverage, ^b Pyrene	Initial Coverage, ^c Stearic Acid	Final Coverage, ^c Stearic Acid	% Loss Pyrene
69.5 ± 1.9	62.7 ± 1.7	-----	-----	9.8 %
72.3 ± 5.9	53.4 ± 7.1	71.6 ± 15	75.5 ± 2.4	26.1 %
72.1 ± 2.6	55.4 ± 3.4	251 ± 5.6	252 ± 4.7	23.2 %
173 ± 3.3	146 ± 5.6	-----	-----	15.7 %
211 ± 7.6	176 ± 4.2	71.6 ± 15	69.5 ± 6.8	16.9 %
174 ± 5.3	141 ± 7.6	254 ± 13	252 ± 9.4	18.8 %

^a stearic acid deposited prior to pyrene

^b µg pyrene/ g fly ash

^c µg stearic acid/ g fly ash

Table 3.11 Illumination of "Low" and "High" Coverage Pyrene for 6 Hours on Coal Fly Ash in the Absence and Presence of Coadsorbed Stearic Acid^a.

Initial Coverage, ^b Pyrene	Final Coverage, ^b Pyrene	Initial Coverage, ^c Stearic Acid	Final Coverage, ^c Stearic Acid	% Loss Pyrene
69.5 ± 1.9	57.1 ± 4.6	-----	-----	17.8 %
72.3 ± 5.9	46.6 ± 2.2	71.6 ± 15	72.7 ± 9.2	35.5 %
72.1 ± 2.6	42.6 ± 3.2	251 ± 5.6	250 ± 6.5	41.0 %
173 ± 3.3	129 ± 2.9	-----	-----	25.7 %
211 ± 7.6	146 ± 2.7	67.4 ± 2.1	69.1 ± 4.1	30.8 %
174 ± 5.3	115 ± 4.2	254 ± 13	249 ± 1.9	33.8 %

^a stearic acid deposited prior to pyrene

^b µg pyrene/ g fly ash

^c µg stearic acid/ g fly ash

"low" and "high" coverage pyrene samples adsorbed on coal fly ash compared with the control samples containing pyrene adsorbed alone on coal fly ash. The increase in the extent of photodecomposition of pyrene was greater for the "low" coverage pyrene samples than for the "high" coverage pyrene samples. In both sets of experiments (3 hr and 6 hr illuminations) an increase in the amount of stearic acid by a factor of 3 produced only a slight increase in the photodecomposition of pyrene; thus, the presence of stearic acid appears to cause an increase in the extent of photodecomposition of pyrene, which does not increase correspondingly with the quantity of stearic acid.

A second set of samples containing vapor deposited stearic acid and pyrene on fly ash was prepared with coverages the same as above ("low" stearic acid with "low" pyrene, etc.); however, pyrene was vapor deposited prior to stearic acid on the fly ash sample. Again, two control samples containing vapor deposited pyrene alone, one having a "low" coverage, and one having a "high" coverage, were prepared. Separate portions of these 6 samples were illuminated for 6 hr each. The coverage of stearic acid and pyrene adsorbed on fly ash was determined prior to and following illumination with the xenon lamp. The photodecomposition of pyrene in the presence of stearic acid was compared with that of the control sample containing only the adsorbed pyrene with approximately the same coverage to determine the effect of the coadsorbed stearic acid on the photochemistry of pyrene. The results of this experiment can be seen in Table 3.12.

From the results it can be seen that the presence of stearic acid increases the extent of photodecomposition of pyrene on coal fly ash following a 6 hr illumination, when pyrene was vapor deposited prior to stearic acid, compared with a control sample containing

Table 3.12 Illumination of "Low" and "High" Coverage Pyrene Deposited Prior to Stearic Acid on Coal Fly Ash for 6 Hours in the Absence and Presence of Coadsorbed Stearic Acid.

Initial Coverage, ^a Pyrene	Final Coverage, ^a Pyrene	Initial Coverage, ^b Stearic Acid	Final Coverage, ^b Stearic Acid	% Loss Pyrene
68.4 ± 8.6	47.4 ± 8.5	-----	-----	30.7 %
80.2 ± 7.1	50.8 ± 4.3	94.5 ± 9.3	92.3 ± 10.6	36.7 %
93.9 ± 3.1	57.2 ± 4.1	174 ± 11.1	177 ± 7.8	39.0 %
175 ± 5.5	131 ± 3.4	-----	-----	25.2 %
177 ± 5.4	126 ± 3.3	87.0 ± 5.5	89.6 ± 8.9	29.0 %
190 ± 3.2	134 ± 4.4	201 ± 10.4	195 ± 8.2	29.7 %

^a µg pyrene/ g fly ash

^b µg stearic acid/ g fly ash

pyrene only. The extent of photodegradation on "low" coverage pyrene samples was greater than that of the "high" coverage pyrene samples. Again, as with the data in Tables 3.10 and 3.11, a large increase in the amount of stearic acid appears to have little effect on the extent of photodegradation of pyrene, causing only a slight increase.

The results of the two 6 hr experiments shown in Tables 3.11 and 3.12 were compared to each other to determine the effect of the order of deposition (i.e., stearic acid followed by pyrene, pyrene followed by stearic acid). This comparison of the two 6 hr illumination experiments is shown in Table 3.13. These results obtained when pyrene was vapor deposited prior to stearic acid on coal fly ash were comparable to those obtained when pyrene was vapor deposited following stearic acid on coal fly ash. Both experiments showed that stearic acid coadsorbed with pyrene on coal fly ash appears to cause an increase in the extent of photodecomposition of pyrene. At the coverage levels used for pyrene and stearic acid in this study, the order of deposition (i.e., pyrene followed by stearic acid or stearic acid followed by pyrene) does not appear to have an influence on the photodegradation of pyrene adsorbed on coal fly ash.

Effect of 2- Undecanone on Pyrene Photodecomposition

For the study of the effects of 2- undecanone on the photochemistry of pyrene adsorbed on coal fly ash, samples of fly ash were prepared with coverages of pyrene and 2- undecanone much the same as for the stearic acid/ pyrene samples. Two samples were prepared with a "low" coverage of vapor deposited pyrene, followed by vapor deposition of 2- undecanone onto one of the samples to give a "low" 2- undecanone coverage, and

Table 3.13 Comparison of 6 Hour Illumination of Pyrene Vapor Deposited Prior To and Following Stearic Acid on Coal Fly Ash.

Order of Deposition	Initial Coverage, ^a Pyrene	Final Coverage, ^a Pyrene	% Loss Pyrene
Pyrene followed by Stearic Acid	80.2 ± 7.1	50.8 ± 4.3	36.7 %
	93.9 ± 3.1	57.2 ± 4.1	39.1 %
	177 ± 5.4	126 ± 3.3	28.8 %
	190 ± 3.2	134 ± 4.4	29.5 %
Stearic Acid followed by Pyrene	72.3 ± 5.9	46.6 ± 2.2	35.5 %
	72.1 ± 2.6	42.6 ± 3.2	40.9 %
	211 ± 7.6	146 ± 2.7	30.8 %
	174 ± 5.3	115 ± 4.2	33.9 %

^a µg pyrene/ g fly ash

vapor deposition of 2- undecanone onto the other sample to give a "high" 2- undecanone coverage. Again, a control sample with a "low" coverage of only vapor deposited pyrene was prepared for comparison with the 2 samples (see fly ash samples with stearic acid and pyrene, p.111-12, for definition of terms "low" and "high"). A portion of each of these 3 samples was illuminated for a 3 hr period, which, considering the results, shown in Table 3.14, did not appear to provide sufficient decomposition of pyrene. Therefore, a portion of each of these 3 samples was illuminated for 6 hr. These results can be seen in Table 3.15.

From Table 3.14 it can be seen that there was apparently virtually no photodecomposition of pyrene on samples with coadsorbed 2- undecanone after illumination for 3 hr, either with a "high" or "low" coverage of 2- undecanone; however, pyrene adsorbed alone on fly ash showed appreciable decomposition. It would appear from this experiment that 2- undecanone inhibits the photodecomposition of pyrene, but comparison of these results to those of Table 3.15 leads to the opposite conclusion. The results of Table 3.15 (6 hr illumination) clearly show that the presence of 2- undecanone, both "low" and "high" coverage, increases the extent of photodegradation of pyrene, when adsorbed on coal fly ash. An increase in the coverage of 2- undecanone of a factor of 2 produced only a small increase in the extent of photodegradation of pyrene. It would seem that, while the presence of 2- undecanone at some level causes increased photodegradation of pyrene, the effect of 2- undecanone on pyrene photodecomposition does not scale with the amount of 2- undecanone present. Upon closer inspection of the data in Table 3.14 (3 hr illumination) it can be seen that there are relatively large

Table 3.14 Illumination of "Low" Coverage Pyrene for 3 Hours on Coal Fly Ash in the Absence and Presence of 2- Undecanone.

Initial Coverage, ^a Pyrene	Final Coverage, ^a Pyrene	Initial Coverage, ^b 2- Undecanone	Final Coverage, ^b 2- Undecanone	% Loss Pyrene
60.3 ± 2.92	48.4 ± 2.24	-----	-----	19.8 %
51.0 ± 12.17	48.3 ± 7.57	58.5 ± 2.71	59.4 ± 3.60	5.3 %
64.7 ± 5.14	60.6 ± 7.94	120 ± 5.9	113 ± 14.8	6.3 %

^a µg pyrene/ g fly ash

^b µg 2- undecanone/ g fly ash

Table 3.15 Illumination of "Low" Coverage Pyrene for 6 Hours on Coal Fly Ash in the Absence and Presence of 2- Undecanone.

Initial Coverage, ^a Pyrene	Final Coverage, ^a Pyrene	Initial Coverage, ^b 2- Undecanone	Final Coverage, ^b 2- Undecanone	% Loss Pyrene
59.7 ± 4.01	45.5 ± 4.11	-----	-----	23.9 %
56.3 ± 5.91	36.9 ± 1.68	56.7 ± 6.72	50.3 ± 6.48	34.5 %
61.8 ± 5.33	37.6 ± 3.82	123 ± 1.2	122 ± 7.9	39.2 %

^a µg pyrene/ g fly ash

^b µg 2- undecanone/ g fly ash

uncertainties associated with the initial and final coverage determinations of pyrene coadsorbed with 2- undecanone when compared with the sample containing only pyrene (compare with the data in Table 3.15). Due to this large uncertainty, there was quite possibly some photodegradation of pyrene on these samples of comparable magnitude to that associated with the sample containing only adsorbed pyrene.

Two samples were also prepared with a "high" coverage of vapor deposited pyrene, followed by vapor deposition of 2- undecanone onto the samples, so that one of the samples contained a "low" 2- undecanone coverage, and the other sample contained a "high" 2- undecanone coverage. Finally, a sample of fly ash containing only adsorbed pyrene with a "high" coverage was prepared for comparison to the samples with coadsorbed 2- undecanone (the same "low" and "high" coverage definitions as on p. apply). A portion of each of these 3 samples was illuminated for 3 hr, which provided sufficient decomposition of pyrene; therefore, these 3 samples were not illuminated for a longer time period. The results of this experiment are shown in Table 3.16.

These results are consistent with those compiled in Table 3.15, indicating that the presence of coadsorbed 2- undecanone increases the extent of photodegradation of pyrene on coal fly ash. As with the "low" pyrene coverage samples, a greater than twofold increase in the coverage of 2- undecanone does not produce a corresponding increase in the extent of photodegradation of pyrene.

Because of the uncertainties associated with the data in Tables 3.10- 3.16, it was wondered whether the % loss of pyrene, when coadsorbed with stearic acid and 2- undecanone on coal fly ash, was statistically different from the % loss of pyrene adsorbed

Table 3.16 Illumination of "High" Coverage Pyrene for 3 Hours on Coal Fly Ash in the Absence and Presence of 2- Undecanone.

Initial Coverage, ^a Pyrene	Final Coverage, ^a Pyrene	Initial Coverage, ^b 2- Undecanone	Final Coverage, ^b 2- Undecanone	% Loss Pyrene
165 ± 2.4	138 ± 3.9	-----	-----	16.6 %
173 ± 4.2	127 ± 5.3	26.3 ± 3.65	26.8 ± 7.84	27.0 %
145 ± 2.3	93.4 ± 6.16	133 ± 4.9	130 ± 1.7	35.7 %

^a µg pyrene/ g fly ash

^b µg 2- undecanone/ g fly ash

alone on coal fly ash, and, if so, at what confidence level. To address this issue, the well-known "t- test" [123] was used to compare the mean values for % loss of pyrene in the absence and presence of co- adsorbate (stearic acid or 2- undecanone). The equation used for "t" is

$$t = (\bar{x}_1 - \bar{x}_2) / s_p \sqrt{(1/n_1 + 1/n_2)}$$

where $\bar{x}_1$ and $\bar{x}_2$ are the two experimental mean values being compared, s_p is the pooled standard deviation, and n_1 and n_2 are the number of replicate data in the two sets of results being compared. A t value was calculated for the mean values of % loss of pyrene being compared, and this t value was compared to the tabulated t value for a two- tailed t test at the 95 % confidence level. If the calculated t value is greater than the tabulated t value, then the difference between the two compared values is considered to be significant at the 95 % confidence level.

Table 3.17 shows the calculated and tabulated t values for Tables 3.10 and 3.11, comparing pyrene adsorbed alone on coal fly ash and pyrene coadsorbed with stearic acid on coal fly ash, with pyrene vapor deposited following stearic acid on the fly ash, illuminated for 3 hr and 6 hr. From the results it can be seen that the increase in the values of % loss of pyrene from "low" coverage pyrene adsorbed alone on fly ash (9.8 %) to "low" coverage pyrene coadsorbed with "low" coverage stearic acid (26.1 %) and with "high" coverage stearic acid (23.2 %) illuminated for 3 hr (Table 3.10 data) are all statistically significant. However, the results show that the increase in the values of % loss of pyrene after a 3 hr illumination (Table 3.10) from "high" coverage pyrene adsorbed alone on fly ash (15.7 %) to "high" coverage pyrene coadsorbed with "low" coverage

Table 3.17 Comparison of % Loss of Pyrene for 3 Hour and 6 Hour Illuminations of Pyrene in the Absence and Presence of Coadsorbed Stearic Acid on Coal Fly Ash^a.

% Loss of Sample w/ Pyrene Alone	% Loss of Sample w/ Py and Stearic Acid	Illumination time	Calculated t	Tabulated t (at 95 % C.L.)	Change Significant at 95 % Confidence Level
9.8 %, s = 3.66	26.1 %, s = 3.73	3 hr	7.66	2.23	Yes
9.8 %, s = 3.66	23.2 %, s = 5.48	3 hr	5.00	2.23	Yes
15.7 %, s = 5.24	16.9 %, s = 3.52	3 hr	0.48	2.23	No
15.7 %, s = 5.24	18.8 %, s = 3.72	3 hr	1.21	2.23	No
17.8 %, s = 4.05	35.5 %, s = 2.56	6 hr	9.06	2.23	Yes
17.8 %, s = 4.05	41.0 %, s = 4.85	6 hr	9.00	2.23	Yes
25.7 %, s = 1.29	30.7 %, s = 3.28	6 hr	3.51	2.23	Yes
25.7 %, s = 1.29	33.8 %, s = 2.75	6 hr	6.57	2.23	Yes

^a stearic acid deposited prior to pyrene

stearic acid (16.9 %) and with “high” coverage stearic acid (18.8 %) were not statistically different at the 95 % confidence level. The increase in % loss of pyrene from “high” coverage pyrene adsorbed alone on fly ash (15.7 %) to “high” coverage pyrene coadsorbed with “high” coverage stearic acid (18.8 %) was statistically significant at the 80 % confidence level, while the increase in % loss of pyrene from “high” coverage pyrene adsorbed alone on fly ash (15.7 %) to “high” coverage pyrene coadsorbed with “low” coverage stearic acid (16.9 %) was not significant, even at the 50 % confidence level. The increases in the values of % loss of pyrene after a 6 hr illumination (Table 3.11 data) from “low” coverage pyrene adsorbed alone on fly ash (17.8 %) to “low” coverage pyrene coadsorbed with “low” coverage stearic acid (35.5 %) and with “high” coverage stearic acid (41.0 %), and from “high” coverage pyrene adsorbed alone on fly ash (25.7 %) to “high” coverage pyrene coadsorbed with “low” coverage stearic acid (30.7 %) and with “high” coverage stearic acid (33.8 %) were statistically significant at 95 % confidence level.

Table 3.18 shows the calculated and tabulated t values for the data in Table 3.12, comparing pyrene adsorbed alone on coal fly ash with pyrene coadsorbed with stearic acid on coal fly ash, with pyrene vapor deposited prior to stearic acid, illuminated for 6 hr. The data show that all increases in the % loss of pyrene from “low” coverage pyrene without stearic acid (30.7 %) to “low” coverage pyrene coadsorbed with “low” coverage stearic acid (36.7 %) and with “high” coverage stearic acid (39.0 %), as well as “high” coverage pyrene without stearic acid (25.2 %) to “high” coverage pyrene coadsorbed with “low” coverage stearic acid (29.0 %) and with “high” coverage stearic acid (29.7 %), were

Table 3.18 Comparison of % Loss of Pyrene for 6 Hour Illuminations of Pyrene in the Absence and Presence of Coadsorbed 2- Undecanone on Coal Fly Ash^a.

% Loss of Sample w/ Pyrene Alone	% Loss of Sample w/ Pyrene and 2- U	Illumination time	Calculated t	Tabulated t (at 95 % C.L.)	Change Significant at 95 % Confidence Level
30.7 %, s = 4.89	36.7 %, s = 3.34	6 hr	2.44	2.23	Yes
30.7 %, s = 4.89	39.0 %, s = 2.06	6 hr	3.82	2.23	Yes
25.2 %, s = 2.62	29.0 %, s = 2.56	6 hr	2.56	2.23	Yes
25.2 %, s = 2.62	29.7 %, s = 2.21	6 hr	3.20	2.23	Yes

^a pyrene deposited prior to stearic acid

statistically significant at the 95 % confidence level.

Table 3.19 shows the calculated and tabulated t values for the data in Tables 3.14-3.16, comparing pyrene adsorbed alone on coal fly ash with pyrene coadsorbed with 2-undecanone on coal fly ash illuminated for 3 hr and 6 hr. It can be seen from Table 3.19 that the change in the % loss of pyrene from "low" coverage pyrene adsorbed alone on fly ash (19.8 %) to "low" coverage pyrene coadsorbed with "low" coverage 2-undecanone (5.3 %) and with "high" coverage 2-undecanone (6.3 %) illuminated for 3 hr (Table 3.14 data) is statistically significant at the 95 % confidence level, as is the increase in the % loss of pyrene from "low" coverage pyrene adsorbed alone on fly ash (23.9 %) to "low" coverage pyrene coadsorbed with "low" coverage 2-undecanone (34.5 %) and with "high" coverage 2-undecanone (39.2 %) illuminated for 6 hr (Table 3.15 data). In addition, the increase in the % loss of pyrene from "high" coverage pyrene adsorbed alone on coal fly ash (16.6 %) to "high" coverage pyrene coadsorbed with "low" coverage 2-undecanone (27.0 %) and with "high" coverage 2-undecanone (35.7 %) illuminated for 3 hr (Table 3.16 data) is statistically significant at the 95 % confidence level.

Conclusions

From the results compiled in the current study, it appears that the presence of both stearic acid and 2-undecanone coadsorbed with pyrene leads to statistically significant increases in the extent of photodecomposition of pyrene compared with that of pyrene adsorbed alone on coal fly ash. However, there was no dramatic increase in the effect of either coadsorbate on the extent of pyrene photodecomposition as the quantity of

Table 3.19 Comparison of % Loss of Pyrene for 3 Hour and 6 Hour Illuminations of Pyrene in the Absence and Presence of Coadsorbed 2- Undecanone on Coal Fly Ash.

% Loss of Sample w/ Pyrene Alone	% Loss of Sample w/ Pyrene and 2- U	Illumination time	Calculated t	Tabulated t (at 95 % C.L.)	Change Significant at 95 % Confidence Level
19.8 %, s = 2.32	5.3 %, s = 8.24	3 hr	4.80	2.15	Yes
19.8 %, s = 2.32	6.3 %, s = 9.25	3 hr	4.01	2.15	Yes
23.9 %, s = 3.61	34.5 %, s = 3.86	6 hr	5.71	2.15	Yes
23.9 %, s = 3.61	39.2 %, s = 4.12	6 hr	7.90	2.15	Yes
16.6 %, s = 2.91	27.0 %, s = 4.23	3 hr	5.74	2.15	Yes
16.6 %, s = 2.91	35.7 %, s = 4.13	3 hr	10.71	2.15	Yes

coadsorbate was increased. In the case of stearic acid as coadsorbate, the order of deposition (i.e., pyrene before or after stearic acid) did not appear to have any significant effect on the extent of photodegradation of pyrene. As discussed on p.103, it was not possible to interchange the order of deposition of pyrene and 2- undecanone.

In previous work by this research group, 2 organic compounds, succinic acid and n-decane, were utilized as coadsorbates in a study similar to the current study [64]. It was found that succinic acid only slightly increased the photodecomposition of pyrene, while n-decane slightly inhibited the photodecomposition of pyrene when adsorbed on several different fractions of coal fly ash (see p.44). The previous work was performed on a fly ash on which the extent of pyrene photochemistry in the absence of coadsorbates was known to be very small, whereas the ash used in the current work was an ash on which pyrene photodecomposition had been shown to be moderately efficient [110]. In addition, it was later discovered that succinic acid decomposed under the oven conditions used for vapor deposition; hence, the validity of the results for all experiments involving succinic acid is questionable. Thus, the previous study provided little in terms of solid results regarding the effects of coadsorbates on the photochemistry of pyrene adsorbed on coal fly ash. The conclusion of the present work is that, if present in significant quantities, coadsorbed organic compounds will tend to increase the susceptibility to photodecomposition of pyrene adsorbed on coal fly ash.

It has been proposed that one way in which coadsorbates might enhance or inhibit photodegradation of PAHs would be by altering the exposure of the PAH molecules to incident light by filling the pores of the ash particles and displacing the PAH molecules to

surface “adsorption sites”, which would tend to *increase* the power of radiation to which adsorbed PAH molecules were exposed or, alternately, by scattering or reflection of incident light [64], which would *decrease* the amount of incident light reaching the PAH molecules. These are plausible explanations for the observed behaviors of PAHs in the presence of coadsorbates on coal fly ash, given the physical characteristics of fly ash particles, especially when relatively high coverages of coadsorbate are used. These high coverages of the coadsorbate, when deposited prior to the PAH, might allow for “covering” of the particle surface and filling of adsorbent pores in which PAH molecules might otherwise be “hidden”, leading to *greater* exposure of the PAH to incident light, or alternately, when deposited following the PAH, result in “covering” of the adsorbed PAH, causing scattering or absorption of the incident light, and thus *reducing* the power of incident radiation actually reaching the adsorbed PAH molecules.

In the present study coverages of both pyrene and the 2 coadsorbates were relatively small. It seems highly unlikely that the small quantities of stearic acid or 2- undecanone present would so strongly reflect or scatter the incident radiation that the incident power to which pyrene molecules were exposed would be altered significantly. In any case, the general effect of the presence of the coadsorbate in the current study was to increase the extent of photodecomposition of pyrene, which is opposite to the effect one would predict on the basis of the “scattering” or “reflection” argument.

At the coverage levels used in these studies, it is possible that a coadsorbate, if deposited prior to pyrene, would tend to occupy pores rather than surface sites in the fly ash, causing the pyrene molecules to be deposited on more accessible surface “sites” (or

perhaps to displace some of the coadsorbate molecules from the internal pore structure of the fly ash). If competition between coadsorbate and PAH molecules for the relatively inaccessible pore "sites" of the fly ash was a significant factor influencing the susceptibility of pyrene to photodecomposition, then the order of deposition (pyrene prior to or following coadsorbate) would be expected to have an effect on the observed extent of photodecomposition of pyrene. However, it was observed that the presence of coadsorbed stearic acid tended to increase the extent of photodecomposition of pyrene, whether deposited prior to or following pyrene.

It should also be noted that the fly ash used in this work has a relatively small specific surface area ($\sim 2 \text{ m}^2/\text{g}$), compared with most other coal fly ashes studied previously by this group ($4\text{--}30 \text{ m}^2/\text{g}$) [124]. None of the reported subfractions of the Texas ash has a specific surface area larger than $3.6 \text{ m}^2/\text{g}$, whereas the specific surface areas of the most adsorptive subfractions of other fly ashes previously studied may be as large as $30 \text{ m}^2/\text{g}$ [124].

It has been presumed that one of the reasons that PAHs exhibit more extensive photodecomposition on the "Texas Lignite" fly ash used in this work than on most other fly ashes is because the "Texas Lignite" fly ash particles are much less porous than those of most other fly ashes [125]; therefore, a greater fraction of the surface adsorption "sites" are accessible to incident light in the "Texas Lignite" ash than in many other ashes [125]. All this tends to support the idea that the effect of stearic acid on the photodecomposition of pyrene on the "Texas Lignite" ash is not likely only to involve "physical" effects of stearic acid on the radiant power to which adsorbed pyrene molecules are exposed.

One must also consider the possibility that the chemical properties of the coadsorbate may play an important role in affecting the photodecomposition of pyrene. A recent article by Reyes, et al.[126], examines the mechanism of pyrene photolysis on activated and unactivated silica by way of the known cation radical intermediate [24,29,127,128]. Based on studies involving identification of pyrene photoproducts and reflectance spectroscopy on silica gel, the authors propose that the pyrene cation radical intermediate is formed by electron transfer from the excited triplet state of pyrene. The pyrene cation radical may then react with adsorbed water on silica to form oxygenated pyrenes, such as mono- and dihydroxypyrenes, which can then further react to form pyrenediones. The authors concluded that electron transfer mechanisms involving singlet oxygen to form the pyrene cation radical could be ruled out, but proposed that O_2 could act as an electron acceptor in a reaction with excited singlet and/ or triplet state pyrene molecules, forming the pyrene cation radical and the superoxide anion radical, $O_2^{\cdot-}$. Other possibilities for electron acceptors not considered by the authors could include the adsorbent surface, adsorbed water, or adsorbed organic compounds.

In another article by Jang and McDow [83], concerning benz[a]anthracene photodegradation in the presence of organic compounds in solution, these authors suggest additional processes of PAH photodegradation, which may be applicable to atmospheric particulate matter surfaces, although their work was performed in liquid solution, rather than on solid particulate surfaces. These processes include 1) direct energy transfer from an organic compound, which acts as a photosensitizer, and 2) hydrogen atom abstraction by excited state species to produce reactive radicals, which react with adsorbed PAHs in

chain reactions. The authors also suggest that the hydrogen donating properties of any adsorbed organic species could be quite influential in the process(es) taking place.

Kamens, et. al. [90] have found that PAHs associated with wood soot particles are highly susceptible to photodegradation, while under the same conditions on fly ash particles, they are highly resistant to photodegradation. Wood soot particles are quite different in composition from fly ash particles. They are mostly organic in nature with a liquid- like surface layer containing water, phenols, ketones, and low- molecular weight alkyl and aryl carboxylic acids. It is therefore not surprising that, in this liquid- like organic environment, photodecomposition of pyrene proceeds more efficiently than on fly ash, or any other "inorganic" solid surface.

In any case, if the pyrene cation radical is considered to be an intermediate in pyrene photolysis, then any coadsorbed species which will enhance the formation of the pyrene cation radical or undergo reaction with the pyrene cation radical once formed, will necessarily enhance the photodecomposition of pyrene.

It should be noted that the necessary experiments needed to determine adequately the mechanism by which coadsorbates affect the photochemistry of adsorbed pyrene would be difficult and possibly infeasible to perform. Previous attempts by this research group to perform reflectance, fluorescence, Raman, and Fourier transform infrared spectroscopic studies of adsorbed pyrene, pyrene photoproducts, and pyrene photodecomposition intermediates have all proven futile. Fly ash adsorbs strongly in the UV- visible and IR regions, in addition to having intense fluorescence, making it virtually impossible to detect pyrene, as well as any pyrene photoproducts, or intermediates by direct in situ optical

spectroscopy.

Likewise, identification of pyrene photoproducts formed on fly ash by means of solvent or supercritical fluid extraction, followed by chromatography or mass spectrometry, has repeatedly proved infeasible, due to low recoveries of the photoproduct species by the extraction procedure. Therefore, no attempts were made in this work to recover and identify pyrene photoproducts. Considering the lack of knowledge regarding the identities of both pyrene photoproducts and photochemical intermediates of pyrene adsorbed on fly ash, either in the presence or absence of coadsorbates, and the probability that any attempts to achieve such identification would prove unsuccessful, further speculation on the process by which coadsorbates affect the photochemistry of pyrene adsorbed on coal fly ash is not warranted.

While fly ash containing relatively small amounts of coadsorbed stearic acid or 2-undecanone is primarily an "inorganic" matrix, highly different in composition from wood soot particles or a solution environment described earlier, the results of the current study seem to indicate that the presence of organic compounds, even as relatively minor constituents of a basically inorganic particulate adsorbent, tend to increase the extent of photodegradation of pyrene.

As discussed in the opening chapter (p.10, p.21), the fact that coadsorbed organic molecules tend to enhance the susceptibility of particle-associated PAHs to photochemical decomposition, does not necessarily have positive implications. The expected photoproducts of pyrene, as well as other PAHs, are more water soluble than their parent compounds, and are more likely to be toxic and/ or mutagenic than the parent

PAH compounds, which increases the health risk to humans, and the potential damage to the entire environment.

REFERENCES

REFERENCES

1. Schwartz, S. E. *Science*, 1989, 243, 753-763.
2. McElroy, M. B.; Salawitch, R. V. *Science*, 1989, 243, 763-770.
3. Dockery, D. W.; Pope, C. A. III; Xu, X.; Spengler, J. D.; Ware, J. H.; Fay, M. E.; Ferris, B. G. Jr.; Speizer, F. E. *New Engl. J. Med.*, 1993, 329, 1753-1759.
4. *Atmospheric Chemistry and Physics*, Seinfeld, J. H.; Pandis, S. N., Eds.; John Wiley and Sons: New York, 1998, Chapter 1.
5. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*, Finlayson-Pitts, B. J.; Pitts, J. N., Jr., Eds.; John Wiley and Sons: New York, 1986, Chapter 1.
6. *Atmospheric Chemical Compounds: Sources, Occurrences, and Bioassay*, Graedel, T. E.; Hawkins, D. T.; Claxton, L. D., Eds.; Academic Press, Inc.: New York, 1986, Chapter 1.
7. *Atmospheric Chemistry and Physics*, Seinfeld, J. H.; Pandis, S. N., Eds.; John Wiley and Sons: New York, 1986, Chapter 12.
8. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*, Finlayson-Pitts, B. J.; Pitts, J. N., Jr., Eds.; John Wiley and Sons: New York, 1986, Chapter 13.
9. Baek, S. O.; Field, R. H.; Goldstone, M. E.; Kirk, P. W.; Lester, J. N.; Perry, R. *Water Air Soil Pollut.*, 1991, 60, 279-300.
10. National Research Council Subcommittee on Airborne Particles, *Airborne Particles*, University Park Press: Baltimore, 1979, Chapter 1.
11. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*, Finlayson-Pitts, B. J.; Pitts, J. N., Jr., Eds.; John Wiley and Sons: New York, 1986, Chapter 12.
12. Harrison, R. M.; Jones, M. *Sci. Tot. Environ.*, 1995, 168, 195- 214.
13. Oanh, N. T. K.; Reutergårdh, L. B.; Dung, N. T. *Environ. Sci. Technol.*, 1999, 33, 2703-2709.

14. Huntzicker, J. J.; Heyerdahl, E. K.; McDow, S. R.; Rau, J. A.; Griest, W. H.; MacDougall, C. S. *J. Air Pollut. Cont. Assoc.*, 1986, 36, 705-709.
15. Dyremark, A.; Westerholm, R.; Övervik, E.; Gustavsson, J.- A. *Atmos. Environ.*, 1995, 29, 13, 1553-1558.
16. Schroeder, W. H.; Lane, D. A. *Environ. Sci. Technol.*, 1988, 22, 240-246.
17. Saxena, P.; Hildemann, L. M. *J. Atmos. Chem.*, 1996, 24, 57.
18. Seinfeld, J. H. *Science*, 1989, 243, 745-752.
19. Nielsen, T.; Ramdahl, T.; Bjørseth, A. *Environ. Health Perspect.*, 1983, 47, 103-114.
20. Pitts, J. N., Jr. *Environ. Health Perspect.*, 1983, 47, 115-140.
21. Valerio, F.; Bottino, P.; Ugolini, D.; Cimberle, M. R.; Tozzi, G. A.; Frigerio, A. *Sci. Tot. Environ.*, 1984, 40, 169-188.
22. Storey, J. M. E.; Luo, W.; Isabelle, L. M.; Pankow, J. F. *Environ. Sci. Technol.*, 1995, 29, 2420-2428.
23. *Atmospheric Chemistry and Physics*, Seinfeld, J. H.; Pandis, S. N., Eds.; John Wiley and Sons: New York, 1986, Chapter 7
24. Ames, B. N.; McCann, J.; Yamasaki, E. *Mutat. Res.*, 1975, 31, 347-364.
25. *Carcinogenesis- A Comprehensive Survey, Vol. 1 Polynuclear Aromatic Hydrocarbons: Chemistry, Metabolism, and Carcinogenesis*, Freudenthal, R.; Jones, P. W., Eds.; Raven Press: New York, 1976.
26. *Polynuclear Aromatic Hydrocarbons: Third International Symposium on Chemistry and Biology- Carcinogenesis and Mutagenesis*, Jones, P. W.; Leber, P., Eds.; Ann Arbor Science: Ann Arbor, MI, 1979.
27. Smith, D. J. T.; Harrison, R. M. *Atmospheric Particles*, Harrison, R. M.; Van Grieken, R., Eds.; John Wiley and Sons, Inc.: New York, 1998, Chapter 8.
28. Ren, T. S.; Lin, Z.; Liming, J. *China Environ. Sci.*, 1998, 18, 4, 289.
29. Nikolaou, K.; Masclet, P.; Mouvier, G. *Sci. Tot. Environ.*, 1984, 32, 103-132.

30. Hutzinger, O.; Reischl, A. *Emissions from Combustion Processes: Origin, Measurement, Control*, Clement, R.; Kagel, R, Eds.; Lewis Publishers: Ann Arbor, MI, 1990, Chapter 27.
31. van Cauwenberghe, K. A. In *Handbook of Polycyclic Aromatic Hydrocarbons, Vol. 2: Emission Sources and Recent Progress in Analytical Chemistry*, Bjørseth, A.; Ramdahl, T., Eds.; Marcel Dekker, Inc.: New York, 1985, Chapter 10.
32. van Vaeck, L.; van Cauwenberghe, K. *Atmos. Environ.*, 1978, 12, 2229-2239.
33. Miguel, A., H.; Friedlander, S. K. *Atmos. Environ.*, 1978, 12, 2407.
34. Natusch, D. F. S.; Tomkins, B. A. In *Polynuclear Aromatic Hydrocarbons*, Jones, P. W.; Freudenthal, R. I., Eds.; Raven Press: New York, 1976, 145.
35. Schure, M. R.; Natusch, D. F. S. In *Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry*, Cooke, M.; Dennis, A. J.; Fisher, G. L, Eds.; Battelle Press: Columbus, OH, 1982, 713.
36. Rayan, P. A.; Cohen, Y. *Chemosphere*, 1986, 15, 21.
37. Masclet, P.; Bresson, M. A.; Mouvier, G. *Fuel*, 1987, 66, 556-562.
38. Peters, J. A.; Deangelis, D. G.; Hughes, T. W. In *Polynuclear Aromatic Hydrocarbons: Chemical Analysis and Biological Fate*, Cooke, M.; Dennis, A. J., Eds.; Battelle Press: Columbus OH, 1981, 571-582.
39. *Atmospheric Chemical Compounds: Sources, Occurrences, and Bioassay*, Graedel, T. E.; Hawkins, D. T.; Claxton, L. D., Eds.; Academic Press, Inc.: New York, 1986, Chapter 15.
40. Pankow, J. F.; Isabelle, L. M.; Buchholz, D. A.; Luo, W.; Reeves, B. D. *Environ. Sci. Technol.*, 1994, 28, 363-365.
41. Wehry, E. L.; Mamantov, G. In *Aquatic and Surface Photochemistry*, Helz, G. R.; Zepp, R. G.; Crosby, D. G., Eds.; Lewis Publishers: Ann Arbor, MI, 1994, 173-180.
42. Pitts, J. N., Jr.; Sweetman, J. A.; Zielinska, B.; Atkinson, R.; Winer, A. M.; Harger, W. P. *Environ. Sci. Technol.*, 1985, 19, 1115.
43. Grosjean, D.; Fung, K.; Harrison, J. *Environ. Sci. Technol.*, 1983, 17, 673-679.

44. Pitts, J. N.; van Cauwenberghe, K.; Grosjean, D.; Schmid, J. P.; Fitz, D. R.; Belser, W. L.; Knudson, G. B.; Hynds, P. M. *Science*, 1978, 202, 515-518.
45. Natusch, D. F. S. *Environ. Health Perspect.*, 1978, 22, 79-90.
46. Metzler, G.; Poliner, J.; Bechtold, W. E.; Eidson, A. F.; Newton, G. J. *Environ. Sci. Technol.*, 1991, 25, 930-935.
47. Fisher, G. L. *Environ. Health Perspect.*, 1983, 47, 189-199.
48. Ting, F. T. C. In *Coal Structure*, Meyers, R. A., Ed.; Academic Press: New York, 1982, Chapter 2.
49. Schobert, H. H. *J. Chem. Ed.*, 1989, 66, 242-244.
50. Renton, J. J. In *Coal Structure*, Meyers, R. A., Ed.; Academic Press: New York, 1982, Chapter 7.
51. Flagan, R. C.; Friedlander, S. K. In *Recent Developments in Aerosol Science*, Shaw, D. T., Ed.; John Wiley and Sons: New York, 1978, Chapter 2.
52. Smith, R. D.; Campbell, J. A.; Nielson, K. K. *Atmos. Environ.*, 1979, 13, 607-617.
53. *Fundamentals of Air Pollution*, Boubel, R. W.; Fox, D. L.; Turner, D. B.; Stern, A. C., Eds.; Academic Press: New York, 1994, Chapter 29.
54. *Electrostatic Precipitation*, Oglesby, S., Jr.; Nichols, G. B., Eds.; Marcel Dekker, Inc: New York, 1978, Chapter 14.
55. Lao R. C.; Thomas, R. S.; Oja, H.; DuBois, L. *Anal. Chem.*, 1973, 45, 908-915.
56. Fisher, G. L.; Prentice, B. A.; Silberman, D.; Ondov, J. M.; Biermann, A. H.; Ragaini, R. C.; MacFarland, A. R. *Environ. Sci. Technol.*, 1978, 12, 447-451.
57. Hulett, L. D., Jr.; Weinberger, A. J.; Northcutt, K. J.; Ferguson, M. *Science*, 1980, 210, 1356-1358.
58. Hulett, L. D., Jr.; Weinberger, A. J. *Environ. Sci. Technol.*, 1980, 14, 965-970.
59. Lauf, R. J.; Harris, L. A.; Rawlston, S. S. *Environ. Sci. Technol.*, 1982, 16, 218-220.
60. Norton, G. A.; Markuszewski, R.; Shanks, H. R. *Environ. Sci. Technol.*, 1988, 20, 409-413.

61. Griest, W. H.; Harris, L. A. *Fuel*, 1985, 64, 821-826.
62. Dunstan, T. D. J.; Mauldin, R. F.; Zhong, J.; Hipps, A. D.; Wehry, E. L.; Mamantov, G. *Environ. Sci. Technol.*, 1989, 23, 303-308.
63. Mahajan, O. P. In *Coal Structure*, Meyers, R. A., Ed.; Academic Press: New York, 1982, Chapter 3.
64. Holder, P. H. *Photochemical Transformation of Polycyclic Aromatic Compounds Sorbed on Coal Stack Ash in the Absence and Presence of Coalsorbates*, Ph.D. Dissertation, University of Tennessee, Knoxville, 1993.
65. El- Mogazi, D.; Lisk, D. J.; Weinstein, L. H. *Sci. Total Environ.*, 1988, 74, 1.
66. Miller, V. R.; Wehry, E. L.; Mamantov, G. *Environ. Toxicol. Chem.*, 1990, 9, 975-980.
67. Roy, W. R.; Griffin, R. A.; Dickerson, D. R.; Schuller, R. M. *Environ. Sci. Technol.*, 1984, 18, 734-739.
68. Harrison, F. L.; Bishop, D. J.; Mallon, B. J. *Environ. Sci. Technol.*, 1985, 19, 186-193.
69. Schauer, J. J.; Kleeman, M. J.; Cass, G. R.; Simoneit, B. R. T. *Environ. Sci. Technol.*, 1999, 33, 1578-1587.
70. Yamasaki, H.; Kuwata, K.; Miyamoto, H. *Environ. Sci. Technol.*, 1982, 16, 189-194.
71. *Atmospheric Chemistry and Physics*, Seinfeld, J. H.; Pandis, S. N., Eds.; John Wiley and Sons: New York, 1998, Chapter 13.
72. Broddin, G.; Cautreels, W.; van Cauwenberghe, K. *Atmos. Environ.*, 1978, 12, 2229-2239.
73. Garcia, J. P.; Beyne- Masclet, S.; Mouvier, G.; Masclet, P. *Atmos. Environ.*, 1992, 26A, 1589-1597.
74. Schnelle, J.; Jansch, T.; Wolf, K.; Gebefügi, I.; Kettrup, A. *Chemosphere*, 1995, 31, 3119-3127.
75. Hildemann, L. M.; Rogge, W. F.; Cass, G. R.; Mazurek, M. A.; Simoneit, B. R. T. *J. Geophys. Res.*, 1996, 101, 541-549.

76. Kadowaki, S. *Environ. Sci. Technol.*, 1994, 28, 129-135.
77. Mastral, A. M.; Callén, M. S.; García, T. *Environ. Sci. Technol.*, 1999, 33, 3177-3184.
78. Kawamura, K.; Kaplan, K. *Environ. Sci. Technol.*, 1987, 21, 105-110.
79. Grosjean, D.; van Cauwenberghe, K.; Schmid, J. P.; Kelley, P. E.; Pitts, J. N., Jr. *Environ. Sci. Technol.*, 1978, 12, 313-317.
80. Barkenbus, B. D.; MacDougall, C. S.; Griest, W. H.; Caton, J. G. *Atmos. Environ.*, 1983, 17, 1537-1543.
81. McDow, S. R.; Sun, Q.; Vartiainen, M.; Hong, Y.; Yao, Y.; Fister, T.; Yao, R.; Kamens, R. M. *Environ. Sci. Technol.*, 1994, 28, 2147-2153.
82. Jang, M.; McDow, S. *Environ. Sci. Technol.*, 1997, 31, 1046-1053.
83. Jang, M.; McDow, S. *Environ. Sci. Technol.*, 1995, 29, 2654-2660.
84. Odum, J. R.; McDow, S. R.; Kamens, R. M. *Environ. Sci. Technol.*, 1994, 28, 1285-1290.
85. Soltys, P. A.; Mauney, T.; Natusch, D. F. S.; Schure, M. R. *Environ. Sci. Technol.*, 1986, 20, 177.
86. Griest, W. H.; Tomkins, B. A. *Environ. Sci. Technol.*, 1986, 20, 292.
87. Fisher, G. L.; Chrisp, C. E.; Raabe, O. G. *Science*, 1979, 204, 879-881.
88. Fitch, W. L.; Smith, D. H. *Environ. Sci. Technol.*, 1979, 13, 341.
89. Pitts, J. N., Jr.; Pauer, H. R.; Zielinska, B.; Arey, J.; Winer, A. M.; Ramdahl, T.; Mejia, V. *Chemosphere*, 1986, 15, 675-685.
90. Kamens, R. M.; Guo, J.; Guo, Z.; McDow, S. R. *Atmos. Environ.*, 1990, 24A, 1161-1173.
91. Butler, J. D.; Crossley, P. *Atmos. Environ.*, 1981, 15, 91-94.
92. Pitts, J. N., Jr.; Zielinska, B.; Sweetman, J. A.; Atkinson, R.; Winer, A. M. *Atmos. Environ.*, 1985, 19, 911-915.

93. Ingle, J. D., Jr.; Crouch, S. R. In *Spectrochemical Analysis*, Prentice Hall: Englewood Cliffs, NJ, 1988, Chapter 12.
94. Dulin, D.; Mill, T. *Environ. Sci. Technol.*, 1982, 16, 815-819.
95. *Atmospheric Chemistry and Physics*, Seinfeld, J. H.; Pandis, S. N., Eds.; John Wiley and Sons: New York, 1998, Chapter 3.
96. Behymer, T. D.; Hites, R. A. *Environ. Sci. Technol.*, 1988, 22, 1311-1319.
97. Koester, C. J.; Hites, R. A. *Environ. Sci. Technol.*, 1992, 26, 502-507.
98. Falk, H. L.; Markul, I.; Kotin, P. *AMA Arch. Ind. Health*, 1956, 13, 13.
99. Tebbens, B. D.; Thomas, J. F.; Mukai, M. *Amer. Ind. Hyg. Assoc. J.*, 1966, 27, 415.
100. Inscoe, M. N. *Anal. Chem.*, 1964, 36, 2505-2506.
101. Kortüm, G.; Braun, W. *Ann. Chem.*, 1960, 632, 104-115.
102. Lane, D. A. *Gas Chromatographic Analysis and Photomodification Studies of Atmospheric PAH's*, Ph.D. Dissertation, York University, Toronto, Ontario, Canada, 1975.
103. Lane, D. A.; Katz, M. *Environ. Sci. Technol.*, 1977, 2, 137.
104. Lane, D. A. In *Chemical Analysis of PAH Compounds*. Vo-Dinh, T., Ed.; John Wiley and Sons: New York, Chapter 2.
105. Korfmacher, W. A.; Natusch, D. F. S.; Taylor, D. R.; Mamantov, G.; Wehry, E. L. *Science*, 1980, 207, 763-765.
106. Korfmacher, W. A.; Wehry, E. L.; Mamantov, G.; Natusch, D. F. S. *Environ. Sci. Technol.*, 1980, 14, 1094-1099.
107. Behymer, T. D.; Hites, R. A. *Environ. Sci. Technol.*, 1980, 14, 1004-1006.
108. Wehry, E. L. In *Analytical Photochemistry and Photochemical Analysis*. Fitzgerald, J. M., Ed.; Marcel Dekker; New York, 1971, p.173.
109. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*, Finlayson, B. J.; Pitts, J. N., Jr., Eds.; John Wiley and Sons: New York, 1986, Chapter 2.

110. Yokley, R. A.; Garrison, A. A.; Wehry, E. L.; Mamantov, G. *Environ. Sci. Technol.*, 1986, 20, 86-90.
111. Miguel, A. H.; Kirchstetter, T. W.; Harley, R. A. *Environ. Sci. Technol.*, 1998, 32, 450- 455.
112. Marr, L. C.; Kirchstetter, T. W.; Harley, R. A.; Miguel, A. H.; Hering, S. V.; Hammond, S. K. *Environ. Sci. Technol.*, 1999, 33, 3091- 3099.
113. Masclet, P.; Pistikopoulos, P.; Beyne, S.; Mouvier, G. *Atmos. Environ.*, 1988, 22, 639.
114. Mauldin, R. F. *Photochemical and Supercritical Fluid Extraction Studies of PAHs Adsorbed on Coal Stack Ash Fractions*, Ph.D. Dissertation, University of Tennessee, Knoxville, 1990.
115. Korfmacher, W. A. *The Decomposition of Organic Matter Adsorbed on Coal Fly Ash*, Ph.D. Dissertation, University of Illinois, Urbana-Champaign, 1978.
116. Engelbach, R. J.; Garrison, A.A.; Wehry, E.L.; Mamantov G. *Anal. Chem.*, 1987, 59, 2541- 2543.
117. Hipps, A. D. *Photochemical Investigations of Surface Adsorbed Polycyclic Aromatic Hydrocarbons*, M.S. Thesis, University of Tennessee, Knoxville, 1989.
118. Harris, G. D.; Adams, M. V. D.; Moore, W. M.; Sorensen, D. L. *J. Environ. Eng.*, 1987, 113, 612.
119. *Photochemistry*, Calvert, J. G.; Pitts, J. N., Jr., Eds.; John Wiley and Sons: New York, 1966, p.781.
120. Pitts, J. N., Jr.; Cowell, G. W.; Burley, D. R. *Environ. Sci. Technol.*, 1968, 2, 435.
121. Knapp, D. R. *Handbook of Analytical Derivatization Reactions*, John Wiley and Sons: New York, 1979, Chapter 1.
122. Pierce, A. E. *Silylation of Organic Compounds*, Pierce Chemical Co.: Rockford, IL, 1968, Chapters 1- 2.
123. *Statistics for Analytical Chemistry*, Miller, J. C.; Miller, J. N., Eds.; John Wiley and Sons: New York, 1988, Chapters 2-3.

124. Sanders, J. K. *Chromatographic and Spectroscopic Studies of the Interaction of Pyrene with Coal Stack Ash*, Ph.D. Dissertation, University of Tennessee, Knoxville, 1991.
125. Yokely, R. A. *The Photochemistry of Polycyclic Aromatic Hydrocarbons Adsorbed on the Surface of Coal Fly Ash*, Ph. D. Dissertation, University of Tennessee, Knoxville, 1985.
126. Reyes, C. A.; Medina, M.; Crespo-Hernandez, C.; Cedero, M. Z.; Arce, R.; Rosario, O.; Steffenson, D. M.; Ivanov, I. N.; Sigman, M. E.; Dabestani, R. *Environ. Sci. Technol.*, 2000, 34, 415-421.
127. Mao, Y.; Thomas, J. K. *Langmuir*, 1992, 8, 2501.
128. Wilkinson, F.; Worrall, D.R.; Williams, S.L. *J. Phys. Chem.*, 1995, 99, 6689- 6696.

APPENDIX

Chemical Actinometric Procedures

Results and Discussion

A p- nitroanisole (PNA)/ pyridine (PYR) chemical actinometer (see p.75) was used to determine the power and intensity of the xenon lamp used for the photodecomposition experiments involving pyrene and the coadsorbates, stearic acid and 2- undecanone, adsorbed on coal fly ash. The actinometer solution was composed of 5.26×10^{-5} M PNA and 5.48×10^{-4} M PYR. The equation used for calculating power was

$$P_o = n_b / \Phi_b t (1 - 10^{-A_a})$$

where n_b = molecules of product, Φ_b = quantum yield for formation of product, t = time of illumination, and $(1 - 10^{-A_a})$ = fraction of incident light absorbed by the actinometer. The quantum yield for the formation of product was found to be 5.21×10^{-4} M, using the equation

$$\Phi_b = (0.44[\text{PYR}]) + 0.00028$$

for an illuminated PYR concentration of 5.48×10^{-4} M. The time, t (sec), of the illuminations varied, depending on the experiments, as did the number of product molecules (n_b), found using the equation

$$n_a^i - n_a^f = n_b$$

where n_a^i and n_a^f are the number of molecules of PNA present prior to and following illumination, respectively. The amount of product produced was dependent on the limiting reactant, PNA ($[\text{PYR}] / [\text{PNA}] \sim 10:1$). The absorption spectrum of the actinometer solution can be seen in Figure A.1. The absorbance of the actinometer (A_λ) at each 10 nm interval between 410 and 220 nm, along with the normalized power output of the lamp (P_λ)

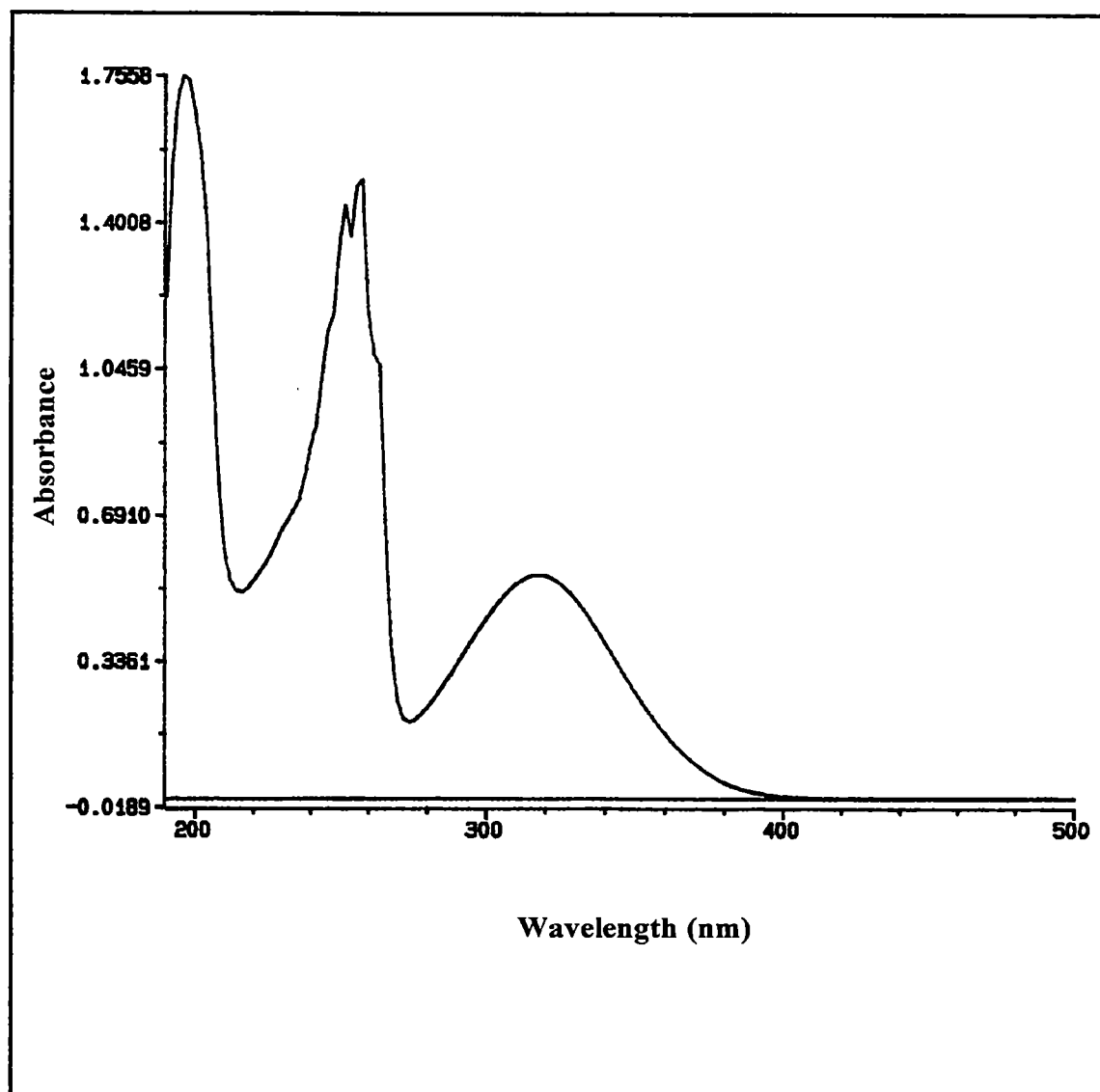


Figure A.1 Absorption Spectrum of PNA/ PYR Actinometer Solution.

at each of the 10 nm intervals, as determined from the emission spectrum of the lamp (see p.68) and equation (4), p.155 , are given in Table A.1. These values were used to calculate the average absorbance (A_a) of the actinometer, which was found to be 0.29.

Two different sets of experiments were used to determine the average values n_p and t , and subsequently the average power of the lamp. In the first set of experiments, called Experiment I, after an initial 10 minute lamp warm- up, four actinometer solutions were illuminated for 30, 20, 10, and 5 minutes, respectively, with the lamp left on continuously throughout the experiments. The power supply was set at 11 A. This set of data was used to determine an optimum illumination time for the subsequent set of experiments, called Experiment II. The results of Experiment I are shown in Table A.2. It can be seen from the data that as the time of illumination increases, the number of product molecules increases, and the power of the lamp appears to decrease. It was determined from these results that 600 s (10 min) would be used for Experiment II to calculate the average power of the lamp. The longer times of 1200 s and 1800 s were determined to be too long for illumination due to the increased possibility of absorbance changes caused by the decreasing concentration of the reactants in the actinometer solution. The shortest time of 300 s was considered too short a time frame to accurately determine the average power of the lamp due to the difficulty in detecting by HPLC the small quantity of product formed. The data obtained from the second set of experiments, called Experiment II, was used to calculate the average power of the xenon lamp. For this set of experiments the lamp was allowed to warm up for thirty minutes prior to illumination, again at 11 A. Following the warm- up period, 3 mL of the actinometer solution was illuminated for ten

Table A.1 Data for Determining the Average Absorbance (A_a) of the Actinometer Solution.

Wavelength of Absorption (nm)	Absorbance of Actinometer [A_k]	Power of Xenon Lamp [P_k] (W/ nm)	$A_k P_k$
410	0.00	1.20	0.00
400	0.01	1.15	0.01
390	0.02	1.10	0.02
380	0.04	1.07	0.04
370	0.09	0.98	0.08
360	0.16	0.93	0.15
350	0.26	0.96	0.25
340	0.38	0.93	0.35
330	0.49	0.93	0.45
320	0.54	1.00	0.54
310	0.52	0.85	0.44
300	0.44	0.82	0.36
290	0.33	0.75	0.25
280	0.23	0.76	0.17
270	0.24	0.74	0.18
260	1.17	0.79	0.92
250	1.34	0.63	0.84
240	0.86	0.52	0.45
230	0.66	0.29	0.19
220	0.54	0.17	0.09

$$\text{Average Absorbance } (A_a) = (\sum A_k P_k) / 20$$

$$A_a = 0.29$$

Table A.2
Experiment I: Data for Determining Optimum Illumination Time for Actinometer.

Time of Illumination t (sec)	Initial Molecules of PNA n_a^i	Final Molecules of PNA n_a^f	Molecules of Product n_b	Power P_o (photons/ s)
0	9.50×10^{16}	0.00	0.00	0.00
300	9.50×10^{16}	7.95×10^{16}	1.55×10^{16}	20.4×10^{16}
600	9.50×10^{16}	7.48×10^{16}	2.02×10^{16}	13.3×10^{16}
1200	9.50×10^{16}	7.00×10^{16}	2.50×10^{16}	8.2×10^{16}
1800	9.50×10^{16}	6.47×10^{16}	3.03×10^{16}	6.6×10^{16}

3 mL of actinometer solution was illuminated
10 min lamp warm- up prior to illumination

minutes (600 s). This was repeated five times, each time with a fresh actinometer solution, for a total of six measurements. The experiments were conducted over a period of three days to allow sufficient cool-down of the lamp between illuminations. The results of Experiment II can be seen in Table A.3

It can be seen from the data in Table A.3 that the power of the lamp appeared to fluctuate slightly from experiment to experiment. The average power of the lamp was calculated to be $1.63 \pm 0.21 \times 10^{17}$ photons/s (95 % confidence interval). The intensity of the lamp was calculated, using equations (6)- (9) given on pp.153-156, to be 245 W/ m^2 (surface area exposed to lamp 3.78 cm^2). The intensity calculated for the current xenon lamp was much greater than that of the lamp used previously by Hipps, which was determined to have an intensity of 137 W/ m^2 [117]. This was possibly due to the fact that a relatively new lamp was used in the present studies (the power output of a xenon lamp tends to decrease markedly as the lamp ages). The average flux of this xenon lamp was calculated to be 432×10^{14} photons/ $\text{cm}^2 \cdot \text{s}$, compared to an average flux of 7.70×10^{14} photons/ $\text{cm}^2 \cdot \text{s}$ for sunlight calculated at 40° zenith angle [95].

Table A.3
Experiment II: Data for Determining Average Power of Xenon Lamp.

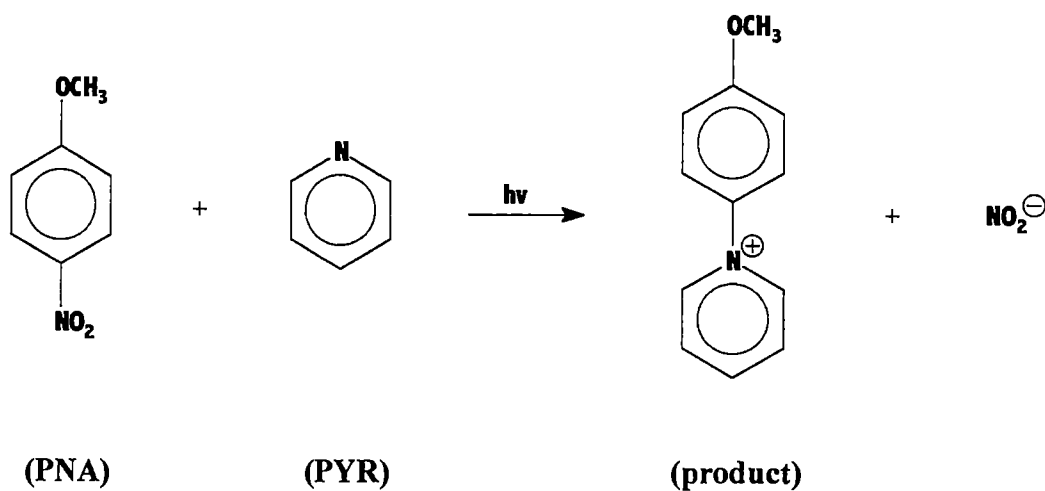
Illumination Number	n_a^i	n_a^f	n_b	P_o (photons/ s)
1	9.50×10^{16}	7.12×10^{16}	2.38×10^{16}	1.56×10^{17}
2	9.50×10^{16}	7.60×10^{16}	1.90×10^{16}	1.25×10^{17}
3	9.50×10^{16}	6.93×10^{16}	2.57×10^{16}	1.69×10^{17}
4	9.50×10^{16}	6.79×10^{16}	2.71×10^{16}	1.78×10^{17}
5	9.50×10^{16}	6.96×10^{16}	2.54×10^{16}	1.67×10^{17}
6	9.50×10^{16}	6.69×10^{16}	2.81×10^{16}	1.85×10^{17}
				$\bar{x} = 1.63 \pm 0.21 \times 10^{17}$

3 ml of actinometer solution was illuminated
 30 min lamp warm- up prior to illumination
 n_a^i = molecules of PNA prior to illumination
 n_a^f = molecules of PNA following illumination
 n_b = molecules of product
 P_o = power of lamp

Calculating Power and Intensity of the Xenon Lamp used for Illumination Experiments

The equations used for calculating the power and intensity of the xenon lamp, as well as descriptions of how the values in the equations were obtained, where applicable, are given below.

Actinometer Reaction:



Equation for power:

$$P_o = n_b / \Phi_b t (1 - 10^{-A_a}) \quad (1)$$

P_o = power in photons/ sec

n_b = number of molecules of product formed

Φ_b = quantum yield for formation of product

t = time of illumination of actinometer in sec

$1 - 10^{-A_a}$ = fraction of incident light absorbed by reactant(s)

The stoichiometry of the actinometer reaction given above is 1:1, PNA to product. The reactant PYR was in excess ($[PYR] \gg [PNA]$); therefore, the quantity of product formed was dependent upon the quantity of PNA. The quantity of PNA (mol/ L) in the actinometer solution was known prior to illumination and the quantity of PNA (mol/ L) remaining in the actinometer solution was determined by HPLC following illumination. From these values and the known stoichiometry of the reaction, the molecules of product (nb) was determined from the following equation:

$$n_a^i - n_a^f = n_b \quad (2)$$

n_a^i = number of molecules of PNA initially (determined from mol/ L)

n_a^f = number of molecules of PNA following illumination (determined from mol/ L)

The quantum yield (Φ_b) for the reaction was dependent on the concentration of PYR (mol/ L), and was determined from the following equation:

$$\Phi_b = 0.44 [PYR] + 0.00028 \quad (3)$$

The fraction of incident light absorbed by the reactants ($1 - 10^{-A_a}$) was determined by first finding the average absorbance of the actinometer (A_a) over the wavelength range in which the absorption spectrum of the actinometer overlaps the emission spectrum of the xenon lamp (410- 220 nm). The average absorbance of the actinometer was used because polychromatic light, such as that produced by the xenon lamp used in this work, is comprised of radiation over a wide range of wavelengths, and absorbance varies as a function of wavelength. In most experimental applications of chemical actinometry, nearly

monochromatic incident radiation is used, so this issue does not arise. It was assumed that the absorbance of the actinometer remained constant over the course of the experiments, due to the short illumination times utilized in the experiments.

The absorbance of the actinometer (A_i) was measured at 10 nm intervals from 410- 220 nm by UV- Vis spectrophotometry (see Table A.1, p.149). The power output of the lamp (P_i in units of W/ nm) at each 10 nm interval from 410- 220 nm was determined from the emission spectrum of the lamp, supplied by the manufacturer (see p.68). The power output at each 10 nm interval (P_i) was normalized to relative power output at each 10 nm interval (P_k) by multiplying each P_i by the wavelength (λ_i) at which it was measured, and dividing this value by the power output (P_j) at 320 nm, the maximum power output over the range 410- 220 nm. The equation is given below:

$$P_k = P_i \times \lambda_i / (P_{(320 \text{ nm})} \times 320 \text{ nm}) \quad (4)$$

The subscript "i" denotes each 10 nm interval.

Thus, for each absorbance value measured for the actinometer, A_k , there was calculated a corresponding normalized power output value, P_k , for the lamp. These values were used to determine the average absorbance of the actinometer (A_a) by the following equation:

$$A_a = [\Sigma(A_k P_k)] / N \quad (5)$$

N = number of 10 nm intervals between 440- 220 nm = 20

Once all the values in the power equation (1) were determined, the average power of the lamp was calculated using equation (1). From the average power of the lamp that was determined, the average intensity of the lamp was calculated using known conversion

factors given below.

$$P_o \text{ (in photons/ sec) } \times (1 \text{ einstein/ } 6.022 \times 10^{23} \text{ photons}) = P_o \text{ (in einstein/ sec)} \quad (6)$$

$$P_o \text{ (in einstein/ sec) } \times (81.7 \text{ kcal/ 1 einstein})_{\text{at } 350 \text{ nm}} = P_o \text{ (in kcal/ sec)} \quad (7)$$

$$P_o \text{ (in kcal/ sec) } \times (1/ \text{ surface area exposed to light} = 3.78 \text{ cm}^2) = I_o \text{ (in kcal/ sec} \cdot \text{cm}^2) \quad (8)$$

$$I_o \text{ (in kcal/ sec} \cdot \text{cm}^2) \times (1 \text{ kW} \cdot \text{sec/ } 0.239 \text{ kcal}) \times (1000 \text{ W/ 1 kW}) = I_o \text{ (in W/ cm}^2) \quad (9)$$

VITA

Sabella Bowers Sauceman was born on February 24, 1970, in Maryville, Tennessee. She grew up in Greeneville, Tennessee, and attended Greeneville High School, from which she graduated in 1988. She then attended East Tennessee State University, in Johnson City, Tennessee, where she graduated magna cum laude with her Bachelor of Science degree in Chemistry in May, 1993. She entered The University of Tennessee, Knoxville, in August 1993 to pursue a Doctorate of Philosophy in Analytical Chemistry, which was awarded in August, 2000.